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Novel Technique for Developing E-Textiles:
Printing MXene Supercapacitors on
Fabrics for Wearable Electronics

A thesis presented to Trinity College Dublin,
The University of Dublin, for the degree of
Doctor of Philosophy in Chemistry

By

Anastasiia Shandra

Under the supervision of

Prof. Valeria Nicolosi

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DECLARATION

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ANASTASIIA SHANDRA

Novel Technique for Developing E-Textiles:
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ABSTRACT

The increasing demand for miniaturized and flexible wearable electronics is driving the rapid growth of electronic textiles (e-textiles). In this context, microsupercapacitors (MSCs) are becoming essential as energy storage solutions, offering high-power density and extended lifespans. Herein, a novel approach is introduced using aerosol-jet printing (AJP) to fabricate e-textiles with additive-free and pseudocapacitive $\text{Ti}_3\text{C}_2\text{T}_x$ MXene ink. AJP offers superior resolution and cost-effectiveness for rapid prototyping, while $\text{Ti}_3\text{C}_2\text{T}_x$ exhibits excellent electrical conductivity, solution-processability, electrochemical activity, and mechanical flexibility. Our printed flexible MXene@Fabric electrodes achieve high areal capacitance of up to 4.387 F cm^{-2} , great rate capability, excellent cyclability, and good washability. The fabricated current collector-free symmetrical MSCs on cotton deliver an areal capacitance of 381 mF cm^{-2} (at 2 mV s^{-1}) in poly(vinyl alcohol)/sulfuric acid gel electrolyte, outperforming up-to-date printed MXene/textile-based MSCs. These findings demonstrate the transformative potential of integrating MSCs via AJP, paving the way for enhanced energy storage in a wide variety of flexible, breathable, and washable textile-based devices, thereby catalyzing a paradigm shift in wearable electronics.

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COMMUNICATIONS

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EDUCATION & PUBLIC ENGAGEMENT

Volunteered at Trinity College Dublin Open Day representing Chemistry, Chemistry with Biosciences, Chemistry with Molecular Modelling, Medicinal Chemistry, and Nanoscience degree programmes (November 23rd 2019, November 4th 2023). Trinity College Dublin School of Chemistry representative at BT Young Scientist Event (January 9th 2020).

Carried Spectroscopy in a Suitcase workshops (January 23rd 2020, February 5th 2020).

Royal Society of Chemistry representative at the Irish Science Teachers Association Conference (February 8th 2020).

Teaching assistant for Transition Year program (March 2nd – 6th 2020).

Invigilated 54th International Chemistry Olympiad (July 10th – 18th 2022).

Teaching assistant for the chemistry elective module TEU00351, “The Chemistry of Periodic Elements for non-science students” at the School of Chemistry, Trinity College Dublin (September 1st - December 2nd 2022).

Carried out a school workshop on the “Energy & Sustainability” scheme (March 22nd 2023).

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LIST OF ABBREVIATIONS

0D – Zero-Dimensional

1D – One-Dimensional

2D – Two-Dimensional

3D – Three-Dimensional

AJP – Aerosol Jet Printing

ADF – Annular Dark-Field

CAD – Computer-Aided Design

CNTs – Carbon Nanotubes

CV – Cyclic Voltammetry

EDL – Electrostatic Double Layer

EDLC – Electrostatic Double Layer Capacitance

EDX – Energy Dispersive X-ray Spectroscopy

EIS – Electrochemical Impedance Spectroscopy

EMI – Electromagnetic Interference

ESR – Equivalent Series Resistance

FDM – Fused Deposition Modelling

FR – Focusing Ratio

GCD – Galvanostatic Charge/Discharge

HAADF – High Angle Annular Dark Field

h-BN – Hexagonal Boron Nitride

IDD – Interdigitated Device

IHP – Inner Helmholtz Plane

IJP – Inkjet Printing

LED – Light-Emitting Diode

MILD – Minimally Intensive Layer Delamination

MSC – Microsupercapacitor

MWCNTs – Multi-Walled Carbon Nanotubes

OHP – Outer Helmholtz Plane

PANI – Polyaniline

PDF – Powder Diffraction File

PEDOT – Poly (3,4-(ethylenedioxy) Thiophene

PET – Polyethylene Terephthalate

PFA – Perimeter Fill Algorithm

PPy – Polypyrrole

PTFE – Polytetrafluoroethylene

PTh – Polythiophene

PVA – Poly(Vinyl Alcohol)

rGO – Reduced Graphene Oxide

SAED – Selected Area Electron Diffraction

SCCM – Standard Cubic Centimetres per Minute

SEM – Scanning Electron Microscopy

SFA – Serpentine Fill Algorithm

STEM – Scanning Transmission Electron Microscopy

SWCNTs – Single-Walled Carbon Nanotubes

TEM – Transmission Electron Microscopy

TPU – Thermoplastic Polyurethane

UA – Ultrasonic Atomiser

XRD – X-ray Diffraction

OBJECTIVES OF THE THESIS

This thesis is dedicated to advancing the field of wearable electronics by developing innovative, high-performance, and flexible energy storage devices integrated into textiles. Utilising additive-free $\text{Ti}_3\text{C}_2\text{T}_x$ MXene inks and the capabilities of Aerosol Jet Printing (AJP), this research aims to establish new benchmarks in e-textile design and functionality.

A central objective of this research is the optimisation and systematic implementation of AJP for the fabrication of MXene-based energy storage devices on textiles. This involves the synthesis of high-purity $\text{Ti}_3\text{C}_2\text{T}_x$ MXene from its Ti_3AlC_2 MAX phase precursor using the MILD method, followed by the formulation of a stable, high-quality ink tailored for AJP deposition. A key focus is the precise control of ink properties and printing parameters to achieve uniform, well-adhered MXene coatings on textiles such as cotton, polycotton, and polyester. Additionally, this study aims to assess the reproducibility of the AJP process by quantifying the relationship between the number of printed layers and mass loading, ensuring scalable and reproducible fabrication.

The next critical objective is to verify the robustness and practical utility of MXene-printed textile electrodes for wearable technologies. Utilising AJP, this work targets fabricating $\text{Ti}_3\text{C}_2\text{T}_x$ MXene electrodes on various textile substrates and assessing their capacitive behaviour, charge-discharge dynamics, and long-term cycling stability. Furthermore, the study seeks to evaluate the durability of these electrodes through up to 100 wash cycles to assess their suitability for integration into wearable electronics.

Building on the insights from electrode fabrication, the final objective is to optimise the design of MXene-printed textile microsupercapacitors (MSCs) and conduct a comprehensive electrochemical analysis. This also includes evaluating their performance under mechanical stress, such as bending, to ensure durability for wearable applications. The study also aims to explore the versatility of AJP by fabricating MSCs in series and parallel configurations. To demonstrate the practical applicability, a tandem MSC device printed in series will be developed and tested for its capability to power an LED.

These objectives establish a systematic approach to optimising AJP for MXene-based textile energy storage, driving the development of high-performance e-textiles for wearable electronics

STRUCTURE OF THE THESIS

CHAPTER 1: INTRODUCTION

This chapter offers a detailed overview of foundational materials science concepts, tracing their historical development to establish context for the thesis. It begins by highlighting key milestones in the evolution of materials, from natural substances to advanced materials. The focus then shifts to nanotechnology, showcasing its impact on manipulating materials at the nanoscale. The chapter also explores the development of wearable electronics and e-textiles, covering their definition, history, current status, and adoption challenges. A section on energy storage devices, particularly supercapacitors, discusses their structure, storage mechanisms, and miniaturisation for wearable applications. The chapter concludes with an in-depth look at MXenes, including their synthesis, properties, and potential in e-textiles for energy storage. Finally, it outlines the thesis objectives and research goals, emphasising their relevance to advancing wearable electronics.

CHAPTER 2: DEPOSITION & CHARACTERISATION TECHNIQUES

This chapter provides a comprehensive analysis of the deposition and characterisation techniques employed in this research. It begins by evaluating various printing technologies and highlighting the advantages and limitations of each method. Particular emphasis is placed on aerosol-jet printing, the primary deposition technique selected for its high precision and compatibility with flexible substrates. The chapter then explores the application of electron microscopy and X-ray diffraction, which are crucial for assessing the material's morphology, phase composition, and deposition quality. Additionally, the chapter discusses electrochemical characterization methods, focusing on the design and operation of electrochemical cells, as well as techniques such as cyclic voltammetry, galvanostatic charge-discharge, and electrochemical impedance spectroscopy, all of which are tailored to the specific requirements of microsupercapacitor characterization.

CHAPTER 3: AEROSOL JET PRINTED MXENE TEXTILES

This chapter explores the innovative application of aerosol-jet printing to incorporate $\text{Ti}_3\text{C}_2\text{T}_x$ MXene inks into textile substrates, with the goal of developing high-performance, flexible e-textiles. It begins by discussing the benefits of using textiles as substrates for

electronic integration. The chapter then details the synthesis and characterization of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene, emphasizing the unique properties that make it ideal for wearable electronics. The synthesis of high-purity MXene is validated using X-ray diffraction, transmission electron microscopy, selected area electron diffraction, and energy-dispersive X-ray spectroscopy, confirming the successful transformation from the Ti_3AlC_2 MAX phase to the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene structure. Following this, the chapter examines the deposition of MXene inks onto textiles using aerosol-jet printing, with an analysis of the resulting surface morphology and structural integrity via scanning electron microscopy and X-ray diffraction. This comprehensive study demonstrates the effectiveness of aerosol-jet printing in fabricating functional e-textiles that combine the electronic capabilities of MXenes with the desirable properties of fabrics.

CHAPTER 4: AEROSOL JET PRINTED MXENE TEXTILE ELECTRODES

This chapter investigates the fabrication of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene-based electrodes on textile substrates using aerosol-jet printing, aimed at developing flexible and high-performance energy storage solutions for wearable electronics. It begins by outlining the advantages of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene, which make it particularly suitable for integration into e-textiles. The chapter then describes the aerosol-jet printing process employed to deposit MXene inks onto textiles like cotton, polycotton, and polyester, achieving uniform coatings that maintain the inherent flexibility of the fabrics. Various electrode thicknesses are produced to analyze the effect of layer number on electrochemical performance. Electrochemical characterization of these electrodes reveals exceptional performance metrics, confirming their viability for wearable applications. Finally, the chapter discusses the broader implications of these findings for advancing e-textile technology and lays the groundwork for the development of MXene-based fabric MSCs, which is explored further in Chapter 6. The results highlight the potential of MXene-printed e-textiles as durable, high-performance components in wearable energy storage devices.

CHAPTER 5: WASHABILITY STUDY OF AEROSOL JET PRINTED MXENE TEXTILE ELECTRODES

This chapter examines the washability of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene-based textile electrodes to assess their durability and functionality in wearable applications. As electronics are increasingly integrated into fabrics, e-textiles must retain performance after repeated washing. The chapter begins by underscoring the importance of washability for e-textiles and the

mechanical and chemical challenges posed by laundering. A systematic study was conducted on MXene-printed textile electrodes for up to 100 wash cycles, using a specialized washability tester in accordance with the ISO 105-C06 test A1M standard. Key metrics were evaluated through cyclic voltammetry and galvanostatic charge-discharge tests. Morphological changes were monitored using scanning electron microscopy and digital microscopy. The results provide valuable insights for the development of durable, washable e-textiles.

CHAPTER 6: PRINTED MXENE TEXTILE MICROSUPERCAPACITORS

This chapter explores the fabrication and performance of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene-based microsupercapacitors printed onto textiles using aerosol jet printing. The integration of microsupercapacitors into fabrics addresses the challenge of embedding energy storage in wearable electronics while maintaining flexibility and comfort. The chapter focuses on optimizing the printing process to create symmetric interdigitated microsupercapacitors on cotton. Electrochemical evaluations reveal high capacitance, energy density, and power density. Mechanical flexibility under bending conditions confirms their durability. The study also explores tandem microsupercapacitors in series and parallel configurations, adjusting energy and power outputs for specific needs. A demonstration of an LED powered by a four-in-series tandem microsupercapacitor device highlights the practical potential. By refining fabrication techniques and showcasing real-world functionality, this chapter advances wearable electronics and integrated energy storage in textiles.

CHAPTER 7: CONCLUSIONS & OUTLOOK

This final chapter synthesizes the key findings of the research, emphasizing the advancements made in developing high-performance, flexible, and durable MXene-based MSCs for wearable electronics. It discusses the broader implications of these developments for the future of e-textiles, highlighting their potential to drive innovations in wearable technology. The chapter also outlines several avenues for future research into e-textiles. It concludes by reaffirming the transformative potential of combining MXenes with aerosol-jet printing, emphasizing their critical role in advancing wearable energy storage technologies.

1 INTRODUCTION

1.1. HISTORICAL EVALUATION OF MATERIALS

The story of materials science is, in many ways, the story of human civilisation. It begins with our ancestors' early encounters with natural materials – stones shaped into tools, bones turned into weapons, and clay moulded into pottery. These simple yet profound innovations marked the dawn of human ingenuity, allowing early societies to hunt more effectively, cook food, and protect themselves.^[1]

As our understanding of materials deepened, so did our ability to manipulate them in increasingly sophisticated ways. The *Bronze Age*, marked by the discovery of how to alloy copper with tin, was a pivotal moment in this journey. The creation of bronze, a material far stronger and more durable than its predecessors, revolutionized many aspects of life.^[2] Stronger tools and weapons enhanced agricultural productivity and military capability, while the increased durability of bronze artefacts supported the rise of trade networks and early urban centres.^[3] This era of innovation laid the foundation for the growth of ancient civilizations, where the ability to produce and control materials became a critical factor in developing complex societies.

Following the Bronze Age, the advent of the *Iron Age* brought even more profound changes. The widespread use of iron and later steel enabled the construction of stronger and more resilient tools, weapons, and infrastructure. Unlike bronze, iron was more abundant and could be produced in greater quantities, which significantly lowered costs and made durable tools accessible to a broader segment of society. The strength and versatility of iron and steel transformed agricultural practices, warfare, and architecture, supporting the expansion of empires and the establishment of vast trade networks.^[4,5]

The *Industrial Revolution* in the 18th and 19th centuries marked another seismic shift in the history of materials science.^[6,7] The development of new metallurgical processes, such as the Bessemer process for mass-producing steel, revolutionized manufacturing and construction.^[8] With its unparalleled strength and flexibility, steel became the backbone of the industrial era, enabling the creation of railways, skyscrapers, and machinery that powered unprecedented economic growth.^[9] This period also saw the emergence of new

materials such as rubber^[10] and cement^[11], expanding the possibilities for industrial and infrastructural development. The ability to produce materials on an industrial scale transformed economies, accelerated urbanization, and laid the groundwork for the modern world.

As we moved into the 20th century, often referred to as the *Digital Age*, the pace of material innovation accelerated at an unprecedented rate, driving transformative changes across virtually every aspect of society.^[12] Among the most groundbreaking developments was the discovery and widespread adoption of semiconductors, particularly silicon.^[13] This material, abundant and uniquely suited for controlling electrical conductivity, became the cornerstone of modern electronics.^[14] The invention of the transistor in 1947, a small device capable of amplifying and switching electronic signals, revolutionized the industry. Unlike the bulky and fragile vacuum tubes that preceded it, the transistor allowed for the miniaturization of electronic circuits, laying the groundwork for developing smaller, faster, and more reliable devices.^[15,16] The subsequent creation of integrated circuits, which packed millions of transistors onto a single chip, marked the dawn of the digital age. This leap in technology enabled the development of computers, which transitioned from room-sized machines to personal devices that could fit on a desk. The ripple effects of this innovation are profound –leading to the proliferation of smartphones, laptops, and other digital devices that have become integral to our daily lives.^[17] The mastery of semiconductor materials not only reshaped technology but also fundamentally altered how we communicate, work, and interact with the world.

In parallel with these advances in electronics, the field of energy storage was also undergoing significant transformation. Early batteries, such as the lead-acid battery, played a vital role in powering the first wave of electrical devices, but their limitations in size, weight, and energy capacity became apparent as technology advanced.^[18] The invention of the lithium-ion battery in the late 20th century was nothing short of revolutionary. By leveraging lithium's light weight and high electrochemical potential, scientists developed a battery that offered unprecedented energy density and longevity. This innovation was critical in supporting the growth of portable electronics, from laptops to smartphones, and later became the driving force behind the rise of electric vehicles.^[19] The success of lithium-ion batteries was made possible by a deep and precise understanding of materials at the atomic level, enabling the optimization of electrode materials and electrolytes to maximize performance and safety.^[20]

Chapter 1: Introduction

As we entered the late 20th and early 21st centuries, materials science ushered in what is now known as the *Nanotechnology Age*, a transformative period characterized by the exploration and manipulation of materials at the nanoscale.^[21] This era's roots can be traced back to 1959 when physicist Richard Feynman delivered his seminar lecture "There is Plenty of Room at the Bottom".^[22] In this talk, Feynman alerted the scientific community to the vast, untapped potential of nanomaterials, planting the seeds for the innovations that would follow.

Building on Feynman's insights, researchers began to push the boundaries of what was possible in science and technology, leading to the discovery of materials with extraordinary properties. Among the most groundbreaking discoveries of this age was graphene – a single layer of carbon atoms arranged in a hexagonal lattice. Known for its exceptional strength, flexibility, and conductivity, graphene quickly became a focal point for research across various fields, including flexible electronics, advanced sensors, and energy storage systems. Its ability to conduct electricity more efficiently than any other material, combined with its mechanical robustness, made it an ideal candidate for next-generation technologies.^[23] Alongside graphene, carbon nanotubes (CNTs) – cylindrical structures composed of rolled-up graphene sheets – also garnered significant attention. These nanomaterials exhibit remarkable electrical, thermal, and mechanical properties. Stronger than steel yet lighter than aluminium, CNTs possess excellent electrical conductivity, making them suitable for a wide range of applications, from high-performance composites to nanoelectronics.^[24,25] In recent years, the discovery of MXenes – two-dimensional transition metal carbides, nitrides, and carbonitrides – has added a new dimension to the field of advanced materials. MXenes, with their metallic conductivity and hydrophilic surfaces, are particularly promising for applications in energy storage, electromagnetic interference (EMI) shielding, and environmental remediation. In energy storage, MXenes have shown tremendous potential in enhancing the performance of supercapacitors and batteries due to their high surface area, excellent conductivity, and tunable chemical properties. Their versatility and adaptability continue to drive ongoing research aimed at integrating MXenes into various high-performance, flexible, and durable technologies.^[26]

1.2. NANOTECHNOLOGY

Nanotechnology is a multidisciplinary field that has redefined the boundaries of science and engineering, focusing on manipulating and controlling matter at the nanoscale – typically between 1 and 100 nanometers. To put this into perspective, a nanometer is one-billionth of a meter (i.e., 10^{-9}), roughly the size of 10 hydrogen atoms lined up in a row. At this scale, the properties of materials can change dramatically, giving rise to unique physical, chemical, and biological characteristics that are not observed in bulk materials. Nanotechnology itself is broadly defined as the application of nanoscience – the study of phenomena and manipulation of materials at the nanoscale – to create new materials, devices, and systems that exhibit novel properties and functions due to their small size. *Nanoscience*, on the other hand, is concerned with understanding these nanoscale materials – how they behave, how their properties differ from those of bulk materials, and how they can be harnessed for specific applications. The interdisciplinary nature of nanoscience draws from fields such as physics, chemistry, biology, materials science, and engineering, making it one of the most integrative areas of research today.^[21]

Materials at the nanoscale often exhibit properties that differ significantly from those at the macroscopic level.^[27] These differences arise due to a few key factors. Firstly is a *surface area-to-volume ratio*. At the nanoscale, the surface area of a material becomes much larger relative to its volume. This increased surface area can enhance the material's chemical reactivity, strength, and other properties.^[28] For instance, nanoparticles of gold can behave as catalysts, accelerating chemical reactions, something bulk gold does not do.^[29] Secondly, *quantum effects* become significant when materials are reduced to the nanoscale. These effects can alter the material's optical, electrical, and magnetic properties.^[28] For example, quantum dots – tiny semiconductor particles – emit different colours of light depending on their size, a property exploited in advanced display technologies.^[30] And lastly, nanoscale materials often exhibit enhanced *mechanical properties* such as increased strength, hardness or elasticity.^[31] For example, nanocrystalline ceramics, which consist of grains at the nanometer scale, are far tougher and more fracture-resistant than traditional ceramics. The nanoscale grain boundaries hinder crack propagation, making these ceramics more durable and resilient under stress.^[32] These improved properties make nanocrystalline ceramics ideal for high-durability applications, including cutting tools, protective coatings, and biomedical implants.^[33,34]

Nanomaterials can be categorized based on their dimensionality, which refers to the number of dimensions in which the material is confined to the nanoscale. Understanding the dimensionality of nanomaterials is crucial because it directly influences their physical, chemical, and mechanical properties. The most common classifications are zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) nanomaterials, each with unique characteristics and applications.^[35]

0D nanomaterials are materials that are confined to the nanoscale in all three spatial dimensions. These materials have no dimensions larger than 100 nm, resulting in particles that are effectively point-like.^[36] The most well-known 0D nanomaterials are quantum dots and nanoparticles. Quantum dots are semiconductor materials with unique optical and electronic properties due to quantum confinement effects. When the size of a semiconductor particle is reduced to the nanoscale, the electrons within it become confined, leading to discrete energy levels. This confinement causes quantum dots to exhibit size-dependent optical properties, where the colour of the light they emit changes with their size. Quantum dots are used in applications such as biological imaging, solar cells, and advanced display technologies.^[30,37] Nanoparticles are particles with all three dimensions in the nanoscale range. They can be made from various materials, including metals, oxides, semiconductors, and polymers. Nanoparticles possess a high surface area-to-volume ratio, which enhances their reactivity and enables unique properties. Additionally, they are often surface-functionalized to meet the specific requirements of various applications. As fundamental building blocks in nanotechnology, nanoparticles play a crucial role across a wide range of advanced applications.^[38]

1D nanomaterials are materials that are confined to the nanoscale in two dimensions, leaving one dimension, typically length, extended. These materials include nanowires, nanotubes, nanofibers, and nanorods, characterised by their high aspect ratios (length to diameter).^[39] Nanowires are wire-like structures with diameters in the nanoscale range and lengths extending to several micrometres. These structures exhibit unique electronic, optical, and mechanical properties due to their 1D nature. Nanowires can be made from a variety of materials, including metals, semiconductors, and oxides.^[40] Their applications include nanoscale electronics, photonics, and sensors.^[41,42] CNTs, as introduced earlier, are cylindrical structures composed of rolled-up graphene sheets. They can be single-walled (SWCNTs) or multi-walled (MWCNTs), depending on the number of graphene layers.^[43,44] Nanorods are characterised by their rod-like shape, with diameters in the nanoscale range and lengths that are several times larger. Nanorods can be made from

various materials, including metals, semiconductors, and organic materials.^[45] Their shape and high surface area confer unique optical and catalytic properties, which are particularly useful in applications such as photovoltaic cells, targeted drug delivery, and display technologies.^[46,47] Nanofibers are fibre-like structures with diameters in the nanometer range and lengths spanning from micrometres to centimetres. Nanofibers can be produced from a wide range of materials, including polymers, carbon, ceramics, and metals. Due to their high surface area, flexibility, and mechanical strength, nanofibers are widely used in filtration, tissue engineering, drug delivery systems, and as reinforcement materials in composite structures. Their ability to form highly porous networks makes them particularly valuable in biomedical applications, where they can mimic the extracellular matrix in tissue scaffolds.^[48,49]

2D nanomaterials are materials that are confined to the nanoscale in one dimension, typically thickness, while the other two dimensions, length and width, remain extended. These materials are often described as thin films or sheets and are characterised by their unique properties, which arise from their atomic-scale thickness.^[50] Notably, 2D nanomaterials are characterised by flexibility,^[50,51] large effective surface area,^[52] exceptional mechanical strength,^[53] and distinctive plasmonic, electron confinement, and optical properties.^[50,54] Depending on their specific class, these materials can be tuned to function as superconductors, semiconductors, or insulators.^[50,55] Due to these versatile properties, 2D nanomaterials have garnered significant attention and are extensively explored for applications in electronics,^[56] energy production and storage,^[57] tissue engineering,^[58] sensing,^[59] membranes,^[60] and catalysis.^[61] In addition to the previously mentioned prominent examples of graphene and MXenes, the realm of 2D nanomaterials is vast and includes other significant materials that offer unique properties and applications. One such material is molybdenum disulfide (MoS_2), a layered transition metal dichalcogenide that, like graphene, is composed of single layers of atoms. Although it can be exfoliated into ultrathin layers similar to graphene, each “monolayer” of MoS_2 actually comprises three atomic planes - one molybdenum layer sandwiched between two sulfur layers - rather than a single atomic plane. Unlike graphene, MoS_2 is a semiconductor rather than a conductor, making it particularly attractive for use in electronics and optoelectronics, such as transistors, photodetectors, and flexible displays. MoS_2 also possesses excellent mechanical properties and a high surface area, which enhance its utility in catalysis and energy storage.^[62,63] Another noteworthy 2D nanomaterial is hexagonal boron nitride (h-BN), often dubbed “white graphene”. h-BN

consists of a single layer of boron and nitrogen atoms arranged in a hexagonal lattice, similar in structure to graphene but with different properties. As an electrical insulator with a wide bandgap, h-BN is highly valuable as a dielectric material in electronic devices. Its exceptional thermal conductivity and chemical stability further make it suitable for applications in thermal management, protective coatings, and as a substrate for graphene-based devices.^[64,65]

3D nanomaterials are materials that possess nanoscale features in all three dimensions and offer distinct structural advantages over other dimensionalities.^[66] Their interconnected macro- and mesopores prevent aggregation and maximise surface area, enabling extensive surface functionalisation and defect engineering to enhance reactivity.^[67] The controlled dimensionality allows precise tuning of porosity and pore interconnectivity,^[68] while their morphological versatility enables synthesis in various shapes tailored to specific applications.^[67,68] These structures also support the creation of hybrid nanomaterials by incorporating multiple components, such as combining 3D graphene with metal nanoparticles, and they can be synergistically combined with 0D, 1D, or 2D nanomaterials for enhanced functionality.^[69] Scalable production techniques like templating or printing ensure consistent structural features, and their high porosity and surface area contribute to excellent biocompatibility,^[70] making 3D nanomaterials particularly valuable in energy storage,^[71] catalysis,^[72] environmental,^[73] and biomedical applications.^[67] Metal-organic frameworks, for example, consist of metal ions or clusters coordinated to organic ligands to form a porous 3D structure with nanometer-scale pores that can be tailored for specific uses, including gas storage, drug delivery, and catalysis. Their high surface area and tunable chemistry underscore their versatility across various applications.^[74,75] Aerogels, another type of 3D nanomaterials, are distinguished by their high porosity, low density, and large surface area. The incorporation of nanomaterials, such as CNTs, graphene, and cellulose nanofibers, into the aerogel matrix has been shown to significantly enhance their mechanical, electrical, and thermal properties. These enhancements have broadened the application of aerogels in various domains, including energy storage, environmental remediation, and biomedical engineering. For instance, the integration of graphene oxide into aerogels has led to the development of composites with improved electrical conductivity and mechanical strength, which are highly effective in applications like supercapacitors and sensors.^[76]

In summary, nanotechnology is revolutionizing various industries by enabling the creation of more efficient, sustainable, and high-performance products and processes. From

targeted drug delivery systems in medicine to the miniaturization of electronic devices and advancements in energy storage, the impact of nanotechnology is profound. A particularly exciting application is in the development of wearable electronics, where *e-textiles* emerge as a groundbreaking innovation. These fabrics, embedded with nanoscale electronic components, are set to redefine our interaction with technology. The potential of e-textiles and their implications will be explored in greater detail in the following section.

1.3. FROM WEARABLE ELECTRONICS TO E-TEXTILES: EVOLUTION & TECHNOLOGICAL INTEGRATION

Today, we stand on the brink of a new era in materials science with the rapid development of wearable electronics. These devices integrate advanced electronic systems into wearable formats, enabling users to seamlessly interact with technology throughout their daily lives. The primary aim of wearable electronics is to provide real-time data collection, analysis, and feedback, often in a manner that enhances user experience without intruding upon regular activities.^[77]

Wearable electronics have demonstrated remarkable versatility and adaptability, leading to their application across a wide range of fields. Wearable electronics are increasingly playing a transformative role in healthcare by enabling continuous, real-time monitoring of various physiological parameters essential for the management of chronic and acute health conditions. These devices, ranging from skin-based wearables like electronic tattoos and textile-embedded sensors to advanced biofluidic systems, offer non-invasive methods to track vital signs such as heart rate, blood pressure, glucose levels, and even neurological activity. By integrating advanced materials such as graphene and flexible polymers, these wearables provide comfort and accuracy, making them ideal for prolonged use in both clinical and home settings. Moreover, the incorporation of artificial intelligence and machine learning into wearable systems enhances their diagnostic capabilities, enabling early detection of health issues and the customization of treatment plans. These advancements not only improve patient outcomes but also reduce the burden on healthcare facilities by facilitating remote monitoring and management of diseases.^[78,79]

In the realm of fitness and sports, wearable technology has become an integral part, offering athletes and enthusiasts a sophisticated means to monitor and enhance their physical performance. Devices such as fitness trackers and smartwatches are equipped

with advanced sensors, including accelerometers, gyroscopes, and heart rate monitors, which allow users to track their physical activity, measure performance metrics, and set fitness goals with precision. These wearables are not just for personal use; they play a critical role in professional sports by providing detailed data on movement patterns, exertion levels, and recovery times. This data is invaluable for optimizing training regimens and preventing injuries, as it enables a more tailored and responsive approach to athlete management. The integration of wearable sensors into sports equipment, such as smart textiles and sensor-embedded gear, further enhances the ability to monitor performance without hindering movement, offering a seamless and unobtrusive experience that is crucial for maintaining optimal athletic output.^[80,81]

In the realm of consumer electronics, wearable devices have rapidly evolved into essential tools for managing daily tasks, staying connected, and enhancing lifestyle choices. Smartwatches, for instance, offer far more than just convenient access to notifications, music playback, and contactless payments; they now incorporate advanced features like health monitoring and fitness tracking, which are seamlessly integrated into daily life. These devices have become integral to users' routines, enabling real-time health data collection and personalized feedback, thus blurring the lines between technology and everyday experiences. Moreover, lifestyle-oriented wearables such as augmented reality glasses and wearable cameras further integrate digital functionalities into physical activities, enhancing user engagement with both their environment and digital content. The growing sophistication and utility of these devices underscore their role in not only facilitating connectivity but also in shaping the way users interact with the world around them.^[82]

In industries such as mining, construction, and manufacturing, wearable devices like smart helmets, safety vests, and smart eyewear are equipped with advanced environmental and biosensors. These wearables monitor hazardous conditions, including gas levels, temperature, and worker vitals, thereby reducing the risk of accidents and improving response times during emergencies. Additionally, these devices offer real-time location tracking of workers, aiding in logistics operational management and ensuring prompt evacuation in case of emergencies. Smart eyewear, for example, provides hands-free access to critical information, allowing workers to maintain situational awareness and make informed decisions without interrupting their tasks. The integration of these wearable technologies into industrial settings not only improves worker safety but also enhances operational efficiency by providing real-time data and communication

capabilities, ultimately leading to a more connected, safer, and more productive workplace.^[83,84]

As wearable electronics continue to evolve and diversify, the next frontier in this technological evolution is the integration of electronic functionality directly into textiles themselves – giving rise to the field of electronic textiles, also known as e-textiles. Unlike traditional wearable devices, which are often separate accessories attached to or worn on the body, e-textiles represent a seamless fusion of electronics and fabric.^[77] This integration enables the creation of garments and other textile products that are not only smart but also indistinguishable from conventional clothing in terms of comfort and aesthetics. The emergence of e-textiles marks a significant shift in how we think about wearable technology, expanding its potential applications and redefining the relationship between technology and the human body.

1.3.1. E-TEXTILES

The origins of e-textiles can be traced back to the late 19th century, with early innovations such as illuminated headbands used in the ballet *La Farandole* in 1883. However, it was in the latter half of the 20th century, particularly with the development of conductive polymers in 1977, that e-textiles truly began to take shape. This breakthrough allowed for the integration of electronics directly into textile fibres, laying the foundation for the modern e-textiles industry. This was further advanced by a significant milestone in the mid-1990s when researchers at MIT developed wearable computers that incorporated traditional hardware into textiles.^[85,86] Today, the field of e-textiles is witnessing remarkable growth, fueled by the increasing demand for miniaturized, flexible wearable electronics.^[87] This rapid expansion is underscored by market forecasts, with the global e-textiles market size estimated at USD 9.06 billion in 2023, projected to reach USD 11.74 billion in 2024, and expected to grow at a compound annual growth rate of 29.62%, ultimately reaching USD 55.73 billion by 2030. These figures reflect the increasing recognition of e-textiles as a transformative technology with the potential to revolutionize multiple industries.^[88]

The evolution of e-textiles has seen the development of various methods for embedding electronics into fabrics, categorized into distinct generations. The earliest approach, known as *first-generation* e-textiles, involved attaching rigid electronic components directly onto the surface of garments. This technique often used conductive yarn^[89] to embroider soft

electronic modules onto the fabric, creating both electrical and mechanical connections. While this method remains in use and continues to be refined by some sportswear brands, these early e-textiles are typically bulky and inflexible, making them less ideal for everyday wear. Moving beyond this, *second-generation* e-textiles introduced a more integrated approach by knitting or weaving conductive yarns^[90] directly into the fabric structure, resulting in wearables that are more comfortable and functional. This generation is characterized by smart textiles that incorporate sensors and LEDs within the fabric, offering practical applications like muscle activity monitoring and interactive displays. However, despite being softer and more wearable, second-generation e-textiles still face challenges in achieving optimal comfort and adaptability. The *third generation* represents a significant leap forward, with electronics and sensors embedded^[91] directly within the textile fibres themselves. This innovation allows for a seamless blend of technology and fabric, producing e-textiles that are not only more durable and reliable but also more comfortable and user-friendly. Looking to the future, a *fourth generation* of e-textiles is emerging, although still largely in the experimental and prototype stages. These next-generation textiles aim to fully integrate electronic functions into the fabric while maintaining the essential qualities of softness, flexibility, comfort, washability, and durability. This upcoming generation holds the promise of truly seamless wearable technology that could revolutionize how we interact with our clothing.^[86,92]

The methods of e-textile fabrication are diverse and can be broadly categorized into two main approaches: the use of conductive yarns and additive manufacturing. Each approach brings distinct advantages and presents unique opportunities for integrating electronic functionalities into fabrics.

Conductive yarns are designed with diameters closely matching those of conventional textile fibres. These yarns are produced through a variety of sophisticated processes, including dipping,^[93] spraying,^[94] spinning,^[95] pad-drying,^[96] electroless plating,^[97] chemical vapour deposition,^[98] and sputtering.^[99] This technological innovation allows conductive yarns to be seamlessly integrated into traditional textile fabrication methods such as weaving,^[100] knitting,^[101] and embroidery,^[102] enabling the creation of e-textiles that combine electronic functionality with the familiar qualities of conventional fabrics. As a result, it is now possible to create e-textiles that maintain the familiar feel and mechanical properties of conventional fabrics while embedding electronic functionalities within the textile structure. This integration not only preserves the aesthetic and tactile qualities of the fabric but also enhances its versatility, making it suitable for a wide range of applications, from

wearable technology to smart home textiles. Moreover, the ability to use standard textile machinery for the production of e-textiles significantly lowers production costs and simplifies the scaling up of these innovative materials for industrial manufacturing.^[103]

Additive manufacturing techniques are at the forefront of e-textile innovation, enabling the layer-by-layer construction of electronic devices directly onto textile substrates. Additive manufacturing is particularly well-suited for creating highly flexible, stretchable, and comfortable e-textiles, as it allows for precise control over the deposition of functional materials.^[104] Techniques such as screen printing,^[105] inkjet printing (IJP),^[106] roll-to-roll gravure,^[107] flexographic printing,^[108] are commonly employed in this stream. While these methods share the common goal of adding electronic functionality to textiles, they differ significantly in terms of operational complexity, scalability, cost, resolution, substrate compatibility, and material waste.^[107] These techniques enable the integration of functionalities such as sensing, energy harvesting, and communication into textiles, paving the way for advanced wearable devices.

The specific requirements of the e-textile application determine the choice between these fabrication methods. Conductive yarns are often preferred in scenarios where the mechanical integrity and textile-like properties of the fabric must be preserved. In contrast, additive manufacturing techniques excel in applications requiring precision and the integration of multifunctional components.

E-textiles represent a convergence of textile engineering, electronics, and advanced materials, wherein electronic components are seamlessly integrated into fabric structures. This integration enables traditional textiles to perform "intelligent" functions, such as sensing, heat regulation, touch sensitivity, luminescence, data processing, communication, and even energy storage. These functionalities elevate ordinary fabrics into sophisticated wearable devices capable of interacting dynamically with their environment and users.^[86,103,109,110] The versatility of e-textiles has led to their adoption across various sectors. In healthcare, they facilitate continuous monitoring of vital signs, offering a non-invasive and convenient method for patient care, particularly in remote or outpatient settings. Companies like Hexoskin have developed smart garments that monitor respiratory, sleep, activity, and cardiac data, exemplifying the potential of e-textiles in health monitoring.^[111]

In the fitness industry, e-textiles provide detailed activity tracking and performance analysis with enhanced user experience. For example, smart apparel from Athos uses

electromyography to measure muscle performance, enhancing the training experience for athletes.^[112] Additionally, Sensoria's smart socks, embedded with textile sensors, monitor running form and foot pressure, offering real-time feedback to help runners improve technique and reduce injury risk.^[113]

Moreover, in gaming, these textiles enable interactive and immersive experiences, thereby expanding the possibilities for user engagement and performance enhancement. Interactive gaming gloves developed using spider silk-inspired fibres by the National University of Singapore demonstrate how e-textiles can enhance realism and interactivity in gaming environments. These gloves sense and respond to player movements, offering a more immersive gaming experience.^[114] Furthermore, with the growth of esports, smart clothing equipped with sensors to monitor physiological and psychological states is being developed, providing real-time data to optimize player performance in competitive gaming settings.^[115]

Google's Jacquard thread technology, integrated into garments and accessories, allows users to interact with their devices through gestures and touch, illustrating how e-textiles are revolutionizing personal use and entertainment.^[116] Ralph Lauren's PoloTech shirt, equipped with sensors that track biometrics like heart rate and energy output, further highlights the fusion of fashion and fitness technology through e-textiles.^[117]

Beyond consumer applications, e-textiles are making substantial inroads into the military and defence sectors. Here, they are used in uniforms and gear that provide real-time situational awareness, enhancing both the safety and operational efficiency of personnel in the field. Infoscitex Corp., for example, integrates e-textiles in military garments for a variety of purposes, including kinetic energy harvesting, wearable antennas, and personal status monitoring.^[118] Another significant development is the Broadsword Spine by BAE Systems, which incorporates conductive yarns into the fabric to create a lightweight, wearable power and data network, replacing the traditional, heavy equipment carried by soldiers. This technology enhances mobility and operational capabilities for military personnel in the field.^[119] Additionally, the Smart Shirt, also known as the wearable motherboard, acts as a flexible platform that embeds various sensors and conductive fibres to monitor vital signs such as heart rate and respiration, offering critical real-time health monitoring for soldiers.^[120] The ability of these textiles to incorporate advanced functionalities without compromising comfort or mobility makes them particularly suited for such demanding applications.^[86,103,121]

In addition to commercial products, ongoing research continues to push the boundaries of what e-textiles can achieve. For example, wearable sensors for health monitoring are a major area of focus, with studies demonstrating the use of inkjet-printed graphene-based conductive patterns to monitor heart rate.^[122] These advancements have paved the way for more complex applications, such as real-time glucose monitoring for diabetic patients using e-textile patches that integrate biosensors capable of continuous glucose tracking.^[123]

Similarly, the development of textile-based sweat sensors is another breakthrough, where microfluidic systems embedded in fabrics can monitor dehydration and electrolyte imbalance by analyzing sweat composition in real-time, providing crucial data for athletes and healthcare professionals.^[124] Other research has explored the use of graphene-based composite fibres for a wide range of applications, including motion detection, sleep quality evaluation, and pulse monitoring.^[125] Another exciting advancement involves piezoelectric textiles, which can convert mechanical stress into electrical energy. These fabrics could power small wearable devices like LED lights or sensors, and the energy could be stored for future use.^[126]

Energy harvesting is one of the key areas of development. For instance, researchers have developed textile-based triboelectric nanogenerators that harvest biomechanical energy from body movements to power wearable health-monitoring devices. These energy-harvesting textiles enable continuous and sustainable operation without external power sources, offering a practical solution for self-powered e-textiles used in fitness tracking or long-term health monitoring.^[127,128] Another study showed that photovoltaic textiles can be used as potential power sources for small portable devices, highlighting the ability to integrate solar cells directly into fabrics without compromising their flexibility or comfort.^[129] These textiles are particularly promising for outdoor and military applications, where maintaining power for electronic devices is critical.

In addition, MXene-coated yarns have been developed for use in capacitive pressure sensors, which can be knitted into textiles to create clothing capable of monitoring physiological signals and environmental conditions. These MXene-based sensors offer high sensitivity and durability, making them suitable for long-term wear and extreme conditions.^[90] Similarly, carbon nanotube-based fibres are being explored for their use in strain-sensing textiles, which could detect subtle changes in body posture or movement, providing valuable data for physical rehabilitation and sports performance analysis.^[130,131]

Beyond sensors and energy harvesting, there has been significant progress in integrating stretchable and washable batteries into e-textiles. For example, researchers have developed lithium-ion batteries using flexible polymer electrolytes that can be embedded into fabrics without affecting their wearability.^[132,133] Additionally, flexible supercapacitors using graphene^[134] and MXene^[106] have shown great promise for energy storage in e-textiles, providing fast charging and long cycle life without compromising the comfort and flexibility of the fabric.

Furthermore, there has been a growing interest in integrating e-textiles into augmented and virtual reality systems, where wearable garments embedded with sensors can provide haptic feedback. This development has significant potential in gaming, where users can feel physical sensations corresponding to virtual interactions, creating a more immersive experience.^[135] Researchers are also exploring how e-textiles can be used to measure brain activity through electroencephalogram sensors embedded in caps or headbands, opening up possibilities for cognitive health monitoring or even brain-computer interfaces in wearable technology.^[136]

These examples highlight the innovative approaches being taken to enhance e-textile functionality, demonstrating the vast potential of this field to transform various aspects of daily life, from health monitoring and energy harvesting to adaptive clothing, sports performance, and interactive entertainment. The future of e-textiles is bright, with vast potential for further innovation and application. As materials science continues to advance, the boundaries of what can be achieved with e-textiles will expand, offering new opportunities to enhance the functionality and integration of wearable technologies. This ongoing development underscores the critical role of materials science in shaping the next era of human civilization, where the line between fabric and function continues to blur, leading to increasingly intelligent and responsive textiles that seamlessly integrate into our daily lives.

1.3.2. KEY CHALLENGES FOR E-TEXTILE INTEGRATION

The integration of e-textiles into mainstream applications presents several significant challenges. These challenges span across materials science, electronics, textile engineering, and user experience. Overcoming these challenges is crucial to fully realizing the potential of e-textiles in various industries.

Chapter 1: Introduction

One of the foremost challenges in e-textile integration is ensuring the *compatibility* of electronic materials with textile substrates. E-textiles require the seamless integration of conductive materials, sensors, batteries, and other electronic components with fabrics, which are traditionally designed for comfort, flexibility, and breathability. The materials used for electronic components must not only be flexible and durable but also maintain their electronic properties under the mechanical stresses typical of textiles, such as stretching, bending, and twisting.^[137] For example, conductive inks must adhere well to textile fibres without cracking or delaminating over time. Additionally, the electronic materials must not interfere with the textile's tactile qualities, such as softness and breathability, which are crucial for wearable applications. Balancing these requirements is a complex task that requires innovation in both materials science and textile engineering.^[86]

Providing a reliable and sustainable *power supply* for e-textiles is a major challenge, particularly in the development of thin, flat, and flexible energy storage solutions. Conventional batteries, which are often bulky, heavy, and inflexible, pose significant limitations for wearables where comfort and flexibility are paramount.^[86] Integrating these traditional power sources into textiles can compromise the fabric's properties and lead to discomfort for the wearer. Fabric-integrated solutions, such as embedding batteries into textiles, introduce additional complexities in fabrication, including maintaining consistent performance and ensuring safety under mechanical stress.^[110,138–140] In response to this, microsupercapacitors (MSCs) have emerged as a promising solution. MSCs offer several advantages over traditional batteries, including high-power density, long cycle life, fast energy storage and release, mechanical robustness, and compatibility with flexible substrates.^[140–143] The flexibility and thin form factor of MSCs allow them to be integrated directly into textile fibres or fabrics without significantly altering the textile's flexibility or comfort, making them an ideal energy storage solution for next-generation e-textiles. However, MSCs must also meet the stringent demands of wearable technology, such as surviving the mechanical stress and strain caused by bending, stretching, and other deformations typical of textiles.

Durability and *washability*, therefore, remain critical challenges in the development of e-textiles, particularly for products intended for everyday use.^[86] While traditional textiles are engineered to endure repeated mechanical stresses, environmental exposure, and frequent washing cycles, the integration of electronic components introduces significant vulnerabilities. Conductive pathways, sensors, and other electronic elements are

susceptible to damage from the mechanical agitation and chemical exposure inherent in washing processes. For example, repeated bending and stretching can lead to the cracking of conductive inks or the breaking of conductive fibres, while exposure to water and detergents can corrode sensitive electronic components.^[144] A key issue in making electronic garments market-ready on a large scale is ensuring that these components can withstand the harsh conditions of washing machines, tumble dryers, and high-humidity environments. The standard washing test, a reliability protocol used for all garments, is especially critical for e-textiles.^[145] Many current commercial e-textile products require users to remove batteries before washing, complicating usability and limiting practicality. Ideally, energy storage devices would be fully integrated into the textile, allowing the fabric to endure washing, drying, ironing, and even dry cleaning without needing to remove components. To address these challenges, researchers are exploring various strategies, such as encapsulating electronic components in waterproof coatings and developing inherently water-resistant conductive materials.^[146] This encapsulation should be able to preserve the integrity of the e-textile as well as enhance safety for the wearer by preventing direct contact with the electronic components and potential leakage of electrolytes.

Another challenge is manufacturing *scalability* and *cost*. The integration of advanced electronic components into textiles significantly drives up production costs. This is largely due to the extensive research and development required to design, prototype, and manufacture e-textiles that seamlessly incorporate state-of-the-art electronics while maintaining the desirable properties of conventional fabrics. Additionally, many current e-textile fabrication methods, such as hand embroidery of conductive threads or small-scale printing, are not easily scalable for mass production. The integration of electronic components into textiles is often labour-intensive and costly, especially when high levels of precision and consistency are required. Furthermore, the cost of materials, such as conductive inks and speciality fibres, can be prohibitive, limiting the commercial viability of e-textiles.^[86] Achieving scalability will require the development of automated manufacturing processes capable of producing e-textiles at a large scale while maintaining high quality and performance standards.

Sustainable and *biodegradable* development presents another significant challenge in the field of e-textiles. As the industry moves towards greater environmental responsibility, the need to create eco-friendly and recyclable e-textiles has become increasingly pressing.^[86] The sustainability and biodegradability of these textiles depend heavily on the choice of fibres

and the methods used in their production. Synthetic fibres like polyethylene terephthalate (PET), nylon, and polyester, although popular for their durability and versatility, are inherently resistant to biological degradation. This resistance leads to significant environmental concerns, as these materials contribute to persistent waste and pollution. Additionally, the production processes for these synthetic fibres often involve complex and harmful chemicals, further exacerbating their environmental impact.^[147] Thus, managing the environmental footprint of these materials remains a critical issue. In contrast, natural fibres such as cotton, spider silk, and silkworm silk offer a more sustainable alternative. For instance, silkworm silk and cotton are naturally biocompatible and biodegradable, making them excellent candidates for the production of eco-friendly e-textiles. Their ability to decompose without leaving harmful residues is particularly advantageous in the context of sustainable development.^[148–150] Striking a balance between technological innovation and environmental responsibility is essential for the future of e-textiles, ensuring that these developments benefit both the market and the environment.^[86]

The lack of *standardization* in the e-textile industry is another significant barrier to integration. Currently, there is no universally accepted standard governing the materials, fabrication methods, or electronic components used in e-textiles. This absence of standardization leads to significant variability in product quality and performance, making it difficult to ensure consistent functionality across different applications and products.^[86,151] In response to this, significant efforts are being made by organizations like IPC (The Association Connecting Electronics Industries) and AATCC (The American Association of Textile Chemists and Colorists). For instance, IPC has introduced several key standards, including IPC-8921 (requirements for woven and knitted electronic textiles integrated with conductive fibres and yarns), IPC-8952 (a design standard for printed electronics on coated or treated textiles), IPC-8971 (requirements for electrical testing of printed electronics on textiles), and IPC-8981 (requirements for the quality and reliability of wearable e-textiles, including mechanical testing and washability). Another ongoing project of IPC, in collaboration with Japan Electronics Packaging and Circuits Association, is IPC/JPCA-8911 (standards for conductive yarns: evaluating their electrical, thermal, mechanical, and chemical exposure characteristics). AATCC has also made significant contributions, particularly with AATCC EP13 (procedure for evaluating the electrical resistance of electronically integrated textiles), which was also referenced by other international standards, such as IPC-8921, highlighting the collaborative efforts between

these organizations. The development and adoption of these standards are essential for ensuring that e-textile products meet consistent quality and performance.^[152–154]

Addressing issues related to materials compatibility, durability, power supply, interconnection, user comfort, manufacturing scalability, and standardization will require ongoing research and innovation. Collaboration among researchers, manufacturers, and industry stakeholders will be key to developing the next generation of e-textiles that are not only functional but also practical, comfortable, and commercially viable.

1.4. ENERGY STORAGE DEVICES

As the global population continues to expand, fossil fuels remain the dominant energy source. However, increasing consumption rates have highlighted the urgent need for more efficient energy sources and advanced storage technologies. Consequently, renewable energy sources like wind, tidal, and solar power have been more extensively utilised to meet these growing energy demands. In this context, energy storage technologies have gained prominence. The most prevalent types of energy storage devices include fuel cells, batteries, capacitors, and supercapacitors.^[155] The Ragone plot (**Figure 1**) provides a detailed comparative analysis of these electrochemical energy storage systems.

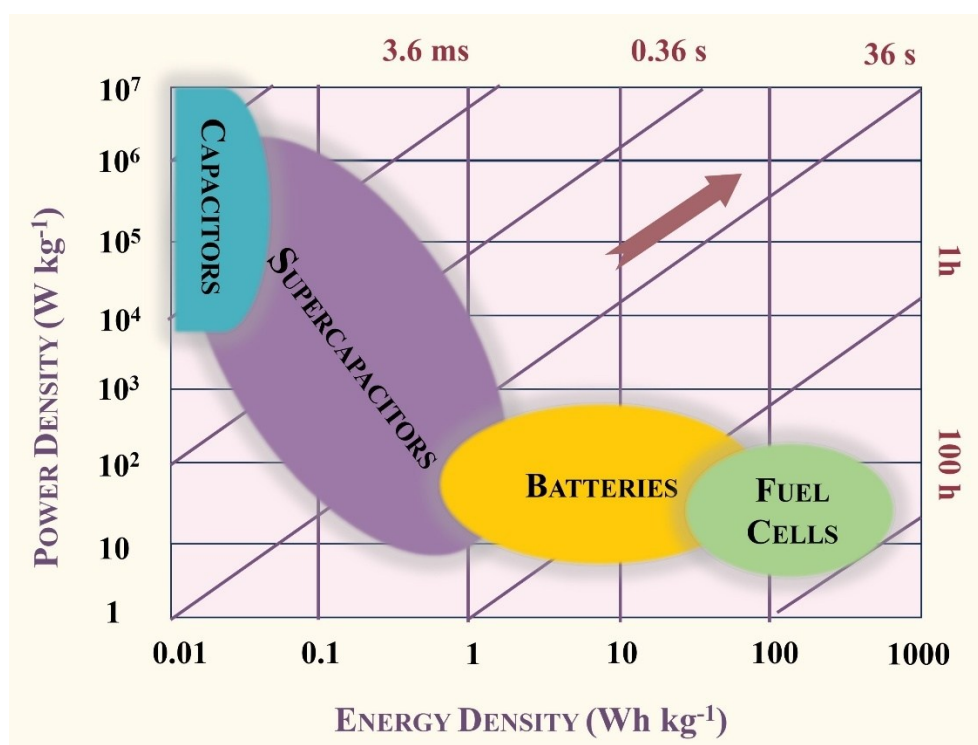


Figure 1: Ragone plot comparing electrochemical energy storage systems, including capacitors, supercapacitors, batteries, and fuel cells. Adapted from Ref^[87].

Ragone plot graphically represents the relationship between *power density* (energy uptake and delivery efficiency, measured in W l^{-1} or W kg^{-1}) and *energy density* (stored and delivered amount of the electrical energy; can be defined gravimetrically as Wh kg^{-1} , or volumetrically as Wh l^{-1}) for each device.^[87] The discharge time capabilities of these devices, indicated by the time scales at the top and right side of the plot, range from milliseconds to hours.^[87]

FUEL CELLS are advanced energy conversion devices that function as thermodynamic systems that harness redox electrochemical reactions to convert chemical energy into electrical energy. Comprising an anode and a cathode separated by an ionically conductive membrane (**Figure 2**), these cells utilize hydrogen as a fuel. At the anode, hydrogen molecules are split into protons and electrons. The electrons flow through an external circuit, creating an electric current, while the protons travel through the membrane. At the cathode, these protons combine with oxygen and electrons to produce water, which is the only byproduct.^[156,157]

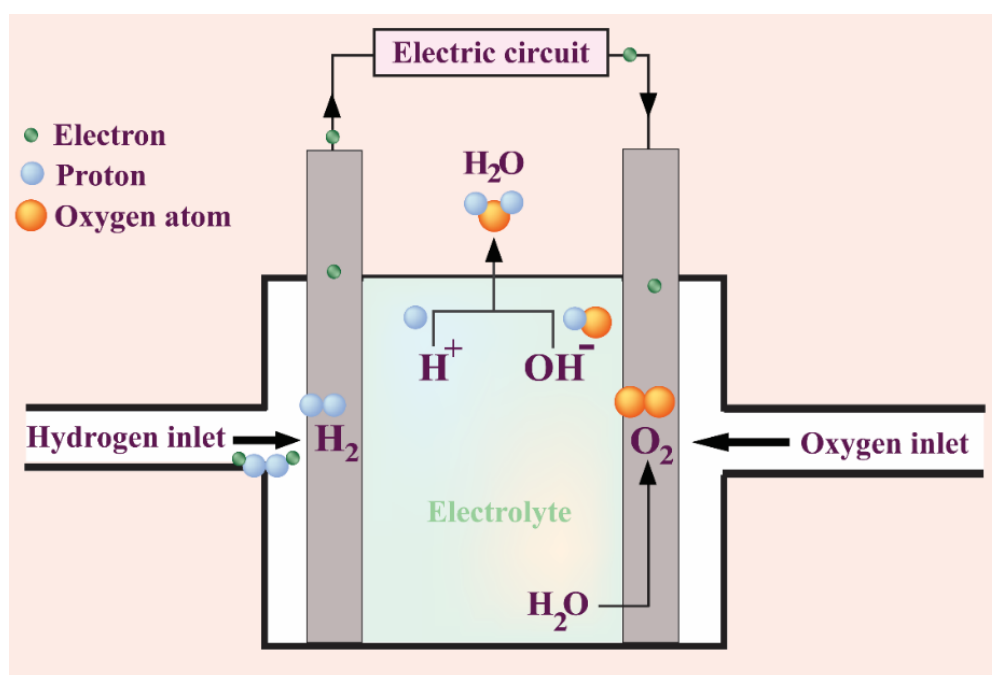


Figure 2: Diagram of a fuel cell, illustrating the electrochemical process where hydrogen at the anode is split into protons and electrons, generating an electric current as electrons flow through an external circuit to the cathode, where they combine with protons and oxygen to produce water. Adapted from Ref^[158].

The efficiency and performance characteristics of fuel cells are highly dependent on the properties of their key components, including the electrolyte, catalyst, cathode, and anode

materials.^[159] Known for their high energy density, fuel cells provide a continuous power supply as long as they have access to hydrogen and oxygen. However, they typically suffer from low power density due to the slow oxygen reduction reaction at the cathode.^[160] Therefore, fuel cells, positioned further to the right in the Ragone plot (**Figure 1**), are known for their ability to store large amounts of energy and deliver it over extended periods, making them suitable for applications requiring sustained power, such as stationary power generation and transportation. Additionally, due to their environmentally friendly and noiseless operation, fuel cells are increasingly being considered for use in powering vehicles, contributing to the reduction of greenhouse gas emissions and noise pollution in urban areas.^[156,157] Despite these advantages, fuel cells face several significant challenges. One major issue is the undefined lifespan, which can vary widely based on operating conditions, complicating the prediction of long-term performance and reliability. The cost of fuel cells remains another critical barrier, as the materials and technologies required for their operation are currently expensive. Furthermore, the lack of an established infrastructure significantly hinders their mass-market adoption.^[156,159]

BATTERIES are situated towards the middle right in the Ragone plot (**Figure 1**), showcasing higher energy density compared to supercapacitors but lower power density and long charging times (up to several hours), enabling substantial energy storage with slower delivery rates.^[161] Batteries, widely used in portable electronics, electric vehicles, and renewable energy systems, offer high energy density, allowing them to store substantial amounts of energy and release it steadily over time.^[162] Lithium-ion batteries, in particular, have become the industry standard due to their high efficiency, energy density, and long cycle life.^[163,164] However, batteries undergo significant volume changes and sometimes phase transformations during cycling. These changes compromise the integrity of the electrode materials over time, which, in turn, drastically reduces the overall lifespan of the device.^[161,165]

Batteries convert chemical energy into electrical energy through redox reactions occurring at the active materials of the positive and negative electrodes within one or more interconnected electrochemical cells separated by an electrolyte. They can be divided into two categories: primary batteries, which are non-rechargeable, and secondary batteries, which are rechargeable by applying an electric current.^[166] A typical lithium-ion battery (**Figure 3**) includes two electrodes, the anode and the cathode, which are immersed in an

electrolyte and separated by a membrane that serves as an electronic insulator and ionic conductor, preventing direct contact between the electrodes to avoid short-circuiting.

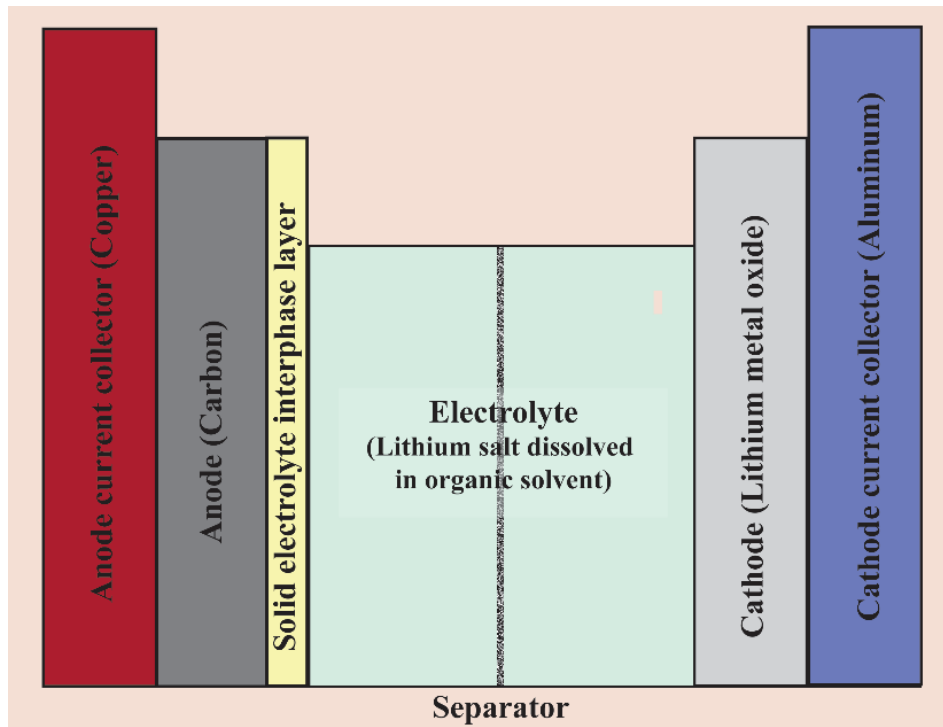


Figure 3: Diagram of a lithium-ion basic battery structure. Adapted from Ref^[167].

The energy storage in such batteries occurs within electrodes made of lithium-intercalation compounds, where oxidation and reduction reactions take place. During charging, lithium ions are extracted from the cathode, travel through the electrolyte, and are inserted into the anode. During discharge, this process is reversed: lithium ions leave the anode, move back through the electrolyte, and re-enter the cathode. The electrons flow through the external circuit and power various devices, completing the cycle.^[164]

CAPACITORS, or more specifically electrostatic capacitors, are electronic devices that function by storing and releasing electrical energy through the separation of charge on two conductive plates (typical parallel plate case in **Figure 4**), which are separated by a vacuum or a dielectric material. When a voltage is applied across the plates, an electric field is established, causing positive charges to accumulate on one plate and negative charges on the other. The dielectric material acts as an insulator, preventing direct electrical conduction between the plates and thereby enabling the storage of energy in the electrostatic field. The capacitance of a capacitor is determined by several factors, including the surface area of the plates, the distance between them, and the dielectric constant of the insulating material.^[168]

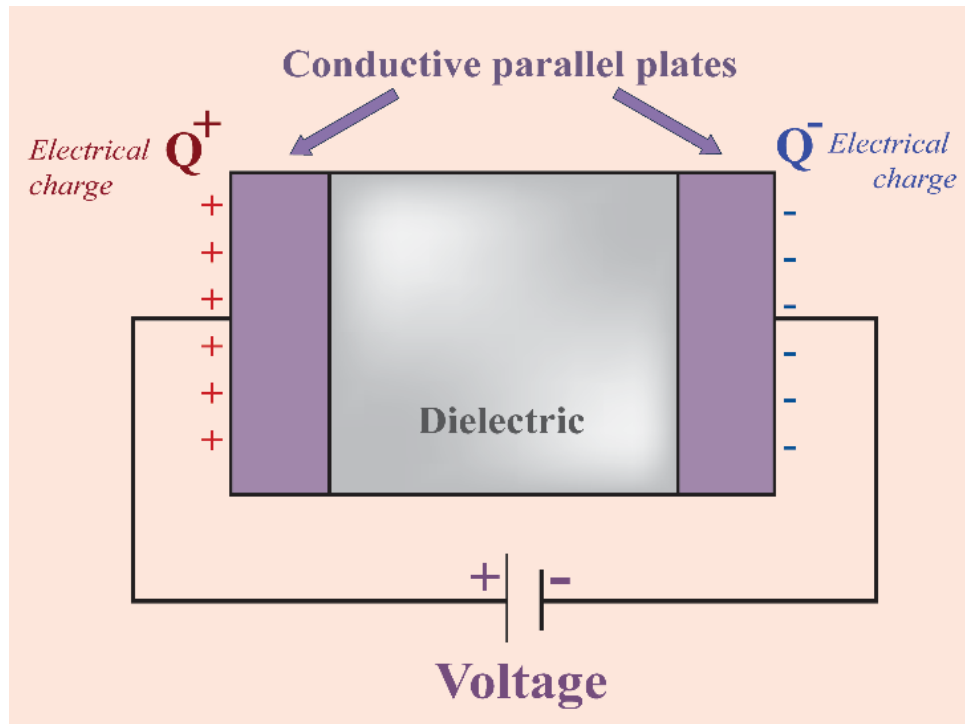


Figure 4: Diagram of a parallel plate capacitor, showing two conductive plates separated by a dielectric material, demonstrating how electric charge is stored on the plates when a voltage is applied across them. Adapted from Ref^[169].

In contrast to fuel cells, capacitors are located in the top-left region of the Ragone plot (**Figure 1**), indicating their ability to deliver high power density with very low energy density, suitable for applications requiring rapid power delivery but minimal energy storage, and so making them ideal for stabilising power supplies and filtering signals in electronic circuits. During the charging process, the capacitor's plates acquire equal and opposite charges, thereby maintaining a net zero charge on the capacitor as a whole. Due to the electrically conductive nature of the plates, a uniform distribution of charge is achieved, leading to the establishment of a potential difference V . The relationship between charge Q (where $Q = |Q^+| + |Q^-|$ and the potential V is governed by the proportionality constant C , which is a capacitance of the capacitor^[168]:

$$Q = CV \quad (1)$$

Capacitance, therefore, based on **Equation (1)**, quantifies the amount of charge required to produce a specified potential difference between the plates. To establish an electrostatic charge on a capacitor's plates, work must be performed by an external driving force. At the onset of charging, the net charge between the plates is zero. When a potential difference is applied, charges begin to accumulate on the conductive plates. As the electric field

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between the plates intensifies, accumulating additional like charges becomes increasingly difficult, necessitating more work. This work, supplied by an external power source such as a battery, converts energy into electric potential energy (**E**), which is stored in the electric field within the dielectric material. The stored energy can be retrieved by discharging the capacitor into a circuit. The work done by a potential difference (**V₀**) for transferring charge on a capacitor is calculated using **Equation (2)**, where the incremental change in charge (**dq**) requires incremental work (**dW**):^[168]

$$dW = Vdq = \frac{q}{C}dq \quad (2)$$

The total potential energy stored in a capacitor is equivalent to the total work performed:

$$E = \int dW = \frac{1}{C} \int_0^q q dq = \frac{q^2}{2C} \quad (3)$$

where the integration is from zero charge to a full charge, **q**. Then, using **Equation (1)**, the stored energy can also be expressed as:

$$E = \frac{(CV_0)^2}{2C} = \frac{CV_0^2}{2} \quad (4)$$

Capacitors can be connected in parallel and in series. When capacitors are arranged in parallel, each capacitor experiences the same potential difference **V₀**. The charge on each individual capacitor **i** is then:^[170]

$$Q_i = C_i V_0 \quad (5)$$

The total charge of the capacitors connected in parallel is:

$$q = \sum_{i=1}^n Q_i = V_0 \sum_{i=1}^n C_i \quad (6)$$

The equivalent capacitance is:

$$C_{eq,p} = \frac{q}{V_0} = \sum_{i=1}^n C_i \quad (7)$$

When capacitors are connected in series to a voltage source with a potential difference V_0 , they experience a sequential charging process rather than having the same potential difference across each capacitor. As a result, each capacitor will theoretically hold the same amount of charge.^[170] The voltage across the plates of each capacitor can be described as:

$$V_i = \frac{q}{C_i} \quad (8)$$

Then,

$$V_0 = \sum_{i=1}^n V_i = q \sum_{i=1}^n \frac{1}{C_i} = \frac{q}{C_{eq,s}} \quad (9)$$

In a series configuration of capacitors, the inverse of the overall capacitance is the sum of the inverses of the capacitances of each individual capacitor:

$$\frac{1}{C_{eq,s}} = \sum_{i=1}^n \frac{1}{C_i} \quad (10)$$

SUPERCAPACITORS, also known as electrochemical capacitors, represent a pivotal advancement in energy storage technology, effectively bridging the gap between traditional electrostatic capacitors and batteries^[171], as shown in **Figure 1**. Supercapacitors are renowned for high power densities (up to 10 kW kg⁻¹),^[172,173] relatively high specific energy (up to 10 Wh kg⁻¹)^[173,174], rapid charge/discharge capabilities (on a second timescale), and exceptional longevity, with lifespans exceeding 100,000 cycles.^[143,170,171] Although their energy density is lower compared to batteries, they excel in the fast delivery of stored charge and exhibit excellent rate capabilities and low maintenance costs.^[155] Furthermore, supercapacitors are highly efficient, with minimal energy loss from cycle to cycle, and can operate across a wide range of temperatures. They are also more environmentally friendly and safer compared to batteries^[168,175,176].

Supercapacitors are increasingly recognized for their versatility and efficiency in modern technology, with applications primarily divided into two categories: backup energy sources and primary energy sources.^[177] In their role as backup energy sources, supercapacitors are typically connected in parallel with a primary power source, such as a battery. This configuration ensures a continuous power supply during outages, voltage drops, or other

disruptions. Historically, supercapacitors have been widely used in devices like memories, microcomputers, and clocks for this purpose. For example, in uninterrupted power supply systems, supercapacitors can serve as temporary backup power, quickly bridging the gap for stationary uninterrupted power supply systems augmented with fuel cells. They are especially suited for providing power during startup and peak load buffering.^[168,171,177] Supercapacitors also show great promise in critical-load operations such as hospitals, banking centres, airport control towers, and cell phone towers. They can effectively bridge the critical time between a power outage and the startup of a generator by providing power within milliseconds to a few seconds after an outage.^[168]

Advancements in energy density have expanded the use of supercapacitors as primary energy sources in various sectors, notably in transportation and portable electronics. In electric vehicles, supercapacitors serve as auxiliary power sources, complementing batteries and fuel cells by providing high energy efficiency, rapid charge-discharge capabilities, and significant energy recovery during braking.^[168,178] This integration is particularly beneficial for enhancing vehicle performance and enabling regenerative braking, which can reduce fuel consumption by approximately 15%.^[177,178] In the realm of portable electronics, supercapacitors are transforming device performance by delivering quick bursts of energy, thereby enhancing functionality and user experience.^[171,177,179]

Despite their numerous advantages, supercapacitors face several significant challenges that must be addressed to enhance their viability as energy storage solutions. A major hurdle is their lower energy density compared to batteries, typically less than 20 Wh kg⁻¹, whereas batteries range from 30 to 200 Wh kg⁻¹.^[175,179–181] Due to their low energy densities, supercapacitors are not yet able to replace batteries fully, and they are currently used alongside them.^[168,175] The expectation is that the high energy densities, low power densities, and limited life cycles of batteries will be effectively complemented by the high power densities, low energy densities, and long lifespans of supercapacitors.^[168] Improving energy density remains a primary research focus, necessitating advancements in manufacturing processes and the discovery of new electrolyte and electrode materials with superior electrochemical performance.

Additionally, supercapacitors require consistent voltage management due to their low-rated voltage (under 2.7 V), which necessitates series connections for practical applications. Overcharging can severely reduce their lifespan, making consistent voltage

monitoring essential.^[182] Furthermore, supercapacitors' capability for instantaneous high-energy throughput demands reliable design frameworks to ensure system stability under varying load conditions and environmental factors, particularly in high-stakes applications such as military and aerospace.^[182]

The rapid development of the supercapacitor industry has also led to disparities in quality and performance, underscoring the need for comprehensive industrial standards. These standards should cover technical specifications, safety requirements, performance testing methods, and guidelines for manufacturing, transportation, recycling, and disposal, promoting cost-effective and environmentally sustainable practices.^[175] Addressing these challenges requires a multifaceted approach, including advanced materials research, innovations in manufacturing, improved design to minimize self-discharge, and the establishment of rigorous standards. With sustained research and development, supercapacitors have the potential to support renewable energy systems and meet the growing demands for portable, wearable, and electric vehicle technologies, underscoring the need for interdisciplinary collaboration and investment to fully realize their potential as a cornerstone of sustainable energy solutions.^[182]

The primary objective of this thesis is the development and optimisation of supercapacitors; accordingly, the subsequent discussions and analyses will focus on these devices in detail.

1.4.1. KEY HISTORICAL MILESTONES IN THE DEVELOPMENT OF SUPERCAPACITORS

The history of supercapacitors is marked by significant milestones that have shaped their development and commercial success. The journey began in 1853 when Helmholtz first explored the charge-storage mechanism of capacitors and introduced the electric double-layer model during his study of colloidal suspensions. This foundational theory provided a crucial understanding of how capacitors store charge, paving the way for future innovations.^[183] In 1957, a major advancement occurred when Becker applied for the first patent for an electrochemical capacitor. This device featured porous carbon electrodes embedded in an H_2SO_4 solution, marking a significant step towards the development of modern supercapacitors.^[168,184] With further modifications, the first practical

supercapacitor was developed by Boos, demonstrating the potential for real-world applications.^[168,185]

The commercialization of supercapacitors took a significant leap forward in 1978 when Japan's NEC Corporation introduced an electrochemical capacitor to the market, coining the term "supercapacitor." This marked the beginning of the recognition and utilization of supercapacitors in practical applications. Further progress was made in 1989 when the USA Department of Energy began supporting long-term research focused on developing high-energy-density supercapacitors. This research aimed to integrate supercapacitors into electric drive systems and hybrid automobile applications, highlighting the potential of supercapacitors in advanced technology and energy solutions.^[186] Today, leading companies such as Maxwell (USA), Nesscap (Korea), and Nippon Chemicon (Japan) have developed a variety of supercapacitors, bringing them into widespread commercial use.^[187] These companies continue to innovate and expand the applications of supercapacitors across numerous industries, demonstrating the significant advancements and ongoing evolution in the field.^[162]

1.4.2. STRUCTURE OF SUPERCAPACITORS

Like most electrochemical energy storage devices, traditional commercial supercapacitors are fundamentally composed of several essential components: positive and negative electrodes, electrolyte, current collector, and separator.^[176,179] Each of these elements plays a crucial role in the device's operation.^[170]

The *positive* and *negative electrodes* are vital for charge storage, each serving as a repository for ions during the charge and discharge processes. The electrode materials store charges, and their choice impacts the energy storage mechanism. Since electrode materials have a high impact on the supercapacitor performance, they have to satisfy the following conditions: having a high electrical conductivity, high chemical and thermal stabilities, large surface area, a mesoporous structure with appropriate pore sizes and pore distributions, a low manufacturing cost, should be lightweight and corrosion-resistant.^[170,188] The scientific progress in nanotechnology plays a crucial role in developing new materials whose properties could be tuned for specific applications. Compared to conventional supercapacitor and battery materials, nanomaterials possess a higher specific surface area, which is critical for applications in the energy storage field. The higher specific surface area allows for enhanced ionic transport, improved electronic

conductivity, higher specific capacities, faster kinetics, more efficient contact of electrolyte ions, faster ion diffusion, more electroactive sites for faradaic energy storage, and high charge/discharge capabilities.^[57,175]

The *electrolyte*, typically a liquid or gel, facilitates the movement of ions between the electrodes, enabling efficient energy transfer. Electrolytes are electronically insulating and ion conductive.^[189] The main requirements for electrolytes include high ionic conductivity, low resistivity, electronic insulation ability, electrochemical stability, wide voltage window, availability at high purity, and low viscosity, volatility, toxicity, and cost.^[143,175] They play a crucial role in determining the power density of supercapacitors on the basis of the equivalent series resistance (ESR).^[170] As ESR decreases, the power density increases; therefore, to minimise ESR, the electrolyte with higher ionic conductivity should be selected.^[179] Supercapacitor electrolytes are typically classified into four types: organic, aqueous, ionic liquids, and solid-state polymer electrolytes. Organic electrolytes, such as tetraethylammonium tetrafluoroborate (TEABF₄) dissolved in solvents like acetonitrile or propylene carbonate, are commonly used in supercapacitors for their ability to provide a wide voltage window and good electrical conductivity. While acetonitrile-based electrolytes can achieve a voltage window of up to 3.5 V, they pose several drawbacks, including higher costs, lower specific capacitance, reduced conductivity, and safety concerns related to flammability, volatility, and toxicity. As a result, propylene carbonate-based electrolytes are often favoured for their safer operation, environmental friendliness, and broader operational temperature range.^[190,191] Aqueous electrolytes, by contrast, provide higher ionic concentration, lower resistance, and superior ionic conductivity. For example, at 25 °C, 1 M H₂SO₄ has an ionic conductivity of ~0.8 S cm⁻¹, and 6 M KOH has ~0.6 S cm⁻¹. Despite these benefits, aqueous electrolytes are limited by a narrower potential window of approximately 1.2 V due to water decomposition.^[179,190] Ionic liquids have gained attention as alternative electrolytes due to their negligible volatility, high thermal, chemical, and electrochemical stability, low flammability, and wide electrochemical stability window of up to 4.5 V. These electrolytes, typically composed of large, asymmetric organic cations paired with inorganic or organic anions, behave like molten salts at room temperature and do not require voltage-limiting solvents. Commonly studied ionic liquids in supercapacitors include those based on pyrrolidinium, imidazolium, and aliphatic quaternary ammonium salts combined with anions such as PF₆⁻, BF₄⁻, TFSI⁻, or FSI⁻.^[190,192]

Solid polymer electrolytes are also increasingly important, particularly in response to the growing energy demands of electronic devices. These electrolytes serve as both ion conductors and separators. Among the three types – dry polymer, gel polymer, and poly-electrolytes. Gel polymer electrolytes are the most extensive. When water is used as a plasticizer, these are known as hydrogel polymer electrolytes, which typically feature three-dimensional polymer networks. Poly(vinyl alcohol) (PVA) has been the most studied polymer matrix due to its ease of preparation, hydrophilicity, excellent film-forming properties, non-toxicity, and low cost. Various PVA-based hydrogel electrolytes, combined with aqueous solutions like H_3PO_4 , H_2SO_4 , KOH, NaOH, KCl, and NaCl, have shown promising results, with PVA/ H_3PO_4 demonstrating the best capacitive performance.^[190,193,194] Wearable and flexible technologies, for example, rely on solid or gel-polymer electrolytes, which offer advantages in the form of minimised internal shortening and leakage and improved flexibility, bendability, and tunability.^[143,179,195]

Current collectors are conductive materials that connect the electrodes to the external circuit, ensuring efficient charge transfer from the active electrode material. They play a crucial role in enhancing the electrochemical performance of supercapacitors by reducing charge transfer resistance between the current collector and the active electrode material, which directly impacts capacitance, cycling stability, and power density. Therefore, selecting an appropriate current collector requires careful consideration of several key factors, including high electrical conductivity (to minimize internal resistance), mechanical strength, thermal and electrochemical stability, lightweight construction, cost-effectiveness, environmental friendliness, and corrosion resistance.^[170]

Separator is a porous membrane that has a primary function to prevent direct contact and electron transfer between the positive and negative electrodes, and so prevents short-circuiting. While acting as a physical barrier, separators must also facilitate the efficient transport of ions between the electrodes, which is essential for the proper functioning of the cell. This ion transfer is enabled by the separator's good ionic conductivity, which allows ions to pass freely while maintaining the necessary electrical insulation between the electrodes.^[170] Typically made from thin, highly porous films or membranes, separators are designed to meet four essential criteria: low resistance to ion transfer, strong electronic insulation, high electrochemical and chemical stability, and solid mechanical strength.^[179] Moreover, the surface morphology, thickness, pore size distribution, and chemical composition of separators can greatly influence the performance of supercapacitors. These factors affect critical parameters like ESR, specific capacitance, and the energy and power

densities of the device. Therefore, careful design and selection of separators are crucial for optimizing the efficiency and reliability of supercapacitors.^[170,179,196] Commonly used materials for separators include cellulose, polymer membranes, and glass fibres, with the choice of material often depending on factors such as the type of electrode, operating temperature, and cell voltage.^[179]

To enhance the performance of supercapacitors, it is essential to consider all these factors simultaneously, aligning them with the desired properties of the device. Each component must be optimized in harmony to achieve improvements in efficiency, reliability, and overall performance. This holistic approach is critical for advancing the capabilities of supercapacitors and meeting the increasing demands of various applications.^[87,175]

1.4.3. MECHANISMS OF ENERGY STORAGE IN SUPERCAPACITORS

Supercapacitors can be classified based on their underlying charge storage mechanisms into three main types: *electrochemical double-layer capacitors* (EDLCs), *pseudocapacitors*, and *hybrid* capacitors. Each type employs a distinct method of storing charge, which influences their performance characteristics and suitability for various applications. EDLCs store charge electrostatically using double-layer electrodes, while pseudocapacitors utilize fast and reversible faradaic processes, such as redox reactions, to transfer charge between the electrodes and the electrolyte, occurring at or near the surface of the electrode material. Hybrid capacitors combine both faradaic and non-faradaic materials to achieve a balanced charge storage mechanism.^[87,175,197]

EDLCs store energy through the electrostatic separation of charges (**Figure 5**). In these electrochemical capacitors, energy storage occurs in the electric double layer (also known as the Helmholtz layer) at the interface between the surface of a conductive electrode and an electrolyte.^[155]

During charging, when a potential is applied between the electrodes, electrons migrate from the negative to the positive electrode. A layer of polarized solvent molecules forms on the electrode surface through Coulomb's force, creating what is known as the inner Helmholtz plane (IHP).^[168] At the same time, counterions from the electrolyte migrate towards the electrode, establishing the outer Helmholtz plane (OHP). This arrangement sets up the characteristic electrostatic double layer (EDL), which functions similarly to a

parallel-plate capacitor, where the OHP acts like a counter electrode, and the IHP, with its polarized molecules, functions similarly to a dielectric.^[198]

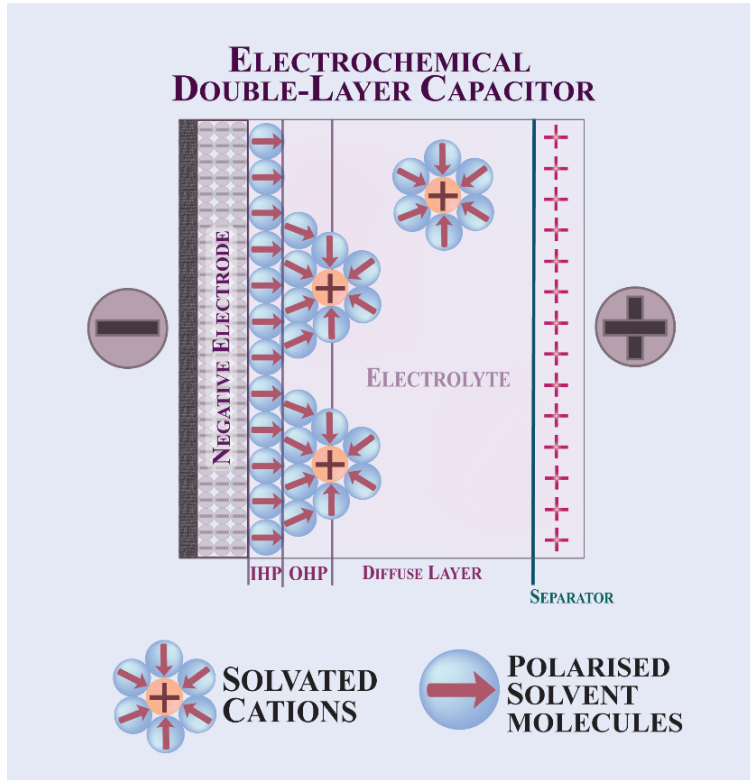


Figure 5: Supercapacitor with EDLC energy storage mechanisms.

Due to thermal fluctuations within the electrolyte solution, net negative (positive) ions are dispersed unevenly, resulting in a higher concentration of these ions near the positive (negative) electrode surface and a lower concentration farther away in the bulk electrolyte solution. This creates the diffuse layer, characterised by a gradient of ion concentration extending from the electrode surface into the bulk of the electrolyte.^[170] The thickness of the diffuse layer is influenced by several factors, including temperature, electrolyte concentration, the charge number carried by the ions, and the dielectric constant of the electrolyte solution. This diffuse layer, combined with IHP and OHP, comprises the complete double-layer structure.

The presence of this diffuse double layer significantly impacts the electrochemical properties and energy storage efficiency of the system.^[168] The double-layer capacitance, therefore, can be estimated as:^[171]

$$C = \frac{\epsilon_0 \epsilon_r A}{d} \quad (11)$$

where ϵ_0 represents the permittivity of vacuum, ϵ_r denotes the relative permittivity of the electrolyte, A refers to the electrode surface area, and d is the effective thickness of the double-layer, which, in this context, corresponds to the charge separation distance, known as the Debye length.^[198] Even though the charge storage mechanism is similar, the significantly greater capacitance of EDLCs compared to conventional capacitors is primarily due to their much larger electrode surface areas and extremely small dielectric distances, on the order of a few Angstroms (0.3–0.8 nm).^[199] These factors enhance the ability of EDLCs to store more charge, resulting in substantially higher specific capacitance and energy density.

Energy in EDLCs is stored through the formation of the double layer, without any charge transfer reactions like faradaic reactions occurring.^[170] Since the energy stored (E) is proportional to the square of the voltage (V) as described by **Equation (4)**, tripling the voltage results in approximately a tenfold increase in the stored energy, assuming the capacitance remains constant.^[171] This charge storage mechanism facilitates rapid energy uptake and delivery, resulting in superior power performance. The absence of chemical reactions during ion movement facilitated by the electrolyte in EDLCs, along with the lack of swelling in the active materials during charging and discharging, enhances the structural stability and longevity of EDLCs.^[155,168,174] As a result, EDLCs are known for their high power density and excellent cycle stability, making them ideal for applications requiring rapid charge and discharge cycles, such as power backup systems and regenerative braking in vehicles.

Despite these advantages, EDLCs face a significant challenge: their limited energy density.^[171] While they excel in power density and cycle stability, their capacity for energy storage is comparatively low. This limitation has driven current research efforts to focus predominantly on enhancing the energy performance of EDLCs and extending their operational temperature range beyond the capabilities of conventional batteries.^[171] Addressing this limitation is crucial for the broader adoption and application of EDLC technology in advanced energy storage systems. Innovations in material science and electrode design are necessary to overcome this challenge and unlock the full potential of EDLCs in various high-energy applications. The primary factors enhancing electrical double-layer capacitance are the porosity and surface area of the material.^[199]

In commercial EDLCs, the choice of electrolyte and electrode materials plays a critical role in determining overall performance. Typically, organic electrolytes in EDLCs are

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composed of conductive salts like tetraethylammonium tetrafluoroborate (TEABF₄), dissolved in solvents such as acetonitrile or propylene carbonate (PC), as previously noted. Acetonitrile offers high salt solubility but poses environmental risks, whereas PC-based electrolytes are more environmentally friendly, providing a wide voltage window, broad operating temperature range, and good electrical conductivity. As a result, TEABF₄/PC has become a widely used electrolyte in EDLC research.^[190,191]

Aqueous electrolytes are divided into acidic (e.g., H₂SO₄), neutral (e.g., Na₂SO₄), and alkaline (e.g., KOH) solutions and are also frequently used in carbon-based EDLCs due to their widespread applicability and effectiveness.^[190,191] These electrolytes generally enable higher capacitance values, ranging from 100 to 300 F g⁻¹, compared to organic electrolytes, where capacitance typically falls below 150 F g⁻¹.^[200]

When selecting ionic liquid electrolytes for EDLCs, the challenge lies in finding options that provide high ionic conductivity, a broad potential window, and a wide operating temperature range. Fluorine-free and solvent-free pyrrolidinium dicyanamide ionic liquids have emerged as promising candidates due to their high ionic conductivity.^[190,192]

In terms of electrode materials, EDLCs mainly employ nanoporous carbons, such as graphene, activated carbon, CNTs, nano-architected carbon, and carbon aerogels. Carbon is particularly appealing as an electrode material for supercapacitors because of its unique combination of properties, including high conductivity, a wide surface area range (~ 1 to > 2000 m² g⁻¹), excellent corrosion resistance, high-temperature stability, controlled pore structure, ease of processing, compatibility with composite materials, cost-effectiveness, availability, established industrial production.^[173,174,199,201–205] Activated carbons are the most prevalent material used for EDLC electrodes, largely due to their affordability and widespread use in commercial applications. The specific capacitance of activated carbon electrodes can range from 40 to 300 F g⁻¹ capacitances depending on the electrolyte and activation method.^[188,206]

Numerous studies have also been done on graphene, as it exhibits outstanding mechanical and morphological properties, excellent electrical conductivity, high carrier mobility, large surface area, and remarkable chemical stability.^[200,207] For example, 3D surface-microporous graphene electrodes were shown to attain up to 200 F g⁻¹ gravimetric capacitance and ultrahigh 1.28 F cm⁻² areal capacitance.^[206] CNTs are also exciting as electrode materials due to their exceptional characteristics, including a highly accessible external structure with a large specific surface area, a complex internal network of

mesopores, excellent chemical and thermal stability, superior electrical conductivity, and low mass density.^[200] For example, in flexible supercapacitor applications, SWCNTs have demonstrated specific capacitances reaching up to 180 F g^{-1} , highlighting their potential as high-performance electrode materials. SWCNTs are also known as promising electrode materials, especially for flexible supercapacitor applications with specific capacitances reaching up to 180 F g^{-1} .^[208,209]

As previously mentioned, the capacitance of EDLCs is impacted by the porosity of the material.^[199] Carbon electrodes are typically engineered with a range of pore sizes to optimize both energy storage and power delivery. Micropores ($< 2 \text{ nm}$) incorporation significantly increases the surface area available for ion adsorption, thereby enhancing the electrode's capacitance. Meanwhile, the presence of mesopores ($2 - 50 \text{ nm}$) and macropores ($> 50 \text{ nm}$) plays a critical role in facilitating efficient ion transport, especially under dynamic polarization conditions. These larger pores serve as pathways that reduce resistance and accelerate ion movement, which is essential for maintaining high power output during rapid charge-discharge cycles.^[177,210,211]

By precisely engineering the electrode structure, paired with the appropriate choice of electrolytes, a well-balanced performance of EDLC can be achieved, combining high energy density with fast charge-discharge capabilities, making them highly effective for a variety of energy storage applications.

PSEUDOCAPACITORS are electrochemical capacitors that store energy through fast and reversible faradaic processes, including redox reactions, electrosorption, and ion intercalation, at the surface or near-surface of the electrode materials.^[168]

Unlike EDLCs, they rely on charge transfer processes involving electron and ion exchange between the electrode and the electrolyte. These faradaic processes enable pseudocapacitors to achieve significantly higher specific capacitance and energy density.^[175] Since electrochemical processes occur both on the electrode surface and within the near-surface bulk of the material, pseudocapacitors achieve capacitance levels that are 10 to 100 times greater than those of EDLCs. However, this increased energy storage capacity comes with certain trade-offs. Pseudocapacitors typically exhibit lower power density than EDLCs because the faradaic processes involved in charge storage are inherently slower than the non-faradaic mechanisms in EDLCs. Additionally, the redox

reactions occurring at the electrode can lead to reduced cycling stability, presenting challenges similar to those encountered in batteries.^[141,177]

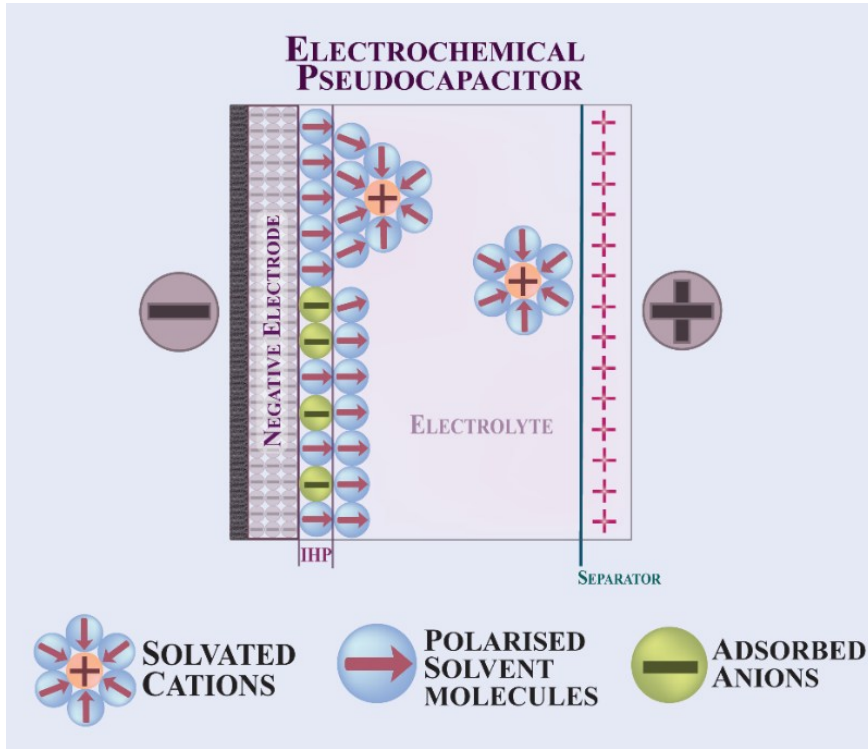


Figure 6: Supercapacitor with pseudocapacitive energy storage mechanism.

The overall faradaic process can be described as:



where $O_{ads.}$ and $R_{ads.}$ represent the oxidized and reduced states of the adsorbed species, respectively, within the electrode material in contact with the electrolyte; and ne^{-} denotes the number of electrons exchanged per active site during the reaction.^[177]

Note that in pseudocapacitors, the charge-storage mechanism involves a combination of the EDLC process and contributions from reversible solid-state redox reactions.^[177] Therefore, the overall capacitance of the pseudocapacitor can be represented as a sum of EDL capacitance and pseudocapacitance associated with the leakage current across the EDL structure due to the faradaic processes within the system.^[141,177]

Three primary faradaic mechanisms that contribute to capacitive electrochemical behaviour, namely, underpotential deposition, redox pseudocapacitance, and intercalation pseudocapacitance, are identified. Each of these mechanisms plays a distinct role in enhancing the overall capacitive performance of materials.^[141]

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Underpotential deposition occurs when metal ions form an adsorbed monolayer on the surface of a different metal at a potential that is higher than their standard redox potential.^[212] This process is exemplified by the deposition of lead on a gold electrode, where a thin layer of metal atoms is adsorbed before bulk deposition begins. This mechanism increases the surface area available for charge storage, thereby enhancing capacitance.^[213]

Redox pseudocapacitance involves the electrochemical adsorption of ions onto or near the surface of a material coupled with a faradaic charge transfer. This mechanism is well illustrated by the behaviour of $\text{RuO}_2 \cdot x\text{H}_2\text{O}$, where ions are adsorbed onto the surface, contributing significantly to the material's capacitive properties. The rapid and reversible redox reactions enable high capacitance values, making this mechanism crucial for materials used in supercapacitors.^[141,212,214]

Intercalation pseudocapacitance occurs when ions intercalate into the tunnels or layers of a redox-active material, accompanied by faradaic charge transfer, but without inducing a crystallographic phase change.^[212] This mechanism is characteristic of materials with layered or tunnelled structures, which permit the reversible intercalation of ions. The absence of phase changes during cycling ensures the structural integrity of the material, contributing to the stability and longevity of the electrode. A typical example of this phenomenon is the intercalation of Li^+ ions into materials like Nb_2O_5 or MnO_2 .^[212,215]

Although these mechanisms arise from different physical processes and involve various materials, they share a common electrochemical signature. This similarity is due to the relationship between the applied potential and the extent of charge development, which is influenced by adsorption/desorption processes at the electrode/electrolyte interface or within the material's inner surface.^[141]

The usefulness of pseudocapacitive materials is often constrained by several key factors, including the reversibility of the redox reactions, the range of reaction potentials, and the associated material costs. The reversibility of redox processes is crucial for maintaining the stability and efficiency of the device over numerous charge-discharge cycles; any deviation can lead to capacity fading and reduced lifespan. Additionally, the reaction potential range directly impacts the energy storage capacity, as a limited range restricts the amount of energy that can be stored and delivered. Furthermore, the high cost of materials,

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particularly those with optimal pseudocapacitive properties, presents a significant barrier to large-scale implementation and commercialization.^[168]

Also, similar to battery systems, redox reactions can induce mechanical stress due to the repeated expansion and contraction of the electrode material during charge and discharge cycles. This volumetric change can lead to significant mechanical instability, causing the electrodes to degrade over time. Consequently, one of the main challenges facing pseudocapacitive materials is their relatively low cycle life, as mechanical degradation reduces the long-term durability and reliability of these devices. Addressing this issue requires the development of more robust electrode materials that can withstand the mechanical stresses associated with redox reactions, thereby enhancing the overall lifespan and performance of pseudocapacitors.^[174]

The choice of electrolyte plays a crucial role in influencing the behaviour of pseudocapacitive materials. For a pseudocapacitive material to be effective in energy storage, its redox reactions must occur within the electrolyte's stability window. The electrolyte not only affects the operating voltage range and reactivity but also has a significant impact on the power output of the entire system. Additionally, the electrolyte can alter the cycle life of the pseudocapacitive material, thus affecting its overall performance in long-term applications.^[168]

Pseudocapacitor electrodes are typically made from transition metal oxides and conducting polymers.^[168,171,216] Transition metal oxides are particularly valued for their high surface area, high ionic conductivity, mesoporous structure, and significant specific capacitance, which enable efficient faradaic reactions on their surfaces.^[170,217] These oxides are also distinguished by their ability to exhibit multiple oxidation states at specific potentials. By selecting materials with multiple stable oxidation states within the potential window of the electrolyte, one can achieve enhanced capacitance.^[168] Additionally, transition metal oxides are less toxic, more environmentally friendly, and more cost-effective.^[218] Among these, ruthenium oxide (RuO_2) stands out as the most extensively researched and widely used, owing to its outstanding reversibility, exceptionally high capacitance, and impressive cycle life. It has demonstrated a gravimetric capacitance of up to 1450 F g^{-1} .^[168,219]

Another notable transition metal oxides are manganese dioxide (MnO_2) and nickel oxide (NiO), which have demonstrated significant potential as supercapacitor electrode materials. MnO_2 is recognized for its specific capacitance values that can reach up to 1380 F g^{-1} , making it particularly promising as a supercapacitor electrode material

due to its excellent cycling stability and cost-effectiveness. Similarly, NiO-based supercapacitors have shown impressive performance, with capacitances ranging from 100 to 1000 F g⁻¹, depending on the synthesis method and the morphology of the NiO electrode. NiO is also environmentally sustainable. However, a common challenge faced by both MnO₂ and NiO-based supercapacitors is their inherently low electrical conductivity. This limitation leads to increased internal resistance, which can restrict power density and overall device performance.^[218]

In comparison to metal oxides, conducting polymers offer higher energy density, lower series resistance, and reduced costs.^[220] These polymers are valued for their relatively high electrical conductivity, ease of synthesis, and cost-effectiveness. However, despite these benefits, the commercial application of conducting polymers in supercapacitors is often limited by their low specific capacitance, poor cyclic stability, and inadequate mechanical durability.^[221] Examples of conducting polymers include polyaniline (PANI), polypyrrole (PPy), polythiophene (PTh), and poly (3,4-(ethylenedioxy) thiophene) (PEDOT), with respective theoretical capacitances of 750 F g⁻¹, 620 F g⁻¹, 485 F g⁻¹, and 210 F g⁻¹.^[222]

The selection of an appropriate electrolyte is crucial for optimizing the performance of pseudocapacitors, as it directly influences the pseudocapacitive behaviour of electrode materials and the overall efficiency of the device. Among strong acid electrolytes, sulfuric acid (H₂SO₄) is the most commonly employed due to its high ionic conductivity and ability to facilitate significant pseudocapacitance. However, the corrosive nature of H₂SO₄ poses challenges for long-term stability. Strong alkaline electrolytes, particularly potassium hydroxide (KOH), are widely used with transition metal oxides like NiO, Co₃O₄, and MnO₂, which exhibit high pseudocapacitance due to efficient ion intercalation and deintercalation processes. The performance of these electrolytes is also affected by the ionic size, with smaller ions, such as Li⁺, promoting better intercalation and higher capacitance. Neutral electrolytes, such as sodium sulfate (Na₂SO₄), lithium sulfate (Li₂SO₄), and potassium sulfate (K₂SO₄), offer a balance between ionic conductivity and electrochemical stability, providing a wider operating potential window compared to acidic and alkaline electrolytes. This results in higher energy densities and improved cycle life, particularly when used with materials like MnO₂. The careful selection and optimization of electrolyte properties, considering factors such as ion size, concentration, and compatibility with electrode materials, are essential for maximizing the pseudocapacitive performance and overall energy storage capabilities of pseudocapacitors.^[179]

MXenes, a family of 2D transition metal carbides, nitrides, and carbonitrides, have emerged as a highly promising class of materials for supercapacitor electrodes.^[223] MXenes are able to exhibit both EDLC and pseudocapacitive behaviour, depending on the specific type of MXene and the electrolyte used.^[224,225] The MXene family is vast and diverse. Among the many MXenes, some notable examples including Ti_2CT_x , $\text{Ti}_3\text{C}_2\text{T}_x$, Mo_2CT_x , $\text{Mo}_{4/3}\text{CT}_x$, $(\text{Mo}_2\text{Ti})\text{C}_2\text{T}_x$, V_2CT_x , $\text{V}_4\text{C}_3\text{T}_x$, and $\text{Nb}_4\text{C}_3\text{T}_x$ are actively being explored for their electrochemical properties.^[225–233] $\text{Ti}_3\text{C}_2\text{T}_x$ is the most extensively researched MXene. When tested in an alkali KOH electrolyte, $\text{Ti}_3\text{C}_2\text{T}_x$ MXene paper has shown a capacitance of 450 F cm^{-3} operating via an EDLC mechanism.^[225,234] However, it is able to demonstrate remarkable capacitance values, achieving up to 900 F cm^{-3} in 1 M H_2SO_4 and 1500 F cm^{-3} in 3 M H_2SO_4 when exhibiting pseudocapacitive behaviour.^[226,235] As an intercalation pseudocapacitive negative electrode material in H_2SO_4 solution, $\text{Ti}_3\text{C}_2\text{T}_x$ possesses several key features that contribute to its performance. The high conductivity of the MXene layers facilitates rapid electron transport, while the layered structure allows for fast ion intercalation and transport along open channels. Additionally, the presence of a transition metal with variable valence states enables efficient charge transfer, and the surface termination with $-\text{O}$ functional groups provides redox-active sites, aligning well with the characteristics of intercalation pseudocapacitive materials.^[190,216,236] A more detailed and comprehensive exploration of MXenes, including their synthesis methods, unique properties, and wide-ranging applications, will be provided in a subsequent Section 1.5.

HYBRID supercapacitors have emerged as a promising solution in energy storage, combining the characteristics of EDLCs with those of pseudocapacitive or battery-like electrodes to optimize device performance. This integration merges the strengths of both systems, allowing hybrid supercapacitors to achieve intermediate performance levels that effectively bridge the gap between traditional supercapacitors and batteries.^[87,174]

The design involves the hybridization of two distinct types of electrodes, resulting in a novel capacitor structure with the energy storage mechanism being a combination of the electrostatic processes typical of EDLCs and the reversible solid-state redox reactions characteristic of pseudocapacitors and battery-like electrodes. The overall performance of a hybrid supercapacitor is thus determined by the synergy between these two mechanisms, as the charge-storage process is governed by both faradaic (redox) and non-faradaic (electrostatic) contributions.^[177] Both EDLC and faradaic capacitance mechanisms operate

simultaneously, although one typically dominates. To achieve high capacitance, the electrode materials must possess key properties such as a large surface area, an optimal pore-size distribution, and high electrical conductivity.^[175]

This approach not only enhances the electrochemical properties within a single cell but also allows for electrochemical behaviour over a broader voltage range. Consequently, this broad voltage range extends the overall operating voltage window and significantly increases the specific energy density – often exceeding that of cells utilizing a single electrode type.^[87] Recent studies have shown that hybrid capacitors are capable of achieving significant specific energy, typically ranging from 36 to 61 Wh kg⁻¹, along with specific power outputs between 500 and 1250 W kg⁻¹.^[237–239]

The primary approach in developing hybrid capacitors focuses on designing devices where the cathode, such as a porous carbon electrode, functions within a broad voltage window in an aqueous solution, while the anode, often a battery-like electrode, operates within a relatively narrow voltage range. Limiting the depth of discharge of the anode is essential to achieving high cyclability, which in turn ensures a longer lifespan for the device.^[177]

It is also crucial to carefully manage the charge balance between the electrodes. The charge exchanged between the anode and cathode must be equivalent, which necessitates the proper selection of active material masses. This balance is essential to prevent water electrolysis at the electrode with lower capacitance (typically the EDLC) during the charge-discharge cycles occurring at the higher capacitance electrode (typically the pseudocapacitor). Generally, the anode has a narrower voltage window compared to the cathode. Therefore, utilizing EDLCs as the cathode and pseudocapacitors as the anode can significantly enhance the stored energy by achieving a higher cell voltage.^[177]

Hybrid supercapacitors can be broadly classified into three main categories: asymmetric hybrids, composite hybrids, and battery-supercapacitor hybrids. Each category represents a different approach to combining the strengths of EDLCs and faradaic materials, tailored to meet specific performance requirements.^[240]

In *composite hybrid* supercapacitors, a single electrode is composed of a composite material that integrates both EDLC and faradaic charge storage mechanisms. This hybrid assembly typically combines carbon materials with either conducting polymers or metal oxides, allowing for dual charge storage through both physical and chemical processes within the electrode. The carbonaceous materials contribute to the EDLC by providing a capacitive

double layer and an expansive surface area; meanwhile, the metal oxides or conducting polymers function as pseudocapacitors, offering high capacity. The increased surface area also facilitates better contact between the embedded pseudocapacitive material and the electrolyte, further boosting the electrode's overall performance. By leveraging the strengths of both EDLC and faradaic mechanisms, these composite materials significantly improve the overall cell voltage, energy density, and power density of the supercapacitor.^[240] For example, by preparing a composite from mesoporous carbon and RuO_2 , a capacitance of up to 243 F g^{-1} could be reached (while mesoporous carbon by itself attains a capacitance of up to 100 F g^{-1}).^[241,242] Another example is a composite of MnO_2 with activated carbon, which can achieve a capacitance of up to 1126 F g^{-1} in 1 M KOH electrolyte.^[241,243] Fabricating hybrid supercapacitors with MXenes is also currently a highly researched topic. For instance, a study showed that $\text{Ti}_3\text{C}_2\text{T}_x/\text{PANI}$ positive electrode can achieve an ultrahigh rate capability and volumetric capacitance of up to 1632 F cm^{-3} .^[244]

Asymmetric hybrid supercapacitors are designed by utilizing two different materials for the positive and negative electrodes, optimizing both energy and power density. Typically, the negative electrode is made of a high-capacitance material such as activated carbon, which operates on the principle of EDLC, while the positive electrode consists of a battery-type material like metal oxides or conducting polymers that undergo faradaic reactions. This combination leverages the strengths of both materials, with the activated carbon providing long-term cycling stability and reversible non-faradaic charge storage and the battery-type material contributing high capacitance. In such systems, the asymmetric configuration is crucial for improving the overall performance of the supercapacitor. For instance, a common example is the use of activated carbon as the negative electrode paired with a conducting polymer as the positive electrode. Although conducting polymers, when used alone, may show limited performance as pseudocapacitors, their incorporation into an asymmetric hybrid supercapacitor enhances efficiency, resulting in elevated power and energy density, along with improved cycling stability. The performance of an asymmetric hybrid supercapacitor is influenced by the operational voltage of each electrode, with the overall electrochemical behaviour determined by the full supercapacitor cell rather than by the individual characteristics of each electrode. This integrated approach in electrode material selection and design significantly enhances the energy storage capabilities of the system, providing a balanced improvement in energy and power densities.^[240,245]

Battery-supercapacitor hybrids are innovative devices that integrate the features of both batteries and supercapacitors within a single system. The battery electrode, made from materials such as lithium intercalated compounds or metal oxides (e.g., LiCoO_2 , LiFePO_4), provides high energy density through faradaic processes. These materials undergo intercalation or conversion reactions, allowing them to store large amounts of energy, albeit with slower kinetics compared to supercapacitors. This is typically achieved by combining a supercapacitor electrode with a battery electrode, often in a series configuration. Such a design enhances the energy and power density of the hybrid device but also ensures rapid energy delivery and prolonged cycling stability, addressing key challenges in energy storage applications.^[240]

As in EDLCs and pseudocapacitors, the choice of electrolyte in hybrid supercapacitors is a critical factor that significantly influences the overall electrochemical performance, stability, and applicability of the device, as it not only facilitates ion transport between the electrodes but also determines the operating voltage window, ionic conductivity, and thermal stability of the supercapacitor. In hybrid supercapacitors, where one electrode may operate on a faradaic (battery-like) mechanism and the other on a capacitive mechanism, the electrolyte must be chosen to accommodate both processes effectively. This involves ensuring compatibility with the electrode materials to avoid detrimental side reactions and selecting an electrolyte that supports the desired voltage window without compromising the device's longevity.^[179]

1.4.4. MINIATURISATION OF SUPERCAPACITORS

The growing importance of compact microscale power sources and self-powered integrated systems is increasingly recognized across various fields, including environmental monitoring, healthcare, medical technology, industrial applications, and military operations. These systems are essential for supporting microelectronics, which typically require low power levels (from nanowatts to milliwatts) to function effectively.^[246–249]

The commercialization of energy storage devices, particularly for portable and wearable applications, hinges on the development of scalable manufacturing methods and advanced nanomaterials that facilitate effective miniaturization.^[250] In the rapidly evolving field of portable and wearable technologies, the demand for compact yet efficient energy storage solutions is critical. Traditional aqueous-based supercapacitors are not well-suited for self-

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powered microsystems due to their bulky design, lack of flexibility, their assembly methods are not compatible with the fabrication techniques used in the microelectronics industry, and the risk of electrolyte leakage caused by gas evolution during charge-discharge cycles. This has led to a growing demand for lightweight, flexible, and ultrathin energy storage solutions, driving the development of MSCs and micro-batteries that are ideally suited for integration into wearable, portable, and miniaturized electronic devices.^[162,251–253]

However, as these storage devices are miniaturized, their energy density often becomes inconsistent due to the reduced size and surface area of the electrodes, which fails to meet the stringent performance standards required for modern applications. To address this issue, there is a pressing need for versatile, reliable, reproducible and smart fabrication and advanced electrode designs with high specific energy densities, whether measured by area or volume, that can satisfy the energy storage demands of microelectronic devices while being integrated within limited spaces.^[142,253]

The term "microsupercapacitor" is used to describe supercapacitor devices that can be seamlessly integrated with microelectronics. These MSCs typically exist in two primary forms: thin-film electrodes arranged in a sandwich structure with a thickness of less than 10 μm or arrays of planar microelectrodes with dimensions on the microscale in at least two directions. More recently, the concept of MSCs has been broadened to include fibre-based electrodes with a core-shell structure.^[246,253]

Supercapacitors are typically constructed in a sandwich configuration, where a separator (electrolyte) is placed between two electrodes.^[254] However, when this design is adapted for MSCs, it introduces several challenges. These include the risk of short-circuiting, dislocation of the film electrodes, and lack of precise control over the distance between the electrolyte and electrodes, which can lead to increased ion transport resistance and power loss.^[142,255] Such limitations underscore the need for more precise fabrication techniques in modern energy storage solutions.

In contrast, the planar interdigitated device (IDD) configuration offers a more suitable alternative for MSC applications. This design is particularly advantageous because it provides a shorter ion diffusion path, greater exposure of electrode materials to the electrolyte, and improved compatibility with microelectronic systems.^[143,254] It also eliminates the need for a separator or membrane, allowing electrolyte ions to move more directly between the electrodes. This streamlined ion transport pathway enhances both the

cycling stability and rate performance compared to the traditional sandwiched MSC configuration.^[251,252]

The basic IDD configuration (**Figure 7**) features finger electrodes and current collectors arranged on the same plane, separated by insulating gaps. The electrolyte is coated on top and between these finger electrodes, facilitating electron transfer along the electrodes.^[254]

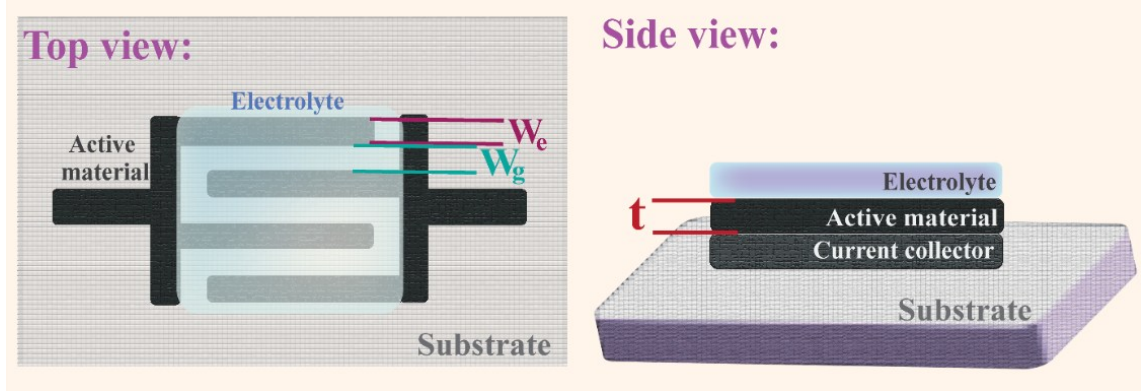


Figure 7: Schematic diagram of the MSC with in-plane IDD electrode configuration, where W_e denotes the width of the finger electrodes with thickness t , and W_g represents the width of the insulating gap.

For MSCs, the overall footprint of the device is typically limited to the centimetre or even millimetre scale. Given that the electrode mass constitutes only a small portion of the device's total mass, the device's size becomes the critical limiting factor. This makes size the primary consideration for miniaturized power generators and energy storage units.^[255] Therefore, performance metrics for IDD-configured MSCs, such as areal capacitance, areal energy, and power densities, are particularly relevant because the weight of the electrodes is minimal compared to the overall device, and the thickness depends on the fabrication method.^[143,254,255]

IDD configurations offer several advantages over conventional structures. They can modify ESR and, in turn, power densities by adjusting the widths of finger electrodes (W_e) and insulating interspacing (W_g). Additionally, specific capacity and energy density can be enhanced by increasing electrode thickness (t) without impacting ion diffusion length and power density.^[254,256,257]

Furthermore, IDD's miniaturization enables seamless integration with wearable and portable electronics on diverse substrates, maintaining mechanical properties and electrochemical performance.^[256] Modifying the interspacing between the adjacent finger

electrodes can impact the average ionic diffusion pathway, ESR, capacitance, energy, and power of the MSC.^[254,258,259] Additionally, if the electrodes are made from highly conductive materials, the design further eliminates the need for metal current collectors, simplifying the device structure while maintaining high performance.^[252] This adaptability makes the IDD configuration a highly promising design for future MSC applications.

One of the key strengths of MSCs is their remarkable cycling performance, capable of sustaining over 100,000 charge-discharge cycles with minimal degradation. This high level of cycling durability ensures long-term reliability, which is critical for various applications. Additionally, MSCs are distinguished by their high power density, enabling them to deliver rapid and efficient energy bursts, a vital characteristic for powering microelectronics. Moreover, their high Coulombic efficiency indicates that they can store and release energy with minimal losses, making them highly effective in applications where both sustained performance and energy efficiency are essential.^[142,143,251]

To achieve optimal performance in MSCs, similar to traditional supercapacitors, the selection of electrode materials is critical, as these materials must balance high surface area, conductivity, and electrochemical stability. Nanomaterials offer significant advantages, including a higher specific surface area, which allows for enhanced ionic transport, improved electronic conductivity, higher specific capacities, faster kinetics, more efficient contact of electrolyte ions, faster ion diffusion, more electroactive sites for faradaic energy storage, and high charge/discharge capabilities.^[57,175] These properties lead to higher specific capacities and more rapid ion diffusion, which are critical for boosting the overall performance of energy storage devices. Furthermore, the versatility of nanomaterials makes them particularly well-suited for integration into portable, flexible, and wearable electronics.^[57]

Porous carbon materials, such as reduced graphene oxide (rGO),^[260] graphene,^[261] small-diameter CNTs,^[262] activated carbon,^[263] and carbide-derived carbon,^[264] are frequently utilized as high-surface-area electrodes in the fabrication of MSCs. These materials exhibit EDLC mechanisms and are particularly valued for their extensive surface areas, which enhance charge storage via electrolyte ion adsorption on the electrode surface. However, this surface-limited charge storage mechanism can restrict the overall energy density of MSCs.^[251,265] To overcome this limitation and boost energy density while preserving other essential electrochemical properties, redox-active pseudocapacitive materials such as transition metal oxides (e.g., MnO_2 ,^[266] RuO_2 ,^[267] Nb_2O_5 ,^[268] WO_3 ,^[269] and Fe_2O_3 ^[270]),

black phosphorus,^[271] conducting polymers,^[272] and electrodes derived from metal-organic frameworks^[273] have been investigated as alternative electrode materials. These materials introduce faradaic charge storage mechanisms, significantly enhancing the energy densities achievable in MSCs.^[251]

The incorporation of efficient 2D electrode materials is vital for enhancing the electrochemical performance of MSCs. In this regard, inspired by the exceptional qualities of graphene, research has expanded to explore other promising 2D materials. These include transition metal dichalcogenides (such as MoS₂, WS₂, MoSe₂, WSe₂, and MoTe₂),^[274] layered metal oxides and hydroxides,^[275] graphitic carbon nitride (g-C₃N₄),^[276] h-BN,^[277] and MXenes.^[223,278] The unique architecture of 2D MXenes, characterized by their conductive transition metal cores and diverse surface terminations, provides abundant electroactive sites and exceptional electron transport efficiency. These features make MXenes ideal candidates for electrodes in high-performance MSCs. To significantly improve the energy density of these devices, it is essential to replace traditional low-capacity carbon-based electrodes with 2D MXenes. Their versatility not only overcomes conductivity challenges but also allows for seamless integration into portable, flexible, and wearable electronics through a range of manufacturing techniques, thereby expanding the application potential of MSCs in advanced electronic devices.^[270]

The *fabrication* process plays a pivotal role in determining the electrochemical performance of MSCs. The methods used to create the electrode structures and devices can lead to significant variations in the final properties due to several critical factors. Firstly, even slight modifications in the fabrication process can result in different microstructures for the same electrode material, directly influencing ion and electron transport within the device. Secondly, the precise dimensions of the electrodes and the spacing between them, which are crucial for the electrochemical performance of MSCs, are also affected by the fabrication technique used.

Common fabrication techniques for MSCs have their respective strengths and limitations, and the choice typically depends on the application.^[257] For example, screen printing^[279,280] and IJP^[258,281] are popular due to their ease of use, cost-efficiency, and suitability for large-scale production. Screen printing allows for the sequential layering of electrode materials and current collectors, making it ideal for manufacturing at scale.^[282] In contrast, IJP provides high precision and flexibility in substrate selection, though it may be less efficient in terms of production speed.^[257]

Photolithography,^[272,283] known for its high-resolution capabilities, is frequently employed to create detailed electrode structures, making it particularly useful for applications that require complex designs. However, this method is more intricate and expensive, which can limit its scalability.^[257] Laser scribing^[284,285] offers a simpler and faster alternative by using a high-energy laser beam to pattern materials, enabling the direct transformation of polymer films into active materials and facilitating the production of high-capacitance devices. This makes laser scribing a compelling option for the production of MSCs.^[257] Mask-assisted filtering^[286,287] is another straightforward and cost-effective method involving the vacuum filtration of liquid electrode materials through a template. While this technique is efficient, it can be limited by the time-consuming preparation of masks and the need for additional steps to transfer the MSCs onto different substrates.^[257] Emerging techniques, such as stamping^[288] with 3D-printed templates and the use of automated scalpel^[289] technologies in combination with coating processes, are also being investigated for their potential to fabricate flexible and high-performance MSCs.^[257]

Aerosol jet printing (AJP) is an emerging technique for fabricating MSCs, offering high precision in producing fine, detailed patterns suitable for complex microscale structures. It supports direct printing of various materials, including conductive inks, onto diverse substrates, making it ideal for flexible and wearable devices. Additionally, it ensures high material utilization with minimal waste, contributing to cost-effective production.^[290–293] However, the process is relatively slow compared to methods like screen printing, which may limit scalability for large-scale manufacturing. Despite this, its ability to create intricate, high-performance MSCs makes it a valuable tool in the field. A more in-depth discussion of AJP will be provided in Section 2.2. Each fabrication method brings its own set of strengths and limitations, and the selection of the appropriate technique can significantly influence the overall performance and scalability of MSCs.

The scale at which fabrication proceeds also plays a crucial role in the electrochemical performance of the printed devices. For instance, nanoscale structuring often requires methods like photolithography and laser processing, which, while precise, are costly and may be limited in scalability. Conversely, direct-writing techniques like inkjet and aerosol jet printing allow for the production of highly structured electrochemical devices at micro-, meso-, and macroscales. This versatility enables extensive performance improvements and control. For example, electronic and ionic conductivities, redox characteristics, active surface area, capacity, energy, and power densities of electrochemical cells can be optimized at the microscale by controlling deposition. At the mesoscale, performance can

be further refined by adjusting the composition of the functional inks. The ability to work on a macroscale facilitates seamless integration with a wide range of substrates, which is critical for developing portable, flexible, and wearable electronics.^[189]

MSCs hold significant potential for a variety of practical applications in advanced technologies. They can function as standalone power sources or be integrated with energy harvesters to enhance the functionality and integration capabilities of various Internet of Things devices.^[294] Their applications extend to self-powered wireless sensors^[295] as well as photoresponsive^[296] and stimuli-responsive systems.^[297] MSCs can be connected in parallel or series to meet specific voltage, capacity, and current requirements, making them versatile for different uses. For instance, when combined with triboelectric nanogenerators, they can efficiently convert mechanical energy into electrical energy, powering devices in wearable and implantable applications.^[298] Furthermore, their integration into radio frequency energy-harvesting systems on flexible platforms demonstrates their potential in autonomous biomedical devices.^[299] Additionally, MSCs offer advantages in AC line filtering, presenting a viable alternative to traditional aluminium electrolytic capacitors by effectively managing AC ripples in electronic devices.^[300]

The advancement of MSCs marks a pivotal step in energy storage technology for modern electronic devices. Through the careful optimization of design configurations, material choices, and fabrication techniques, MSCs are being engineered to meet the stringent demands of compact, flexible, and high-performance electronic systems. This synergy of innovation across various aspects of MSC development ensures that these devices not only deliver exceptional electrochemical performance but also integrate seamlessly into a wide range of applications.

1.5. OVERVIEW OF MXENES

MXenes, a groundbreaking family of 2D nanomaterials discovered in 2011,^[301] have rapidly become a game-changer in the field of materials science, igniting unprecedented interest across diverse research areas. Their unique combination of exceptional properties, such as unparalleled electrical conductivity (up to $\sim 24,000 \text{ S cm}^{-1}$),^[302] prominent hydrophilicity,^[303] vast specific surface areas (up to $\sim 368 \text{ m}^2 \text{ g}^{-1}$),^[304,305] tunable work functions,^[306] biocompatibility,^[307] excellent thermal stability (above 1000°C under vacuum),^[308] and remarkable mechanical properties^[309], has unlocked new possibilities for innovation. These materials are revolutionizing applications in energy storage,^[310,311] catalysis,^[312,313] energy harvesting,^[314,315] environmental remediation,^[316,317] electronics,^[318,319] and nanomedicine.^[320,321] The versatility and potential of MXenes to address critical challenges in these fields make them one of the most exciting advancements in recent scientific history, poised to shape the future of technology and industry.

MXene is a family of 2D layered transition metal carbides, nitrides, and carbonitrides with the general chemical formula $\text{M}_{n+1}\text{X}_n\text{T}_x$. Here M represents early transition metal (e.g. Sc, Y, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W), X denotes C and N, and T_x indicates the surface terminations originating from the etching (e.g., -F, -Cl, -O, -OH, -Br), with n ranging from 1 to 4. This formula also reflects the arrangement within MXene materials where $[n+1]$ M layers cover $[n]$ X layers in $[\text{MX}]_n\text{M}$ manner.^[322–326] The unique structure of MXenes, characterized by their 2D layers and surface terminations, contributes to their outstanding properties. The transition metal layers provide a high density of d-electrons, contributing to metallic conductivity, while the surface terminations introduce hydrophilicity and versatility for chemical modifications. MXenes exhibit a hexagonal close-packed crystal structure with a $\text{p6}_3/\text{mmc}$ space group symmetry. In this structure, the transition metal atoms at the M sites form a close-packed arrangement, while the X atoms are positioned in the octahedral sites between the M atomic layers.^[223]

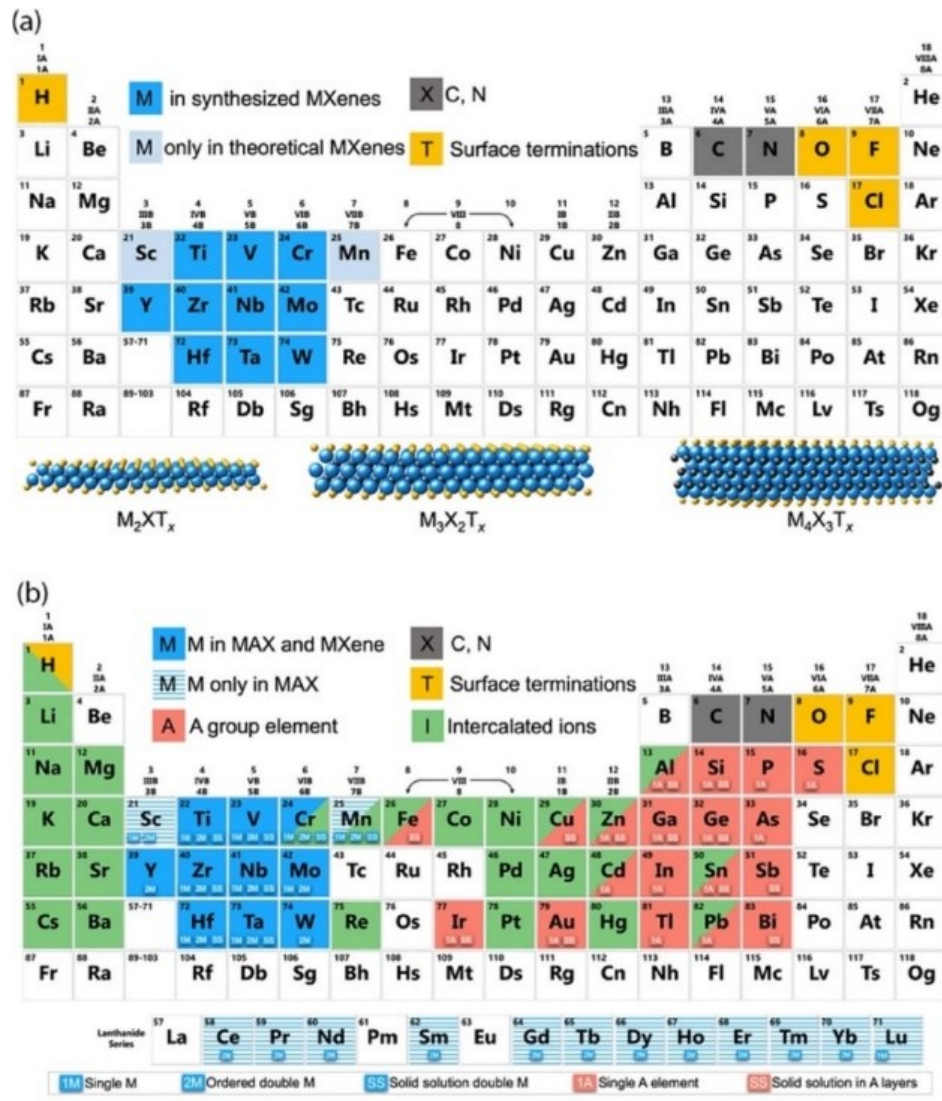


Figure 8: Periodic tables showing compositions of MXenes and MAX phases. (a) Elements used to build MXenes. The bright blue elements represent MXenes that have not yet been experimentally confirmed. The schematics of three typical structures of MXenes are presented at the bottom. (b) Elements used to build MAX phases, MXenes, and their intercalated ions. The elements with a blue-striped background are only reported in MXene precursors (MAX phases), and their MXenes have not yet been synthesized. The elements on the red background are the A elements in MAX phases that can potentially be selectively etched to make MXenes. The green background shows the cations that have been intercalated into MXenes to date. As per the legend at the bottom, 1M and 1A indicate the possibility of the formation of a single (pure) transition metal and A element MAX phase (and MXene). SS indicates the existence of solid solutions in transition metal atomic planes (blue) or A element planes (red); 2M shows the formation possibility of an ordered double-transition metal MAX phase or MXene (either in-plane or out-of-plane). Reprinted with permission from Ref^[327]. Copyright (2019) American Chemical Society.

MXenes are synthesized primarily through two approaches: a *top-down strategy*, which involves the selective etching and exfoliation of MAX phase precursors to produce MXene nanosheets, and a *bottom-up strategy*, which constructs MXene structures directly from atomic or molecular building blocks, allowing for precise control over their composition and morphology. The top-down method remains the most prevalent due to its simplicity and effectiveness, while the bottom-up approach offers the potential for tailoring material properties at the nanoscale. The synthesis conditions play a crucial role in determining the morphology, quality, surface termination, and overall properties of MXenes.^[216]

The top-down technique involves a wet chemical etching process, in which MXenes are primarily synthesized by selectively etching away the reactive A layers from the precursor MAX phases. To understand this process, it is important first to discuss MAX phases, which are a family of layered ternary carbides or nitrides with a unique structure.^[328]

MAX PHASES are layered ternary carbides and nitrides with a general chemical formula $M_{n+1}AX_n$, where M again denotes transition metals (e.g., Sc, Ti, Zr, Hf, V, Nb, Ta, Cr, and Mo), X is C and/or N and $n = 1, 2$, or 3 . A denotes a group 13-16 element (e.g., Al, Ga, In, Si, Ge, Sn, P, As, S, and so on).^[328–330] The chemical formula of MAX phases indicates that transition metal carbides and nitrides, $M_{n+1}X_n$, are interleaved or "glued" with A elements.^[223,323]

MAX phases possess unique properties such as ease in machinability, high damage tolerance, and extreme thermal shock resistance, and some also show oxidation resistance (e.g. Ti_3AlC_2).^[322,331,332] The remarkable properties of MAX phases are attributed to their unique layered structure and the nature of their bonds. The bonds between M and X are strong with mixed metallic/ionic/covalent character, while the bonds between M and A are weaker and are purely metallic.^[323,333] This distinct combination of bonding strengths contributes to the overall stability and versatility of MAX phases, making them suitable for a wide range of applications, such as high-temperature structural materials, protective coatings, sensors, electrical contacts, microelectromechanical systems, and more.^[328]

MAX phases have a hexagonal crystal structure with the space group $p6_3/mmc$. This hexagonal arrangement is maintained in MXenes after the selective etching of the A layers, resulting in MXenes that also have a hexagonal crystal structure with the same space group.^[328] The most common approach for synthesizing MAX phases is through solid-state reactions, such as pressureless sintering. In this method, a mixture of elemental powders or compounds is heated in a crucible under a protective atmosphere at temperatures ranging from 1,000 °C to 1,700 °C for several hours to days. This process ensures the formation of the desired crystalline structure while allowing for precise control over the final material properties.^[332]

Other synthesis techniques, including hot-pressing,^[334] spark plasma sintering,^[335] and self-propagating high-temperature synthesis,^[336] provide alternative routes to achieve the necessary phase formation.^[332] Innovative methods, such as microwave-assisted heating,^[337] allow for rapid temperature increases up to 1,000 °C within minutes, offering

a quicker and energy-efficient pathway to synthesize MAX phases. Additionally, molten salt-assisted synthesis^[338] has emerged as a novel approach, enabling the direct formation of MAX phases under controlled conditions.

For thin films, MAX phases are commonly produced using physical vapour deposition techniques,^[339] which utilize either elemental or compound targets to achieve the desired film composition and structure. Other methods, including chemical vapour deposition^[340] and thermal spraying,^[341] expand the range of available synthesis options. Moreover, a sol-gel-based approach,^[342] involving water-soluble metal precursors and various gel-promoting agents, provides yet another method for synthesizing MAX phases, offering milder reaction conditions and greater processability.^[332]

The chemical composition and synthesis method of the MAX precursors significantly influences the chemistry of the resulting MXenes. The properties, performance, and applications of MXenes are further determined by several factors, including the content and form of the material (such as powder, colloidal solution, film, or fibre), the quality and type of surface terminations (which are influenced by the etching methods), the intercalated species, and the size and quality of the flakes.^[343–346]

With an understanding of the layered structure and composition of MAX phases, the focus can now shift to their role in the synthesis of MXenes. Although the bonds between M and A in the MAX phases are weaker than those between M and X, they are still strong enough that removing the A element through mechanical exfoliation is challenging.^[343] However, the A layers are more chemically reactive, which allows for their selective removal via etching to produce MXenes.^[323] This selective etching process is crucial for transforming the 3D MAX phases into 2D MXene sheets. The key to successful synthesis lies in carefully balancing the temperature and activity of the etchant to effectively remove the A layers while preserving the $M_{n+1}X_n$ structure. Different etching methods and conditions can be tailored to achieve specific MXene characteristics, such as layer thickness, surface terminations, and overall morphology.^[223]

1.5.1. MXENE SYNTHESIS

To accomplish this, various *top-down methods* have been developed, each utilizing different chemical reactions and processing conditions to achieve the desired etching effect. These methods, which include hydrofluoric acid (HF) etching,^[343] in-situ HF generation

using fluorine-containing salts etchants (e.g. $(\text{NH}_4)\text{HF}_2$,^[347] $\text{HCl}/\text{NH}_4\text{F}$,^[348] HCl/NaF ,^[348] HCl/KF ,^[348] HCl/FeF_3 ,^[349] and HCl/LiF ^[226,350]), alkali-based etching (with TMAOH/HF),^[351] electrochemical etching^[352,353] (with dilute aqueous HCl electrolyte), and molten salt etching (molten fluoride salt,^[354] Lewis acidic melts,^[355] ammoniation^[356]), are designed to precisely control the removal of A layers from MAX phases.^[216] Important to note that MXenes may also be synthesised from non-MAX phase precursors also by etching techniques (e.g. $\text{Zr}_3\text{C}_2\text{T}_x$ MXene from $\text{Zr}_3\text{Al}_3\text{C}_5$;^[357] Mo_2CT_x MXene from $\text{Mo}_2\text{Ga}_2\text{C}$ ^[358]).^[328]

Among these methods, HF and HCl/LiF etching are particularly prominent due to their effectiveness in selectively removing A layers and producing high-quality MXenes with controlled surface terminations. HF etching is the most established technique and involves directly using aqueous hydrofluoric acid to selectively remove the A element from MAX phases. This method is highly effective in producing MXenes with a range of surface terminations, predominantly $-\text{F}$ and $-\text{OH}$.^[359] The etching conditions: HF concentration, temperature, and time, are crucial in determining the surface chemistry and structural properties of the MXenes.^[216] The reaction between HF and the A-group elements (e.g., Al in Ti_3AlC_2) produces soluble byproducts like AlF_3 and forms terminal groups on the MXene layers.^[360,361]

MXenes synthesized via HF etching typically have an accordion-like morphology due to van der Waals and hydrogen bonding between the layers.^[301] Milder etching conditions, however, produce thicker multilayer structures with more open interlayer spaces, enhancing ion accessibility and capacitance, reducing defect concentrations, and improving mechanical and electrical properties.^[216,362] Additional delamination is often necessary to achieve monolayer or few-layer MXenes. Mechanical exfoliation methods, such as scotch tape^[363] and ultrasonication,^[364] can separate MXene layers but often result in low yields with the scotch tape method or increased defects with ultrasonication.^[216] MXenes can also be delaminated by chemical intercalation with organic molecules like dimethyl sulfoxide (DMSO),^[365] hydrazine,^[365] urea,^[365] N,N -dimethylformamide,^[365] isopropylamine ($i\text{-PrA}$),^[366] tetrabutylammonium hydroxide (TBAOH),^[367] n -butylamine,^[367] and choline,^[368]. The choice of intercalant depends on the MXene and can affect the properties of resultant MXene differently, and should be, therefore, chosen depending on the application requirements.^[216]

While HF etching is widely used for synthesizing MXenes due to its efficiency in selectively removing A-group layers, the method comes with significant drawbacks, particularly concerning safety and the generation of MXenes with undesirable surface terminations, such as high levels of -F groups. These -F terminations can negatively affect the electrochemical performance of MXenes, especially in applications where high capacitance and specific surface functionalities are critical. Moreover, the hazardous nature of hydrofluoric acid necessitates stringent safety measures and handling protocols, making the process less practical for large-scale synthesis.

To address these issues, a milder and safer alternative, HCl/LiF etching, was developed. Unlike HF etching, HCl/LiF etching introduces Li^+ ions that intercalate between the MXene layers, facilitating delamination and resulting in larger, high-quality flakes with fewer defects. The optimal concentration, typically 7.5 M LiF in 9 M HCl, enables delamination through simple hand-shaking, eliminating the need for sonication or additional intercalation.^[343] MXenes synthesized through HCl/LiF etching exhibit superior hydrophilicity due to the presence of -O surface groups and a high negative surface charge, as evidenced by zeta potential measurements ranging from -30 to -80 mV.^[216] This high hydrophilicity allows these MXenes to be readily dispersed in water, making them suitable for a variety of solution-based processing techniques, such as spin coating,^[369] spray coating,^[370] printing,^[106] direct writing,^[371] and electrophoretic deposition.^[372] Furthermore, the presence of Cl^- anions during etching results in -Cl terminations, which are found to adsorb on the edges of MXene flakes, can enhance interlayer spacing, and potentially assist delamination.^[373] Compared to HF etching, HCl/LiF etching produces MXenes with fewer -F terminations and more -O terminations, which is beneficial for electrochemical applications as excessive -F groups can reduce capacitance.^[323,344] The choice between HF and HCl/LiF etching ultimately depends on the desired properties of the MXenes and the specific requirements of the application.

While top-down methods are the most commonly used for MXene synthesis, *bottom-up* strategies such as chemical vapour deposition and atomic layer deposition also exist and offer alternative approaches. These techniques allow for the direct synthesis of MXenes from atomic precursors, providing precise control over thickness, composition, and structure.^[216,374,375]

Each synthesis approach, whether top-down or bottom-up, leads to MXenes with different structures and surface chemistries. Therefore, it is crucial to select the appropriate

synthesis method based on the desired properties and specific application requirements. There is ultimately no single method that "fits all"; each technique must be tailored to achieve the optimal characteristics for the intended use.

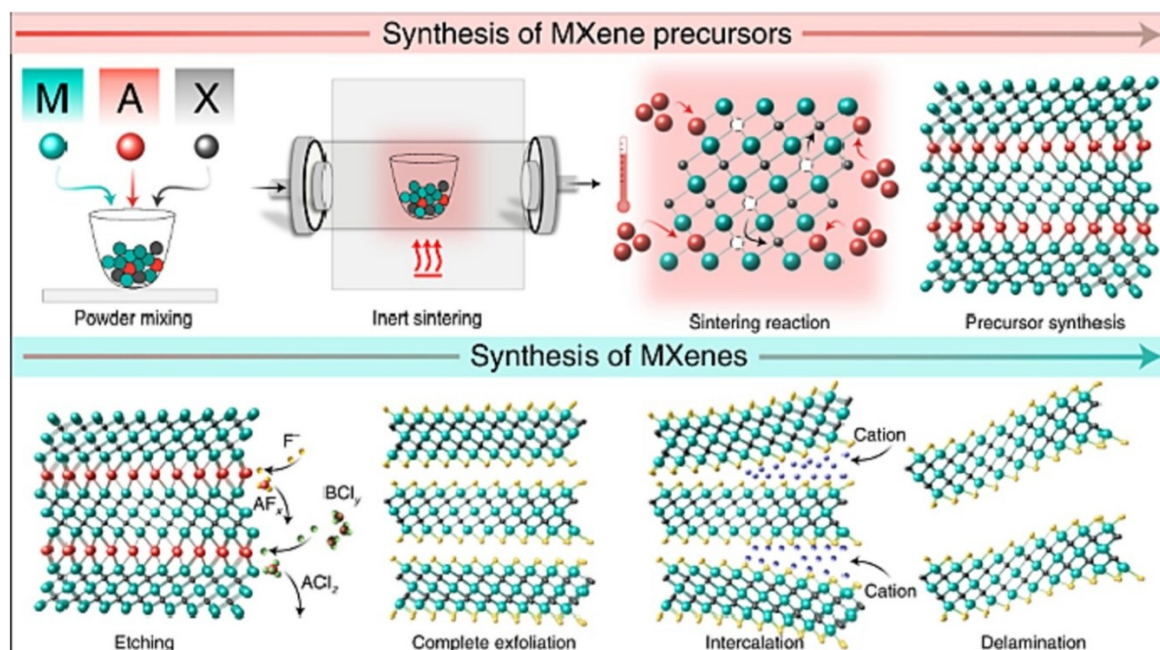


Figure 10: The synthesis of different MXene precursors and MXenes. Reprinted with permission from Ref^[376]. Copyright (2022) Nature Synthesis.

In summary, the extraordinary properties of MXenes unlock a diverse spectrum of applications across numerous fields, pushing the boundaries of what is possible and shaping the future of science and technology.

1.5.2. MXENE E-TEXTILES

MXenes, with their superior electrical, mechanical, and electrochemical properties, are swiftly becoming the material of choice for e-textile innovations, where functionality meets flexibility in a groundbreaking way. Its distinctive characteristics enable a fusion of flexibility and functionality, making it an ideal material to seamlessly integrate cutting-edge technology into the fabrics of our daily lives.

Fibres and yarns form the backbone of the textile industry, and the growing interest in wearable electronics has spurred the demand for fibres and yarns that can be seamlessly integrated into everyday clothing. These fibres must offer high flexibility, mechanical strength, and thermal stability to meet the requirements for textile-based applications. Several methods have been developed to produce functional fibres and yarns incorporating

Ti₃C₂T_x MXenes, such as dip coating, spray coating, electrospinning, wet spinning, and biscrolling. These fabrication techniques can be classified into two main approaches: (i) coating MXene flakes onto pristine fibres/yarns and (ii) developing free-standing fibres/yarns from MXene flakes or MXene/polymer composites.^[377]

Dip coating of woven or knitted fibres or yarns presents a simple, scalable technique for the fabrication of conductive materials. In this process, fibres or yarns are directly immersed in a dispersion of MXene, followed by solvent removal via evaporation. This method has been successfully employed to coat pristine cellulose yarns with Ti₃C₂T_x MXene, producing conductive fibres suitable for textile-based devices. The resulting MXene-coated yarns achieved electrical conductivities up to 440 S cm⁻¹,^[90] approximately three times higher than that of carbon-based materials.^[377,378]

Another method to incorporate MXene into textiles involves transforming MXene dispersions into fibre structures, using techniques such as wet spinning,^[379,380] electrospinning,^[381,382] and biscrolling.^[383,384] Wet spinning, in particular, is an efficient method for fabricating high-performance polymeric fibres. In this process, a material solution is extruded through a spinneret into a coagulant bath to form continuous filaments.^[377] This technique was used to produce pure MXene fibres with high conductivity (up to 7713 S cm⁻¹) and continuous lengths of up to one meter.^[385]

Electrospinning is another versatile technique for creating fibres with a high surface-area-to-volume ratio and intricate structures. This method involves using electric power to produce charged threads of polymer solutions or melt fibres, which are then collected on a substrate.^[377] Electrospinning can produce MXene composite fibres, such as MXene/PAN carbonized fibres, which maintain high conductivity while enhancing mechanical properties through polymer integration.^[386] Bath electrospinning, a modified version of electrospinning that uses a liquid collector, allows for higher MXene content and has been used to produce highly conductive MXene/nylon nanoyarns.^[377,379]

Biscrolling is a unique process where a guest material (e.g., MXene) and a host material (e.g., CNT sheet) are used to produce yarn by twist-based spinning. This method allows for high MXene loading (up to 95 wt.%) and produces highly conductive and mechanically strong fibres, making it ideal for wearable smart garment applications.^[377,387]

Beyond integrating MXene into fibres and yarns, MXenes can also be coated directly onto textile substrates using various methods, including dip coating, spray coating, drop casting,

spin coating, screen printing, and rod casting. These coating methods are generally low-cost, facile, and effective, requiring minimal equipment and infrastructure, making them ideal for large-scale applications.^[377,388]

Similar to its application on fibres and yarns, dip coating has been widely utilized to coat MXene onto textiles. In this process, entire fabric pieces are immersed in an MXene dispersion, followed by a drying step to remove residual solvents. This method produces MXene-coated fabrics with excellent electrical conductivity and robust bonding between the MXene and the textile substrate. However, achieving precise control over the coating thickness remains a challenge, which may impact the uniformity and overall performance of the final product.^[377,389]

Spray coating is a straightforward and rapid method for applying MXene coatings to textiles. In this process, MXene ink is sprayed onto the textile substrate, creating a uniform coating layer. This method has been used to produce MXene-coated textiles with low sheet resistance, high flexibility, and excellent air permeability that are suitable for various applications, including joule heating, EMI shielding, and strain sensing.^[377,390,391]

Drop casting is another technique for depositing MXene layers on textile surfaces. This method involves directly depositing MXene dispersion onto a substrate, followed by drying to achieve the desired coating. Drop casting can produce MXene-coated fabrics with uniform coverage and high conductivity, which are suitable for use as free-standing electrodes in e-textile applications. However, achieving uniform thickness distribution can be a challenge as well, potentially impacting the electrical and mechanical properties of the coated textiles.^[377,392]

In addition to the methods mentioned above, other techniques for depositing MXenes and their hybrid films on fibre surfaces have been explored. These methods include IJP,^[106] which offers precision in patterning and is suitable for creating intricate designs on textiles. Spin coating,^[393] that allows for uniform thin-film deposition, ideal for applications requiring smooth coatings. The vacuum-assisted layer-by-layer assembly^[394] strategy enables the creation of multilayered MXene films with controlled thickness and composition. The roll-to-roll dyeing^[395] process is a scalable approach that integrates MXenes into textiles for large-scale manufacturing. Sol-gel vacuum filtration^[396] is another effective method, particularly for producing MXene-based fabrics with enhanced mechanical and electrical properties. More comprehensive details on printing techniques,

including the nuances of MXene-based ink formulations and printing processes, will be explored in the next chapter.

Integration of MXenes into textiles has opened new avenues for advanced applications. The use of MXene in *energy storage* devices, especially electrochemical capacitors, shows great promise due to its excellent metallic conductivity, redox-active surface, and layered structure. MXene-coated textiles have been designed for supercapacitor applications, offering high capacitance and outstanding durability across many charge-discharge cycles.^[397,398] One study explored the fabrication of high-performance wearable conformable solid-state supercapacitor devices using MXene-coated carbon textiles. The simple and scalable process involved painting MXene ink onto an N-doped carbon fibre textile substrate. The resulting MXene-decorated textile capacitor achieved high spatial energy density ($277.3 \mu\text{Wh cm}^{-2}$) and excellent retention (90% capacitance after 30,000 bending cycles). This demonstrates the feasibility of using MXene-coated textiles for everyday energy storage applications, such as powering wearable electronics and portable devices.^[399] Another innovative approach involved the development of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene-coated nylon for textile-based energy storage devices. Using a bath electrospinning method, the researchers produced MXene-coated yarns that were seamlessly integrated into knitted textiles for supercapacitor applications. These textile-based supercapacitors demonstrated high capacitance (up to 707 mF cm^{-2}) and excellent cycle stability, maintaining performance over 10,000 cycles. This study marks a crucial advancement toward the large-scale production of MXene-based conductive yarns and 3D knitted energy storage devices.^[400]

Energy harvesting is another exciting application area for MXene-based textiles, particularly for developing triboelectric nanogenerators (TENGs) that convert mechanical energy (e.g., exercise, hand clapping/tapping, breathing) into electrical energy.^[377,401] A recent study demonstrated the fabrication of a fabric-based MXene/silicone nanocomposite TENG using a scalable surface treatment method. The MXene-based TENG exhibited significantly improved voltage and current output compared to conventional silicone-based TENGs, achieving a peak power density of 55.47 W m^{-2} . This device was used to harvest energy from various human body movements, such as hand tapping and walking, to power small electronic devices like LED lights and fans. The ability to integrate MXene-based TENGs into textiles opens up new possibilities for self-powered wearable devices, enhancing their functionality and sustainability.^[402]

Joule heating is another significant application of MXene-based textiles, particularly in smart thermotherapy. This technology can provide targeted heating for pain relief in conditions such as muscle pain, rheumatism, sciatica, and sports injuries.^[403] The superior electrical conductivity of $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes allows them to function as efficient heating elements in wearable textiles, offering precise temperature control and rapid heating response.^[377] For instance, an innovative approach was developed for a tri-layer MXene fabric heater using a simple dip-coating process. The device was assembled by layering three sheets of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene-coated fabric, each with different sheet resistances. The outer layers, with low resistance, provided rapid heat generation, while the middle layer, with high resistance, ensured uniform heating distribution. This fabric heater could reach temperatures of 50 °C at an applied voltage of just 5 V, demonstrating its potential for use in wearable thermal therapy applications. Such MXene-based fabric heaters are particularly promising for use in cold environments or for therapeutic purposes in treating muscle stiffness and promoting circulation.^[404]

MXene-based textiles are also gaining attention for their application in wearable *strain sensors*, which are crucial for monitoring human body movements and activities. The exceptional sensitivity of $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes allows these sensors to detect both minor and significant deformations, making them suitable for applications ranging from health monitoring to sports performance analysis.^[405] For example, an innovative application involved spray-coating MXene onto a piezoelectric poly(vinylene fluoride-trifluoroethylene) mat to create a multi-directional strain sensor that can detect various mechanical stimuli, such as head bowing, shoulder rounding, and neck stretching. The ability to monitor subtle changes in posture and movement makes this MXene-based sensor highly suitable for applications in ergonomic assessments.^[406]

The high sensitivity and rapid response of MXene-based sensors make them excellent candidates for *respiratory monitoring*. These sensors can detect subtle movements associated with breathing, providing valuable data for diagnosing and managing respiratory conditions.^[377,407] Researchers developed a smart Kevlar/MXene composite fabric using a continuous wet spinning process. This flexible Kevlar/MXene fabric sensor demonstrated exceptional sensitivity, flame resistance, and a quick response time of 90 ms. When integrated into a medical mask, the Kevlar/MXene fabric could accurately monitor breathing patterns in real time, offering a portable and precise solution for detecting respiratory issues.^[408] The ability to fabricate such sensors from MXene-coated textiles

opens up new possibilities for wearable health monitoring devices that are both effective and comfortable for prolonged use.

MXene-based textiles have shown potential in *environmental monitoring*, particularly for detecting harmful gases. Their unique 2D structure and surface functional groups provide excellent gas-sensing capabilities, making them suitable for wearable gas sensors that can monitor air quality in real time.^[409–411] For instance, a study on $\text{Ti}_3\text{C}_2\text{T}_x$ MXene/rGO composite fibres demonstrated enhanced sensitivity and stability for ammonia (NH_3) sensing at room temperature. These hybrid fibres, produced through a wet-spinning process, showed a significantly better sensing response compared to individual MXene or graphene fibres. The MXene/rGO fibres maintained high efficiency and stability even after being bent for 2,000 cycles, indicating their potential for integration into everyday clothing for continuous environmental monitoring.^[412]

Electromagnetic interference (EMI) shielding is a critical application area for $\text{Ti}_3\text{C}_2\text{T}_x$ MXene-based textiles, particularly given the growing concern over the harmful effects of electromagnetic radiation on human health. MXenes offer a lightweight, flexible, and highly conductive solution for developing wearable EMI shielding materials.^[389,413,414] For example, researchers developed a hydrophobic and highly conductive fabric for EMI shielding by depositing polymerized PPy-modified $\text{Ti}_3\text{C}_2\text{T}_x$ MXene sheets onto PET textiles using a dip-coating method. This PPy/MXene-coated fabric exhibited high electrical conductivity ($\sim 1000 \text{ S m}^{-1}$) and achieved an EMI shielding effectiveness of $\sim 90 \text{ dB}$, surpassing traditional conductive fabrics coated with graphene or other nanomaterials. The study demonstrated that MXene-coated textiles could provide long-term EMI shielding stability, even after multiple wash cycles and extended exposure to environmental conditions.^[377,415]

MXene-based textiles are also being explored for various *biomedical applications* due to their unique properties, such as excellent electrical conductivity, biocompatibility, and antibacterial activity. These qualities make MXene-coated fabrics suitable for applications ranging from wound healing to biosensing and wearable medical devices.^[307,377,416] A recent study demonstrated that MXenes coated onto cellulose fibre nonwoven fabric function as a wound healing textile. The MXene-coated fabric, which is flexible and wearable, offers multifunctional biomedical applications due to its high electrical conductivity, enabling localized heating to kill bacteria and accelerate wound healing.^[417]

Following the promising applications of MXene-based e-textiles, it is essential to address the challenges that accompany their practical use, particularly in ensuring their long-term performance. In addition to the previously discussed challenges of integrating e-textiles, another important consideration is achieving strong adhesion between MXene nanosheets and textile fibres, especially under the mechanical stresses that wearable electronics routinely face. To address this, researchers are focusing on improving the bond between MXenes and fibres through advanced surface treatments and linking agents like O₂ plasma and APTES, which help maintain the necessary stretchability and durability for reliable, long-term use.^[377,418]

1.6. SCOPE OF THE THESIS

The scope of this research focuses on the synthesis and application of Ti₃C₂T_x MXene inks for fabricating energy storage devices that are seamlessly integrated into textile substrates using AJP technology. This thesis provides a comprehensive exploration of the fabrication process, encompassing the synthesis of MXene inks, the optimisation of printing parameters, and the deposition of MXene inks onto various fabric types. Following the fabrication, the study includes an in-depth characterisation using microscopy, spectroscopy, and electrochemical techniques to evaluate the structural, chemical, and functional properties of the printed devices. The research specifically concentrates on MXene materials because of their unique electrochemical properties and significant potential for applications in wearable electronics. Additionally, it focuses on AJP due to its promising capabilities for achieving precise, uniform depositions on flexible substrates, making it an ideal technique for developing advanced e-textiles.

2 DEPOSITION & CHARACTERISATION TECHNIQUES

2.1. PRINTING TECHNOLOGIES FOR WEARABLE & FLEXIBLE ELECTRONICS

Printing technologies have become essential in the fabrication of flexible and wearable electronic devices, facilitating the development of components for e-textiles and energy storage devices with enhanced functionality and adaptability. Unlike traditional manufacturing methods that rely on subtractive processes, printing techniques enable the additive deposition of materials directly onto various substrates, including textiles. This additive approach allows for the creation of intricate patterns with high precision and minimal material waste, making it particularly well-suited for applications requiring miniaturization and flexibility. As a versatile additive manufacturing method, printing also offers significant advantages for large-scale, cost-effective device production. It simplifies the fabrication process to just three main steps: substrate pretreatment, material deposition, and post-treatment, typically involving drying or occasional heat treatment. However, despite advancements in printing technologies, the fields of functional printing and ink development are still relatively early in their evolution, mainly due to the challenges of creating high-performance, additive-free inks that maintain stability and functionality across diverse applications.^[419]

The field of printed electronics encompasses a variety of printing techniques, each offering unique capabilities in terms of resolution, scalability, material compatibility, and cost. These techniques can broadly be categorized into screen printing, inkjet printing, roll-to-roll gravure printing, flexographic printing, extrusion 3D printing, and aerosol jet printing.

Screen printing is a versatile, widely used, and easy contact printing technique that applies ink onto a substrate through a stencil mesh. The stencil has blocked areas to prevent ink passage and open areas for the desired pattern, allowing ink to pass through selectively.^[419] The process can be executed in two main modes: flat-bed and rotary. The flat-bed method presses ink through a flat screen onto the substrate, enabling multilayer deposition through repeated applications, while the rotary method employs a cylindrical screen to continuously apply ink as it rolls over the substrate. Screen printing can be manual or automated, with fully automated flatbed presses achieving speeds up to 70 m min⁻¹ while roll-to-roll reaching up to 100 m min⁻¹.^[420]

Despite its simplicity and cost-effectiveness, the method requires inks with specific rheological properties to ensure optimal performance. Inks for screen printing must possess high viscosity (0.5 - 50 Pa s), to prevent the ink from spreading excessively and to maintain the shape and precision of the printed pattern.^[397,421] Shear-thinning behaviour is essential, allowing the ink to flow smoothly under the pressure of the squeegee during printing and then regain its viscosity to hold its shape once applied. Thixotropy is also beneficial, as it helps the ink level out after printing and reduces mesh marks on the final print. Additionally, a high yield stress is desirable to keep the ink in the screen's open areas and prevent it from dripping or bleeding, ensuring clean and well-defined prints. However, if the viscosity is too high, the ink may stick to the squeegee, creating issues during the printing process. Therefore, achieving the right balance of viscosity, yield stress, and shear-thinning properties is crucial for successful screen printing.^[419,421]

Screen printing offers several advantages, including the ability to produce thick patterns with high aspect ratios and the flexibility to easily adjust the thickness of the printed layers. It is also a cost-effective method suitable for mass production, making it ideal for large-scale applications. However, this technique typically results in lower resolution and higher surface roughness compared to other printing methods, which may impact the quality and precision of the final printed products.^[388]

Inkjet printing (IJP) is a digital, non-contact printing technique valued for its precision and efficiency in both research and industrial settings. The process involves ejecting ink droplets from a printhead nozzle, which are then directed onto the substrate in a controlled manner to create the desired pattern.^[422] This method is highly versatile and can be used on a variety of substrates, including flexible and stretchable materials like textiles. The main advantages of IJP include high resolution, which enables the creation of complex,

custom patterns without the need for masks or screens; the digital nature of the process allows for rapid prototyping and easy customization of designs; as well as minimal ink usage (1 – 2 mL).^[420] IJP is categorized into two main types based on droplet formation mechanisms: continuous (C-IJP) and drop-on-demand (DOD-IJP). C-IJP, often used in industrial applications, produces a continuous stream of ink droplets ($\sim 100\text{ }\mu\text{m}$) using the Rayleigh instability of a liquid column, which is then directed or deflected by an electric field. In contrast, DOD-IJP is more suited to research environments and allows for finer control over droplet size and placement by generating droplets (20 to 50 μm) only as needed through pressure pulses, either thermal or piezoelectric.^[419,423]

IJP requires inks with carefully balanced properties to ensure optimal performance. The jettability of the ink, as well as the behaviour of the droplets once deposited, depend heavily on the ink's surface tension and rheological characteristics. These properties influence every stage of the printing process, from droplet formation and stable jetting to droplet impact and spreading on the substrate. For instance, the ink's viscosity must be low enough to allow smooth ejection through the nozzle, while the surface tension needs to be just right to form stable droplets and prevent undesirable effects like satellite droplet formation or splashing upon impact. The interaction between droplets and the substrate, as well as between adjacent droplets, determines the resolution and accuracy of the printed patterns. To avoid the coffee-ring effect, which causes uneven particle distribution during drying, multi-component solvents or solvent modifications are used to promote uniform deposition. Managing these parameters is crucial for achieving precise control over the final printed features, particularly in applications where high resolution is essential.^[422,423] Despite these challenges, IJP excels in applications requiring precise deposition of thin, uniform layers, making it a popular choice for fabricating electronic components such as transistors,^[424] sensors,^[425] organic light-emitting diodes^[426], and energy storage devices^[258].

Roll-to-roll gravure printing uses gravure rollers to transfer a pre-engraved pattern onto a substrate through the application of pressure. The gravure printing system consists of an ink trough and a metal doctor blade, which removes excess ink from the surface of the roller, ensuring that ink only fills the recessed areas of the engraved pattern. To transfer the ink, the substrate is passed between the gravure roller, which holds the ink, and an impression roller that presses the substrate against the gravure roller.^[388] Gravure printing is commonly used for large-scale applications, such as packaging, due to its ability to achieve high resolution (10 to 50 μm) and print speeds of up to 1000 m min^{-1} . The typical

ink viscosity used for gravure printing is $0.1 - 1 \text{ Pa s}$.^[388] However, the use of gravure printing for functional materials has been limited, primarily due to the higher initial costs and larger ink volumes needed for prototyping compared to other printing methods.^[420]

Flexographic printing is a relief printing technique where ink is transferred onto a substrate using a series of rollers. Ink is first applied to a screened roller cylinder, with excess ink removed by a doctor blade to ensure even coverage on the anilox roller. The ink then moves from the anilox roller to a raised flexographic plate, which prints the pattern onto the substrate.^[422] Flexographic printing uses raised surfaces for ink transfer and allows for high-resolution printing of $45 - 100 \text{ }\mu\text{m}$ at speeds up to 500 m min^{-1} for typical applications. The ink viscosity used for gravure printing is $0.05 - 0.5 \text{ Pa s}$.^[388] For printing functional materials, speeds are usually reduced to around 100 m min^{-1} to accommodate specific material requirements.^[420]

Extrusion printing is an additive manufacturing process that involves depositing viscous or gel-like inks through a nozzle to build structures layer by layer, following a computer-aided design (CAD) model. This technique is widely used in both 2D and 3D printing, with 3D extrusion printing particularly effective for creating complex geometries due to its precise, layer-by-layer approach.^[419,427] Methods like fused deposition modelling (FDM) and 3D dispensing fall under this category. FDM uses thermoplastic filaments that melt and extrude through a nozzle, forming layers to build detailed structures.^[420] In contrast, 3D dispensing employs fluid precursors, such as shear-thinning inks or hydrogels, which solidify after extrusion through physical or chemical processes.^[420] To ensure stability and accuracy in 3D printing, inks must possess high viscosity and yield stress, preventing collapse and maintaining the shape of printed objects.^[419]

Aerosol jet printing (AJP) is a cutting-edge printing technology that offers several advantages over traditional methods, particularly in terms of resolution and versatility.^[292] It is capable of achieving fine details down to $10 \text{ }\mu\text{m}$, ensuring high precision in printing. For example, the resolution and uniformity of printed MSC configurations play a crucial role in determining their electrochemical performance. For instance, adjustments in the interspacing between adjacent finger electrodes can significantly impact the average ionic diffusion pathway, ESR, capacitance, energy, and power of the MSC.^[254,258,259] These parameters are vital in optimising the overall performance and functionality of the energy storage system. Additionally, AJP does not require direct substrate contact, eliminating the risk of surface damage or defects. This non-contact feature contributes to preserving the

substrate's integrity and allows for printing on planar and non-planar surfaces.^[292,293,428,429] Furthermore, AJP is a cost-effective method as it minimises ink waste by utilising only small quantities. Another advantage lies in its digital nature, obviating the need for masks during printing. This digitalised approach enhances efficiency and flexibility in fabrication. Finally, AJP enables the exploration of a broader range of functional materials with varying viscosities, expanding the possibilities for material selection and optimisation.^[189,290–292]

The choice of printing technique is crucial in the fabrication of MSCs and e-textiles, as it directly affects the device's performance, scalability, and suitability for specific applications. For example, printed MSCs require precise, high-resolution patterns to optimize their electrochemical performance, so techniques like IJP and AJP are particularly suited.^[254,258,259] Screen printing, while useful for its low cost and high throughput, is less effective for MSCs where fine features and precise control over layer thickness are essential.^[254,430,431]

Functional inks are at the heart of printed electronics, determining the electrical, mechanical, and electrochemical properties of the final device. The choice and formulation of these inks are critical to the success of any printing process, especially in applications requiring high performance and reliability.^[254] These inks must possess high electrical conductivity, adhesion, appropriate viscosity, and stability while meeting specific requirements for electrochemical energy storage devices, such as high electrochemical activity, carrier mobility, mechanical integrity, safety, and eco-friendliness.^[189,432,433] Typically, inks include active materials, solvents, binders, and additives, influencing substrate selection, fabrication method, post-treatment, scalability, environmental impact and cost.^[434,435] Notably, nanomaterials have revolutionized this landscape, offering enhanced ionic transport and electronic conductivity, enabling integration into portable, flexible, wearable electronics compatible with various manufacturing techniques.^[57]

For energy storage applications, the ink must satisfy a series of key aspects to yield a high-performing electrode. These include high electrical conductivity (impacts electron charge transfer), good electrochemical performance (affects cycling stability, power and energy densities), optimal physical properties (such as surface tension, rheology, viscosity, drying rate), minimised aggregation and precipitation (to reduce clogging of the nozzle), stable, homogeneous and resistance to oxidation, and good adhesion to the desired substrate.^[254,436,437] Even though the electrochemical properties of the MSCs depend on the

active materials used, not many of the nanomaterial dispersions could be readily used as printable inks. The physical properties, drying behaviour, wettability, dispersion stability, uniformity, and compatibility with substrates could be optimised by solvents and incorporation of binders and additives, collectively termed "varnish".^[422] However, these components are typically non-capacitive and reduce conductivity, which impacts the performance of the printed device. Therefore, proper techniques for removing those substances to limit undesirable properties after printing must also be considered.^[254,290,422] Such post-treatments are usually either complex washings or high-temperature annealing, which may affect the structure of the printed pattern and its mechanical properties.^[254]

The ideal ink formulation would, therefore, be water-based and with no or limited amount of additives. Water as a solvent is advantageous both from environmental and processing perspectives, i.e. water can be easily evaporated to solidify the active material.^[258,422]

To optimise the performance of the MSCs, it is critical to ensure that junction resistance between the electrode and current collector is minimised.^[254] Printing technology is very suitable since it allows the current collector and electrode to be fabricated in complete contact.^[290] Typically, it is achieved by printing the current collector into the interdigitated configurations using metal nanoparticle conductive suspensions or pastes. Such materials typically require annealing post-treatment to recover the electrical conductivity, which, unfortunately, may cause loss of mechanical stability (e.g. brittleness, cracking).^[254] However, even when the materials are printed in full contact, the interface between electrodes and the current collector still might delaminate. The best solution to avoid this issue is to use the same materials to print both of these MSCs parts. Such devices are then referred to as "current collector-free configurations". To achieve this, the requirement for high conductivity for the functional ink must be satisfied.^[254,438] This simplifies the printing process, improves mechanical properties, and enhances electron transfer, which improves the rate performance.^[254,288]

MXenes have emerged as highly promising materials for use in functional inks due to their unique combination of properties,^[216,250,288,422] as discussed in detail earlier in Section 1.5. The presence of abundant surface functional groups on MXenes simplifies the formulation of MXene-based inks, often eliminating the need for additional additives that are typically required for other materials.^[419,439] These surface groups not only enhance colloidal stability but also significantly influence the rheological properties and film formation behaviour of the inks. They interact with the carrier solvent, affecting surface tension and

adhesion, which are crucial for achieving high-quality prints. As a result, the overall properties of MXene inks are largely dictated by the MXene's surface chemistry and the characteristics of the solvent used.^[419]

The formulation of MXene inks requires careful consideration to ensure stability, appropriate viscosity, and good substrate adhesion. Aqueous MXene inks are particularly advantageous due to their environmental friendliness and ease of processing. However, MXenes in suspension are prone to oxidation,^[440,441] which can compromise their electrical conductivity, a critical property for many applications. While oxidation can be beneficial for certain uses (e.g., energy storage,^[442] sensing,^[443]), it is generally undesirable where high conductivity is needed.^[419] Therefore, ink formulations often include antioxidants (e.g., sodium L-ascorbate^[444], polyanionic salts^[445]) to mitigate this challenge. These additives help to preserve the functional properties of MXenes by forming protective barriers around the flakes, reducing the oxidation rate, and extending their shelf life.^[419,441]

MXene inks have been investigated for a range of applications in printed electronics, taking advantage of their excellent conductivity and mechanical flexibility. However, since MXenes are still in the early stages of research and development, their typical printing deposition has so far been limited to just three reported methods: inkjet, screen, and extrusion printing.^[419]

Several inkjet-printable MXene inks have been developed with optimized surface tension and viscosity for stable printing.^[397] One formulation involved using surface tension modifiers and a capping ligand to enhance the oxidative stability and dispersion of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene inks, which remained stable for around 80 days. For effective IJP, the lateral size of the MXene nanosheets must be much smaller than the nozzle diameter to prevent clogging. In this case, nanosheets of about 200 nm allowed for uniform printing on photo paper without issues.^[446] In another instance, additive-free MXene inks were formulated in organic solvents (ethanol, DMF, NMP, DMSO), enabling the printing of high-resolution conductive patterns on untreated substrates. These inks featured nanosheets with lateral sizes between 1 and 2.1 μm and demonstrated optimal jetting properties with Z values within the stable range. While most inks remained stable for up to 12 months, the DMSO ink sedimented after 6 months, showing varying degrees of stability. The MXene inks exhibited shear-thinning behaviour, making them suitable for creating durable printed patterns with consistent line widths that are stable for up to 24 months.^[258]

MXene-based inks, including both pure and composite formulations, have been developed for screen printing. These inks exhibit non-Newtonian, shear-thinning behaviour, allowing controlled flow during printing. This property is crucial for screen printing, ensuring smooth transfer through the mesh and minimizing spreading.^[397] For example, inks made from MXene, MXene with silver nanowires (AgNW), and composite inks with $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ nanoparticles have demonstrated ideal rheological properties, maintaining a solid-like state before yielding and becoming more fluid under higher shear stress.^[447]

MXene-based inks have recently attracted considerable attention for their use in 3D extrusion printing. To maintain the shape and stability of the printed structures, the inks need to have a high viscosity, which helps them retain their form immediately after extrusion. The rheological properties, such as shear-thinning behaviour, are critical for controlling the printing process and achieving high-quality, precise patterns. MXene inks formulated for extrusion-based 3D printing have been designed to meet these specific requirements.^[397] For example, 3D printable MXene ink made from 2D $\text{Ti}_3\text{C}_2\text{T}_x$ flakes can be used to create freestanding architectures with high specific surface areas. The rheological properties of these inks are tuned to form strong, solid-like structures, which prevents collapse and allows for the creation of robust, durable 3D forms. Additionally, the alignment of MXene flakes during extrusion, influenced by shear stress, ensures that the flakes orient horizontally in the direction of printing, enhancing the stability and mechanical integrity of the printed structures.^[250]

MXene inks have become highly versatile materials for printed electronics. They have been shown to be particularly well-suited for printing energy storage devices like MSCs, where their high electrical conductivity and large surface area contribute to enhanced electrochemical performance.^[388] For instance, $\text{Ti}_3\text{C}_2\text{T}_x$ MXene inks have been used in both inkjet and extrusion printing to create high-resolution MSCs. Inkjet-printed MSCs achieved a specific areal capacitance of 12 mF cm^{-2} with 25 printed layers, while extrusion-printed reached 43 mF cm^{-2} with just 5 printed layers. Both techniques fabricated MSCs with excellent cyclability and capacitance retention.^[258]

Another example is a screen-printed asymmetric microscale hybrid device that utilizes $\text{Ti}_3\text{C}_2\text{T}_x$ MXene as the negative electrode, and Co-Al layered double hydroxide as the positive electrode. This device configuration achieved an impressive areal capacitance of 28.5 mF cm^{-2} at a current density of 0.75 mA cm^{-2} . The screen-printed MXene-based device demonstrated excellent capacitance retention and mechanical flexibility, making it

suitable for integration with force sensors as a power source for portable electronic applications.^[448]

In addition to this, MXene inks have also demonstrated significant potential in applications for printed electronics, optoelectronics, sensors, and actuators.^[388] The integration of MXenes into textile-based printed electronics represents a significant advancement in the field of wearable and flexible electronics. MXenes are well-suited for textile applications due to their flexibility, conductivity, and ability to form stable dispersions, while the hydrophilic nature of MXenes allows for good adhesion to various textile substrates, and their mechanical robustness ensures that printed patterns remain intact under bending and stretching.^[250,302,309,446,449] MXene inks have been used to create flexible printed textile-based sensors,^[450] and energy storage devices,^[106,451] highlighting the versatility and effectiveness of these materials in diverse applications.

Printing MSCs on textiles using MXene inks leverages the unique properties of both the materials and the substrates. MXenes' high conductivity and mechanical flexibility complement the textile's stretchability, creating a robust, flexible energy storage device that can be integrated seamlessly into wearable electronics. Printing also allows for the optimization of the MSC architecture, such as adjusting the interspacing between finger electrodes to achieve the desired electrochemical performance. Parameters such as the interspacing between finger electrodes, layer thickness, and uniformity of the printed pattern can significantly affect the capacitance, energy and densities of the MSC devices.^[254,258,259] By optimizing these factors, it is possible to achieve high-performance MSCs that are both flexible and durable, suitable for use in a wide range of wearable applications.

MXene inks are at the forefront of research in printed electronics, and ongoing innovations promise to expand their applications even further. This section has explored the range of printing techniques revolutionizing the fabrication of wearable electronics. Each method's unique capabilities and the essential role of functional inks, particularly innovative MXene inks, were highlighted as key drivers of progress in this field. As printing technologies and materials advance, they open up new horizons for creating more adaptable, high-performance devices. The next section will dive deeper into AJP, an emerging technique that promises to push the boundaries of precision and versatility in printed electronics.

2.2. AEROSOL JET PRINTING

AEROSOL JET PRINTING (AJP) stands at the forefront of advanced additive manufacturing, offering the unique ability to deposit functional inks with exceptional precision across a wide range of substrates and intricate geometries.^[292] Although AJP is still considered a niche technology compared to more traditional and widely adopted printing methods, it offers a range of benefits that other techniques find challenging to match.^[292,452,453]

One of the key advantages of AJP is its ability to handle a wide range of ink viscosities — from as low as 1 cP to as high as 1000 cP^[189,454] — far surpassing the viscosity limitations of IJP, which is typically restricted to under 20 cP.^[455] This versatility allows AJP to deposit nearly any aerosolisable material. Moreover, the material deposition process in AJP allows it to function in a manner that transcends traditional 2D printing techniques. AJP can achieve what is known as 2.5D^[456–458] or even fully 3D^[459–462] printing, enabling the creation of intricate, free-standing structures. Reports have documented its use in depositing various conductive inks, including those with silver nanoparticles,^[463,464] graphene,^[465,466] CNTs,^[467,468] transition metal dichalcogenides,^[469,470] perovskites,^[459,471] and MXenes.^[472,473] In addition to these conductive materials, AJP has also been successfully used to print polymers,^[474,475] ceramics,^[476,477] and proteins.^[478,479]

Given its compatibility with a broad range of materials, AJP has found extensive application in the production of printed circuits,^[480,481] transistors,^[482,483] energy storage devices,^[484,485] high-frequency communication systems,^[486,487] photovoltaics,^[488,489] high energy photodection,^[459,490] and wearable electronics,^[491] particularly for advanced sensing applications.^[491,492] The ability to print fine features on flexible substrates is especially beneficial in these contexts.

AJP's operational mechanism, which utilizes aerodynamically focused deposition,^[293,456] offers greater stability during the printing process compared to IJP.^[189] The droplet sizes achieved with atomization in AJP are significantly smaller than those produced by IJP which helps achieve finer details and higher resolution.^[493] This enhanced stability, combined with AJP's ability to achieve finer line widths, makes it ideal for applications that require high-resolution patterning.^[429]

In AJP, a collimated aerosol beam is created from atomized ink and precisely directed towards the substrate, enabling high-resolution printing with line widths as narrow as $\pm 10 \mu\text{m}$,^[292,494,495] which depends on the material and surface.^[496] Moreover, AJP offers the distinct advantage of fabricating without traditional masks, significantly minimizing material waste by precisely depositing inks at digitally defined locations on the substrate. This mask-free process is digitally controlled, allowing direct printing from CADs under ambient atmospheric conditions.^[292,491,494] The printing pattern always has a start and end position and is achieved with the shutter's opening to allow the focused aerosol beam to form a printing line. During transitions, the shutter automatically closes.^[429]

Additionally, AJP's ability to deposit inks on both flat and complex, non-planar surfaces significantly broadens its application range, making it particularly advantageous for the development of flexible electronics. This versatility opens new avenues in the field of e-textiles by enabling the use of fabric substrates. With AJP, advanced technologies can be seamlessly integrated into garments while ensuring that the electronics remain fully functional under dynamic conditions. The process benefits from a contactless printing approach, facilitated by a standoff height of up to 5 mm,^[496,497] which minimizes the risk of substrate damage during printing. AJP's standoff height and a movable stage in x, y, and z directions facilitate printing in all directions, even on the tilted (up to 45°) surfaces.^[456]

There are two ways to fill a pattern: a perimeter fill algorithm (PFA) or a serpentine fill algorithm (SFA). During PFA, the material is deposited continuously in the shape of decreasing squares, starting from the outer border and proceeding inward. In SFA, the material is deposited bidirectionally in a discontinuous line manner.^[429] Studies have shown that the difference between applying these algorithms is that PFA produces more rough layers than SFA. This roughness is related to the time between the interaction of successive printed lines; it takes longer for lines to interact in PFA than in SFA.^[429]

While AJP is extensively used in academic research, it faces several limitations that complicate its broader adoption. Although AJP can handle a wide range of inks, determining optimal print parameters is often challenging and sensitive to changes.^[498–500] Achieving consistency and reproducibility requires frequent adjustments, such as ink replacement, which hampers its scalability for production. Moreover, parameters optimized for one ink type do not usually translate to others, necessitating time-consuming empirical optimization for each new material.^[292] Overall, functional inks need to be stable (constant over time), jettable (able to form drops), and homogeneous (with a uniform

distribution of particles within the solvent. The viscosity and surface tension of the ink are essential parameters in determining the jettability of AJP. Additionally, particle sizes and distributions must be optimized to ensure ink stability, minimize nozzle clogging, and enhance the porosity and functionality of the printed layers. Solvent vapour pressure also plays a critical role in preventing premature evaporation during transport, which can lead to clogging issues.^[189]

This results from a limited understanding of the AJP process, unlike more established printing methods, for example, IJP, which benefits from well-defined parameters like the Z number.^[423] The Z number provides valuable insights into ink formulation and printability by considering droplet diameter (D), surface tension (γ), density (ρ), and dynamic viscosity (η):

$$Z = \sqrt{\frac{\gamma \rho D}{\eta^2}} \quad (13)$$

The Z number assesses the balance of forces involved in droplet formation, guiding the formulation of inks that are stable and suitable for high-quality printing. A Z number within a specific range (typically 4 to 14) indicates good printability, balancing viscosity, surface tension, and droplet dynamics to achieve reliable droplet generation, allowing for straightforward optimisation of ink properties and print conditions.^[423]

In contrast, AJP lacks such a universal parameter, making it more challenging to achieve consistency and predictability across different inks and substrates. The effectiveness of AJP depends heavily on a comprehensive understanding of the physical principles that control droplet formation, aerosol dynamics, and deposition, as well as a detailed knowledge of ink rheology and behaviour under varying conditions. By exploring these core principles, the operator can develop a more robust framework for optimizing AJP settings, enhancing print quality, and broadening its application potential. This work specifically focuses on the Optomec AJP 300 system (**Figure 11**), a widely used commercially available printer.

AJP is a multi-step process that relies on the aerodynamically focused deposition of functional ink onto substrates using a collimated aerosol beam.^[293,456] The process begins with *ink atomization*, where liquid ink is broken down into fine droplets to create an aerosol.

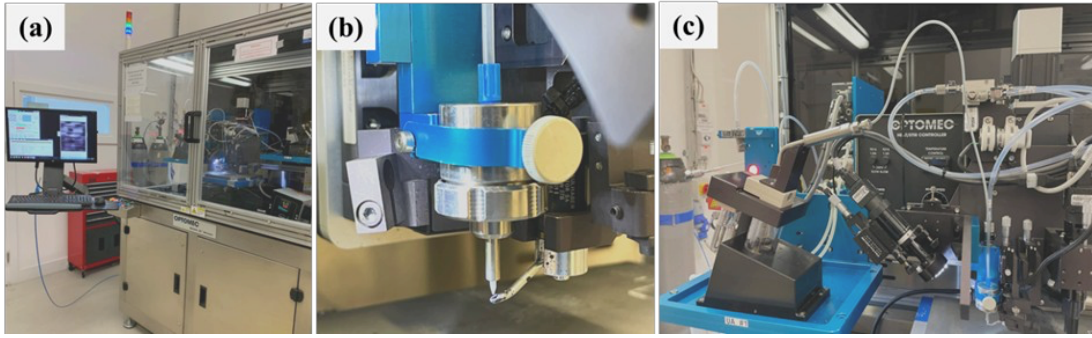


Figure 11: Optomec AJP 300. **(a)** Lab view of the tool. **(b)** Close-up image of the deposition head. **(c)** Detailed overview of the key components during the printing process.

Images captured on-site in our research laboratory.

This aerosol is then *transported* from the atomizer to the deposition head through mist tubing, carried by the atomizer gas flow. Next, the *focusing stage* occurs in the deposition head, where a sheath gas flow is introduced in a surrounding cavity, constricting and guiding the aerosol beam with high precision. In the final *deposition stage*, the focused aerosol beam, accelerated by the sheath gas flow, is directed through the nozzle toward the substrate, forming the desired patterns and structures with high precision. Each stage is crucial for achieving high-quality, accurate printed features.^[292,454,455] This process is depicted in **Figure 12**.

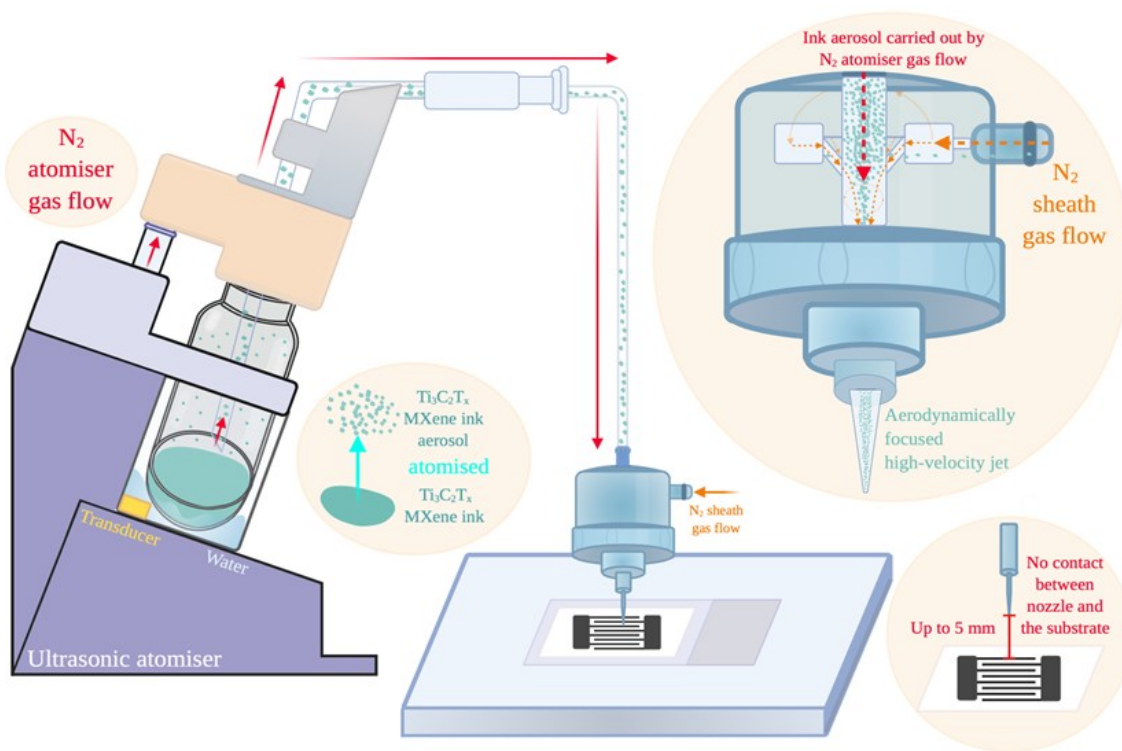


Figure 12: Schematic illustration of the AJP process. Image created using BioRender.com.

INK ATOMISATION is the first critical stage, which is fundamental to the AJP's ability to generate fine droplets from a liquid ink, enabling precise deposition. Atomization involves breaking up the liquid into tiny droplets, forming an aerosol – a suspension of fine solid particles or liquid droplets in a gas. In AJP, this aerosol consists of atomized functional inks, typically producing droplets in the range of 1 to 5 μm in diameter. For optimal printing performance, the aerosol should ideally contain monodispersed, highly concentrated droplets with sufficient inertia to ensure effective deposition onto the substrate.^[292,455] Droplets that are either too large or move too slowly may settle before reaching the nozzle exit, potentially causing blockages and restricting the flow of material, thus affecting the overall print quality.^[292,501]

The Optomec AJP system is equipped with both ultrasonic and pneumatic atomizers, each designed for different viscosity ranges. The *pneumatic atomizer* is capable of processing high-viscosity inks up to 1000 centipoise (cP).^[496] In operation, the pneumatic atomizer utilizes a high-velocity gas stream to break the liquid ink into droplets. Compressed gas is forced through the atomizer nozzle, creating a high-speed jet that draws the ink from the reservoir. As the gas stream exits the nozzle, it breaks the liquid into droplets and suspends them in the flow. This results in a more polydisperse aerosol, where the droplets vary considerably in size.^[500] To achieve the desired droplet uniformity and precision, the aerosol stream requires additional refinement after atomization. This is often accomplished using a virtual impactor, which selectively removes low-inertia droplets from the aerosol stream, enhancing its uniformity and ensuring a consistent droplet size distribution for precise deposition.^[454,496]

The *ultrasonic atomizer*, on the other hand, is optimized for low-viscosity inks, typically within the range of 1 to 10 cP, making it ideal for applications that require fine-feature printing and high resolution. It is particularly suited for small-volume applications, operating efficiently with ink volumes from 0.5 to 3 mL. While ultrasonic atomization can be used for particulate suspensions, the particles must generally be smaller than 50 nm to be effectively incorporated into the ejected droplets. Various inks and materials with a broad range of vapour pressures can be utilized in this setup, but new materials should be tested individually to ensure compatibility.^[496]

Before discussing the detailed mechanics of droplet formation, it is essential to introduce the concept of dimensionless frequency (Ω), which plays a crucial role in determining the behaviour of the atomization process.

The dimensionless frequency Ω is defined as:^[502]

$$\Omega = \omega \left(\frac{\nu^3 \rho^2}{\gamma^2} \right) \quad (14)$$

where ω is the driving frequency, ν is the viscosity, ρ is the density, and γ is the surface tension. This frequency distinguishes between the inviscid and viscous regimes of droplet formation. In the *inviscid regime*, where surface tension and inertial forces dominate, the fluid experiences less resistance to droplet formation, leading to smaller, more uniform droplets. In the *viscous regime*, higher viscosity dominates, increasing resistance to droplet formation and typically resulting in larger, less uniform droplets.^[502] The following discussion will focus exclusively on ultrasonic atomization to meet the specific printing requirements and characteristics of the inks used in this project.

In the ultrasonic atomiser, the atomization is achieved with *ultrasonic waves*, which are sound waves with frequencies higher than the upper limit of human hearing, starting above 20 kHz and extending into the MHz range.^[503] These waves behave similarly to audible sound waves but have much shorter wavelengths due to their higher frequencies. Because of their high frequency, ultrasonic waves can interact with materials in unique ways, making them useful in many different technologies and scientific applications.^[504] Ultrasonic waves require a medium (such as air, water, or a solid) to propagate. They travel through the medium by compressing and expanding the material, creating longitudinal waves that move in the direction of wave propagation.^[505]

These ultrasonic waves are generated by an *ultrasonic transducer*, a device that converts electrical energy into high-frequency pressure waves.^[506] It operates at a frequency of ~ 1.7 MHz.^[496] For effective atomization, ultrasonic energy must be transmitted from the transducer through the coupling fluid and the vial to the material. Therefore, in the set-up, the ultrasonic transducer is submerged in a water bath right below the atomiser ink vial.^[496]

As ultrasonic waves travel through the ink, they cause a disturbance on the liquid's surface. Surface tension, acting as a restoring force at the liquid-air interface, then seeks to minimize the liquid's surface area by attempting to return the surface to its undisturbed state. This balance between the inertial forces of the liquid, which resist acceleration, and the restoring force of surface tension leads to the formation of *capillary waves*.^[507]

When these capillary waves are subject to Faraday instability – a phenomenon where a liquid surface subjected to periodic vertical oscillations develops standing waves – the capillary waves at the phase boundary of the ink can reach an excitation amplitude sufficient to eject droplets from the surface. As the energy input from the ultrasonic waves increases, the amplitude of these capillary waves grows too, eventually reaching a critical threshold where the surface becomes unstable. At this point, the energy concentrated at the wave peaks overcomes the cohesive forces, primarily surface tension, that hold the liquid together, resulting in droplet ejection.^[508,509]

The efficiency of this droplet formation process, characterized by the ejection rate and mean droplet diameter, is highly dependent on the ink's rheological properties, which govern the stability and behaviour of the capillary waves under ultrasonic excitation.^[510]

The wavelength (λ) of the capillary waves is given by the *Kelvin equation*,^[511,512] given by:

$$\lambda = \left(\frac{2\pi\gamma}{\rho f^2} \right)^{1/3} \quad (15)$$

where γ is the surface tension of the ink, ρ is the density of the ink, and f is the frequency of the capillary waves. This equation was later modified by Rayleigh^[511,513] to account for the fact that capillary waves generated by ultrasonic excitation have the frequency half of the driving frequency:^[514,515] The capillary wavelength then can be expressed as:^[515]

$$\lambda = \left(\frac{8\pi\gamma}{\rho \omega^2} \right)^{1/3} \quad (16)$$

where ω is the driving frequency of the ultrasonic waves.

This equation shows how different ink properties (surface tension, γ , and density, ρ) and ultrasonic settings (frequency ω) affect the wavelength of capillary waves. By adjusting these parameters, operators can fine-tune the droplet size to meet specific printing requirements, enhancing print resolution and quality.

The following equation provides a theoretical framework for predicting droplet size based on the properties of the ink and the operational parameters of the ultrasonic waves via:^[512]

$$D_{50} = a\lambda = \left(\frac{8\pi\gamma}{\rho \omega^2} \right)^{1/3} \quad (17)$$

where droplet diameter (D_{50}), also known as the median droplet diameter, represents the average size of the droplets generated during the printing process. The notation D_{50} means that 50% of the total volume of droplets produced has a diameter smaller than or equal to this value, and the other 50% has a diameter larger than D_{50} .^[516]

The empirical constant a was reported based on experimental measurements to be 0.35 ± 0.03 .^[517] This constant indicates that the droplet size is roughly a third of the capillary wavelength (λ), showing a direct proportional relationship between the two. Shorter wavelengths correspond to smaller droplets because more energy is required to form shorter, tighter waves that break up into smaller droplets. In the context of AJP, achieving a specific droplet size is crucial for controlling print resolution, feature size, and overall print quality.

Based on the equation for D_{50} , the droplet diameter is primarily determined by the surface tension (γ) and density (ρ) of the ink. A higher surface tension requires greater energy to overcome the cohesive forces, leading to the formation of larger droplets. Conversely, a higher ink density contributes to greater inertia, which resists the formation of larger droplets and results in smaller droplet sizes. Notably, the droplet diameter is not affected by the ink's viscosity (ν), so it has a minimal impact on the final print quality.^[518]

Building on Faraday's instability, as ultrasonic energy increases, the amplitude of capillary waves reaches a critical threshold where surface tension is overcome, leading to droplet ejection.^[508,509] This process is governed by critical acceleration, a_c , which represents the peak acceleration at the critical amplitude and is used to calculate the critical power (P_c) – the minimum power required to effectively atomize the ink into droplets, which also influences the rate of droplet generation.^[502,519]

Critical acceleration (a_c) can be derived using dimensional analysis and is influenced by the fluid's properties, including surface tension (γ) and density (ρ). The determination of a_c varies depending on whether the fluid is in the *inviscid regime*, where the effects of viscosity are negligible, or the *viscous regime*, where viscosity significantly influences droplet formation and stability.^[502]

The critical power (P_c) required for aerosolisation can be expressed as:

$$P_c \sim \frac{ma_c^2}{\omega} \sim m\nu\omega^2 \quad (18)$$

where ν is the kinematic viscosity of the ink.^[502] In the context of droplet formation, higher viscosity (ν) means the ink is thicker and more resistant to being pulled apart into droplets. This resistance necessitates more power to achieve atomization, explaining why the critical power increases with viscosity. Moreover, the dependence on the square of the frequency (ω^2) indicates that the power requirement escalates quadratically as frequency increases. In AJP, achieving high-resolution printing with small droplets requires higher frequencies, which in turn demands more power to maintain these frequencies.

The mechanisms that determine the critical driving amplitude for Faraday wave instability, leading to the ejection threshold, are fundamentally different from those that govern the size of the resulting droplets, causing these phenomena to behave differently. Although both processes experience a shift from inviscid to viscous behaviour beyond a specific dimensionless frequency,^[502] Ω , this critical frequency is approximately 10^4 times greater when considering the droplet diameter.^[517]

TRANSPORT STAGE: After the aerosol is generated, the carrier N_2 gas flow moves it through the mist tubing to the deposition head (**Figure 12**). This process, which typically takes around 10 seconds under standard conditions, can result in droplet losses due to interactions with the tube walls. Such losses can reduce the deposition rate and cause the material to accumulate, leading to process drift, contamination, or even clogging of the deposition head, thereby shortening the printing lifespan.^[292]

The primary mechanisms behind these transport losses are *gravitational settling*,^[520] which predominantly affects larger droplets; and *diffusion*,^[521] which impacts smaller droplets. These factors define a limited range of droplet sizes that are ideal for deposition and are influenced by the gas flow rate and the design of the mist tube. Higher gas flow rates and shorter mist tubes can minimize losses and expand the range of droplet sizes that reach the substrate, whereas longer tubes require increased flow rates to achieve similar transport efficiency. While transport losses are generally seen as a drawback due to their impact on throughput and printing longevity, they can also serve as a natural filter to control the droplet size distribution. The efficiency of droplet transport, and thus the deposition rate, is a function of aerosol density, flow rate, and transport dynamics.^[292] AJP operators must be aware that while the filtering effect helps control droplet size, it also poses risks. Droplets lost due to transport mechanisms accumulate in the tubing, and if not addressed, these droplets may eventually dislodge, causing unexpected ink splashes on the substrate and

compromising the printed sample. To avoid this, regular cleaning of the tubing is essential to ensure consistent and reliable printing.

FOCUSING STAGE: The transported aerosol is precisely collimated using a sheath gas introduced concentrically around the aerosol stream as it passes through the deposition head, as depicted in the detailed schematic in **Figure 12**. This sheath gas not only serves to narrow the aerosol beam but also aligns and accelerates the droplets, directing them toward the substrate with high precision. The flow rates of both the aerosol carrier and sheath gases are critical parameters that control the degree of collimation and the resulting spot size of the printed features. They are related via the focusing ratio (FR):^[500]

$$FR = \frac{F_S}{F_C} \quad (19)$$

where F_S is the sheath gas flow rate (typically N_2). Higher sheath gas flow rates increase the pressure surrounding the aerosol stream, compressing it and reducing its diameter. F_C is the carrier gas flow rate (also typically N_2). It determines the initial velocity and volume of the aerosol stream entering the focusing region. SCCM stands for $cm^3 \text{ min}^{-1}$ at standard temperature and pressure. As the aerosol jet exits the nozzle, it is typically focused to a diameter that is about 10% to 20% of the nozzle diameter.^[452,522] It is also accelerated to a velocity of $\sim 100 \text{ m s}^{-1}$.^[452,518]

The jet diameter (D_J) is an important factor that affects the resolution and precision of the printed features. D_J then can be estimated using the value for FR, as well as the diameter of the nozzle (D_N) by the following equation:

$$D_J = D_N \sqrt{1 - \sqrt{\frac{FR}{1+FR}}} \quad (20)$$

Since D_N is the physical size of the opening through which the aerosol jet exits, it sets the maximum potential diameter of the jet. The resolution can be estimated using the collimation relation, which depends on the aerosol stream diameter, nozzle diameter, and FR.^[422] A smaller nozzle diameter and a higher FR improve resolution, with an optimal FR value of around 2, providing a balance for adequate deposition and precision.^[292,422] D_J only slightly depends on F_C and has no dependence on either the rheological properties of the ink or droplet size, making it applicable to various types of ink.^[292,452] While

estimating D_j provides a basic reference for evaluating resolution, it is not a complete or perfect measure. This is because the aerosol jet can be influenced by factors such as droplet impaction, incomplete flow development, drying caused by the sheath gas, and potential aerodynamic focusing within the deposition nozzle, which can contribute to variations in resolution.^[292]

DEPOSITION STAGE: The deposition of the aerosol mist is a continuous impinging jet process controlled by the opening and closing of the electromagnetic shutter (located just below the nozzle).^[429] The deposition rate is collectively regulated by the printing parameters. These include atomiser aerosol flow, which is affected by the droplet size distribution, and sheath gas flow, which affects the focusing and the substrate impaction. The deposition rate is directly related to the sheath gas flow, i.e., the higher the sheath gas flow, the higher the deposition rate. However, the extent to which sheath gas flow could be increased is also limited by the pressure in the deposition head; thus, pressure build-up also has a negative impact on the deposition rate.^[292]

Sheath gas flow gives the aerosol droplets the acceleration needed to impact the substrate. The critical-size droplets with appropriate inertia would hit the substrate in a centralized manner, while smaller droplets with lower inertia are typically distributed more broadly around the deposition line, giving rise to the overspray.^[292,429] The overspray droplets are outside of the main focused jet and could generally be minimised by optimising printing parameters and atomisation, as well as ink formulation.^[455] For example, engineering inks with a small amount of a low-volatility co-solvent to increase droplet size can promote more controlled deposition.^[292]

The *Stokes number* (Stk) is typically used to determine the droplet's ability to follow gas streamlines or impact the substrate directly.^[454] Understanding the Stokes number allows for better control over droplet deposition, which is critical for achieving high-resolution and precise patterns in AJP. This parameter is defined by the equation:^[523]

$$Stk = \frac{\rho C_c D V}{4.5 \nu_G D_N} \quad (21)$$

where ρ is the density of the drop, D is the droplet diameter, V is the velocity of the droplet, ν_G is the kinematic viscosity of the surrounding gas, D_N is the nozzle diameter, and C_c is the dimensionless slip correction factor, which accounts for the effects of the

mean free path of gas molecules on small droplets. Optimal focusing is achieved when the $Stk \sim 1$.^[524,525]

When the Stokes number is low ($Stk \ll 1$), it indicates that the inertia of the droplets is very small compared to the drag force exerted by the surrounding gas. In this regime, droplets closely follow the gas flow lines, making them less likely to deviate and impact the substrate directly. A high Stokes number ($Stk \gg 1$) signifies that the droplet's inertia is much greater than the drag force. In this case, droplets have enough momentum to break away from the gas flow and impact the substrate directly. This is typical for larger, denser droplets or those moving at higher velocities.^[454] A high Stokes number indicates that droplets will likely impact the substrate, which is important for achieving precise patterns and minimizing overspray, where droplets spread beyond the intended printing area.^[526] Properly controlling the Stokes number can help minimize overspray and reduce defects such as uneven deposition. This leads to more consistent and reliable printing results. Different inks and substrates may require different droplet behaviours for optimal printing.^[292]

FURTHER CONSIDERATION IN AJP: The quantity of material deposited at a specific location on the substrate is directly influenced by the *process speed*: as the velocity increases, the amount of material deposited per unit length decreases. This relationship is critical for optimising the thickness and uniformity of printed lines. Research indicates that process speed primarily affects line height rather than width. For instance, when the process speed and atomiser gas flow remain constant, increasing the sheath gas flow enhances the line height and layer thickness while narrowing the line width. This adjustment can also influence printing precision by altering the deposition profile.^[429] In AJP, several nonidealities can impact printing quality and efficiency. Rapid deposition of wet ink can cause line spreading and fluid instabilities,^[527] while moderately dry inks may improve resolution but lead to inefficient ink use and airborne particles, posing safety risks. Additionally, high flow rates can result in incomplete flow development within the deposition nozzle, affecting deposition consistency. These challenges, influenced by factors like ink formulation, drying effects, and nozzle geometry, must be managed carefully to optimize deposition rate and resolution.^[292]

While the primary ink properties of viscosity, surface tension, and density are crucial for controlling droplet formation, other ink characteristics also play a significant role in the printing process. For instance, *non-Newtonian fluid behaviour* is also a crucial factor for

certain inks. It refers to fluids whose viscosity is not constant but changes in response to the applied shear rate or stress. Unlike Newtonian fluids, where the viscosity remains consistent regardless of the flow conditions, non-Newtonian fluids can become more or less viscous depending on the forces acting upon them.^[528] This property is particularly relevant in AJP when dealing with inks that contain complex formulations, such as those with high concentrations of nanoparticles, polymers, or other additives.

There are several types of non-Newtonian behaviour. The first one is *shear-thinning fluids*; they decrease in viscosity as the shear rate increases.^[529] This is advantageous in processes like AJP because as the ink flows through the nozzle under high pressure, it becomes less viscous, promoting the formation of smaller droplets and enhancing print resolution. The second type is *shear-thickening fluids*, which increase viscosity as the shear rate increases.^[530] This behaviour can complicate the AJP process because the ink becomes more resistant to flow under high shear, potentially leading to larger, less uniform droplets and difficulty maintaining a stable aerosol stream. The next type is *thixotropic fluids*; they decrease in viscosity over time under constant shear but recover their viscosity when the shear is removed.^[531] This time-dependent shear thinning can be beneficial in AJP if controlled properly, allowing for easier droplet formation during atomization and preventing ink from flowing too freely once on the substrate. Lastly, *rheopectic fluids* increase viscosity over time under constant shear.^[532] While less common, this behaviour can pose challenges in AJP by making the ink progressively harder to atomize if shear forces are maintained for too long.

Non-newtonian fluid behaviour becomes particularly important when dealing with advanced materials. For example, *MXenes* are characterized by their hydrophilic surface functional groups and negative zeta potential to achieve stable dispersion in polar solvents, making them exceptionally well-suited for printing applications.^[533] Notable, MXene inks (e.g. $\text{Ti}_3\text{C}_2\text{T}_x$) often exhibit shear-thinning behaviour primarily due to the high concentrations of 2D flakes dispersed in the solvent.^[534] The viscosity measurements of MXene dispersions were carried out across different shear rates, showing a significant reduction in viscosity at high shear rates. This reduction aligns with the requirements of printing processes, where high shear rates are applied, and low viscosity is desired to ensure smooth ink flow.^[534]

The rheological properties of MXene inks, such as significant elasticity and shear-thinning behaviour, can be fine-tuned to optimize print quality and resolution, depending on the

specific requirements of the application.^[533] When MXene inks exhibit lower viscosity under shear, the risk of nozzle clogging is reduced, as the aligned flakes can pass through the nozzle more smoothly. This property also helps in maintaining a steady flow of ink during printing. For example, tuning the aspect ratio and concentration of MXene flakes could optimize the ink's rheological properties to enhance print quality and resolution.^[250] Furthermore, MXene inks' adaptability extends beyond conventional applications. Due to their tunable viscoelastic properties, MXene inks can be tailored by adjusting the concentration, flake size, and surface chemistry, such as the degree of oxidation or functionalization, to suit specific printing conditions or desired outcomes.^[533]

The *interaction between ink droplets and the substrate* is a crucial aspect as well, and it can significantly affect print quality and adhesion. Two key factors in this interaction are the *surface energy* of the substrate and the *wetting behaviour* of the ink. The extent of this spreading depends on the balance between the ink's surface tension and the substrate's surface energy. For optimal adhesion and consistent line quality, the surface tension of the ink should closely match the substrate's surface energy.^[535] *Substrate temperature* also plays a significant role; heating the substrate can promote faster solvent evaporation, which is beneficial for achieving finer patterns with better adhesion. However, an excessive amount of solvent may cause cracking in the deposited material while drying.^[536] Pre-treatment and surface modification techniques can enhance substrate surface properties to improve ink adhesion and print quality as well.^[537,538]

When applying AJP to fabric substrates, several factors influence the quality of the print, including the fabric's surface energy, porosity, and texture. This adaptability makes MXenes a highly attractive material for AJP, enabling the printing of complex, multifunctional devices with fine structural control. Aqueous MXene inks, such as $\text{Ti}_3\text{C}_2\text{T}_x$, are particularly well-suited for printing on fabric substrates due to their excellent electrical conductivity, flexibility, and strong adhesion. This strong adhesion is facilitated by the abundance of functional groups on the MXene surfaces, which promote robust chemical interactions with textile fibres. The natural roughness of fabrics like cotton further enhances MXene adhesion, as the textured surface improves the adsorption of MXene materials. As a result, the conductive pathways formed by MXene inks remain intact even under mechanical stress, such as washing or bending, making them ideal for developing durable and reliable wearable electronics.^[449,539]

Operating an AJP system requires careful attention to health and safety. Volatile solvents and nanomaterial inks can pose inhalation risks,^[292] making proper ventilation and fume extraction essential to prevent exposure and environmental contamination. Luckily, the Optomec 300 AJP setup includes integrated extraction systems to effectively remove harmful vapours and airborne nanoparticles, ensuring a safer workspace.^[496]

AJP's effectiveness can be enhanced through a combination of process control, understanding of physical phenomena, and careful engineering of nozzle and flow parameters to optimize droplet size distribution and minimize overspray. Together, these factors establish a foundational framework for further refinement and improved precision in AJP applications.

2.3. ELECTRON MICROSCOPY

Electron microscopy has significantly advanced our ability to study the microscopic world by providing exceptional resolution and magnification, allowing for the visualization of structures at the atomic level. Unlike conventional light microscopy, which is limited by the wavelength of visible light, electron microscopy uses electrons as the illumination source. When electrons are accelerated to high energies (10^0 keV – 10^2 keV), they become fine probes with substantial scattering cross sections, ideal for high-resolution characterization at the nanoscale.^[540]

The pursuit of higher resolution in the early 20th century led to the development of electron microscopy. In 1931, Ernst Ruska and Max Knoll invented the first transmission electron microscope (TEM), which used electromagnetic lenses to focus electron beams and allowed for detailed observation of internal structures. Later, the development of the scanning electron microscope (SEM) added the capability to capture detailed images of surface topography.^[541] Together, TEM and SEM have transformed microscopy by enabling in-depth exploration of both internal and surface structures, driving significant advancements in various scientific disciplines.

While both TEM and SEM generate a focused electron beam that interacts with specimens within a vacuum chamber, their applications differ. SEM is designed for analyzing surface features of materials, whereas TEM is used for examining internal structures.^[542] This distinction in function reflects their respective design principles, as depicted in **Figure 13**.

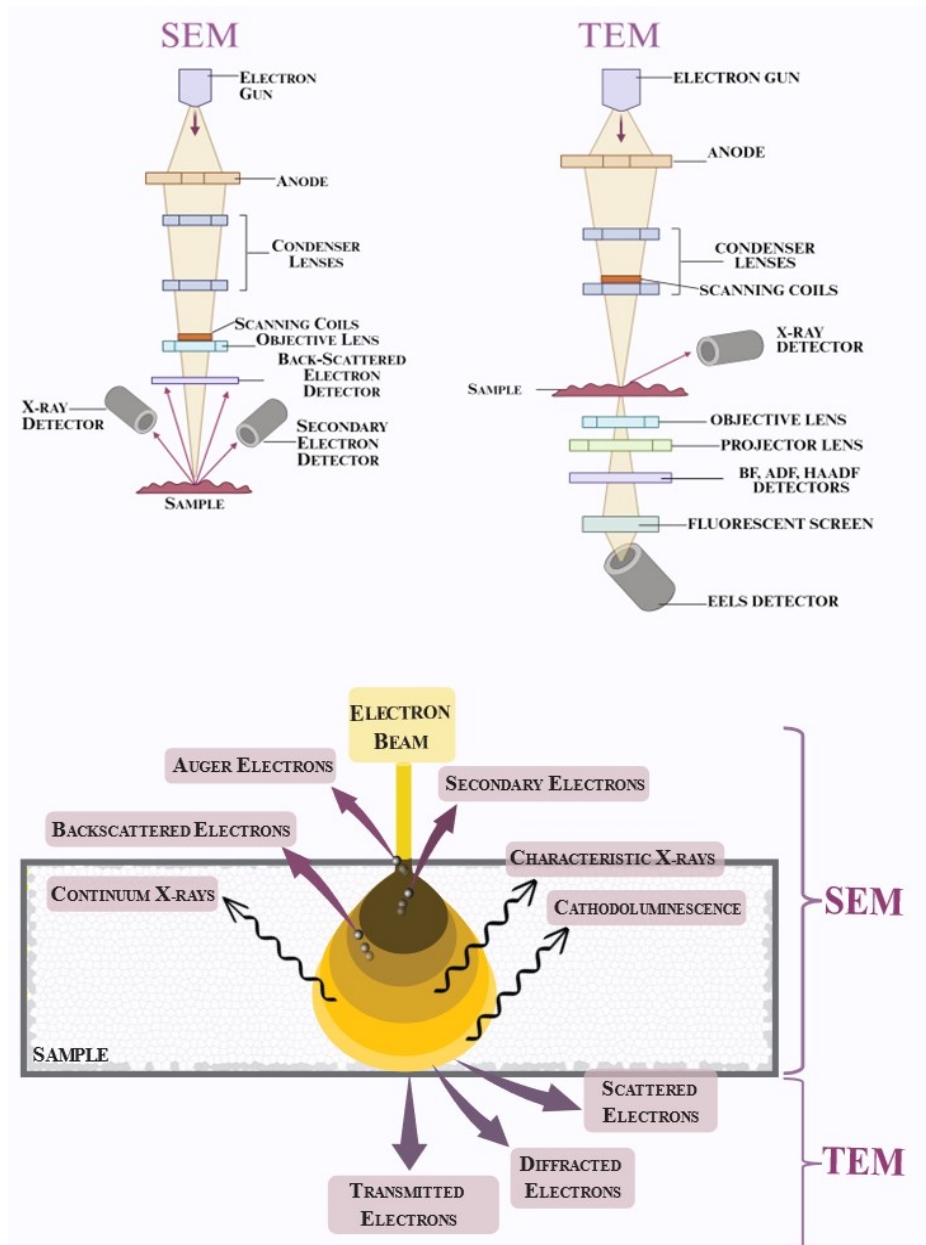


Figure 13: Schematic representation of SEM and TEM: instrument components and the range of electron-specimen interaction signals.

Created with Biorender.com and adapted from Ref^[543].

Electron microscopy relies on the interaction between electrons and materials to produce detailed images. High-energy primary electrons are directed at the specimen, where they interact with atoms, generating various signals. These interactions emit secondary electrons with reduced energy due to energy loss. As primary electrons pass through the specimen, they are scattered based on factors such as atomic structure, element type, and path length.^[542,544]

There are two types of electron scattering: elastic and inelastic. *Elastic scattering* changes the direction of electrons without energy loss, producing electron diffraction patterns useful for crystal structure analysis.^[545] *Inelastic scattering* involves energy loss and generates signals that help characterize the material. Specimen thickness affects scattering behaviour; thicker specimens increase the chances of inelastic scattering and energy loss. The region where these interactions occur is called the interaction volume, and the depth electrons can penetrate before absorption is the electron range. Specimens thin enough to allow primary electrons to pass through with minimal energy loss are considered electron transparent, depending on the electron energy and material composition.^[542]

Electron microscopy relies on various signals generated when electrons interact with a specimen to gather information about its structure and composition. *Secondary electrons* are low-energy electrons (2 – 5 eV) that originate from the specimen's surface. These electrons are produced by inelastic collisions, which excite electrons within the material to energy levels sufficient to overcome the work function. Secondary electrons are ideal for creating high-resolution images of surface features in SEM due to their shallow escape depth of just a few nanometers. *Backscattered electrons* are high-energy electrons generated when primary beam electrons are elastically scattered by the nuclei of atoms, with energies ranging from 50 eV up to the initial energy of the electron beam. Backscattered electrons provide compositional contrast based on the atomic number, as heavier elements scatter more electrons back. They also offer topographic information, although with lower resolution than secondary electrons due to their larger interaction volume. *Auger electrons* and *characteristic X-rays* are generated following the ionization of inner-shell electrons. Auger electrons are emitted when the energy released during the filling of a vacancy is transferred to another electron, which then escapes the atom. These electrons, like secondary electrons, come from a very thin surface layer, making them suitable for surface analysis. Characteristic X-rays, used in energy-dispersive X-ray spectroscopy (EDX), provide elemental composition information based on their unique energy signatures. The interaction depth, or the volume within which these signals are generated, varies depending on the signal type. Secondary and auger electrons are highly surface-sensitive, while backscattered electrons and X-rays originate from deeper within the specimen. The detection and interpretation of these signals, influenced by specimen properties and external fields, allow for detailed surface and compositional analysis, enabling a comprehensive understanding of both the surface and internal characteristics of materials in electron microscopy.^[542,546,547]

TRANSMISSION ELECTRON MICROSCOPY (TEM) is a powerful tool for analyzing the internal structure of materials at the atomic level. In TEM, a highly accelerated electron beam, typically in the range of 80 – 300 kV, is directed through an ultrathin specimen.^[548] As these electrons interact with the specimen, they are scattered either elastically or inelastically, which provides detailed information about the specimen's structure and composition. The resolution in TEM is superior because of the shorter wavelength of electrons compared to visible light, allowing atomic-level imaging. TEM is equipped with electromagnetic lenses positioned sequentially along the path of the electron beam in what is known as the electron column. Condenser lenses, located before the specimen, focus the electrons into a beam with a specific diameter and convergence. The objective lens then focuses the transmitted electrons to create a diffraction pattern and an initial image, which is subsequently magnified by projector lenses onto the detection system.^[542,548]

TEM has various imaging modes, such as bright-field and dark-field imaging, which are used to highlight different features within the sample based on electron scattering. High-resolution TEM (HRTEM) and scanning TEM (STEM) offer even more detailed views, with atomic-scale resolution possible when aberration-corrected lenses are employed. In STEM mode, bright-field images are produced from unscattered electrons, while annular dark-field (ADF) images use electrons scattered at specific angles. High-angle annular dark field (HAADF) imaging, a specialized ADF technique, captures electrons scattered at very high angles, providing strong contrast based on atomic number (Z-contrast) for detailed atomic-scale chemical analysis. Specimen preparation for TEM requires samples to be very thin, generally less than 100 nm, to be electron transparent. Due to the sensitivity of TEM, the environment must be highly controlled to minimize vibrations, electromagnetic interference, and temperature fluctuations.^[542,544]

SCANNING ELECTRON MICROSCOPY (SEM) is widely used for detailed surface analysis and topographical imaging. SEM operates by directing a focused beam of high-energy electrons, typically accelerated through a voltage ranging from 1 to 30 kV, toward a specimen's surface. The interaction of these electrons with the atoms at the sample's surface generates various signals that are detected and analyzed to produce high-resolution images and gather compositional data. In SEM, various detectors collect signals generated by electron-specimen interactions, including secondary electrons, which provide high-resolution surface images; backscattered electrons, which offer compositional contrast

based on atomic number; and X-ray detectors, which facilitate elemental analysis. The choice and combination of detectors and imaging modes enable SEM to deliver comprehensive surface characterization and material analysis.^[547]

Both TEM and SEM are equipped with X-ray detectors that enable *energy-dispersive X-ray spectroscopy* (EDX). These detectors convert incoming X-rays into electron-hole pairs, producing an electronic current that is proportional to the X-ray's energy. Over a collection period of a few minutes, the detector measures X-rays at different energies from a specific point on the specimen, generating an energy-dispersive X-ray spectrum that facilitates the determination of elemental composition. In TEM, EDX achieves higher spatial resolution for chemical analysis because X-rays are emitted only from the very thin, electron-transparent area that the electron beam penetrates, reducing the interaction volume to less than 200 nm. Advanced techniques like STEM-EDX in TEM further improve spatial resolution, enabling nearly atomic-scale elemental mapping. In contrast, the larger interaction volume in SEM limits the spatial resolution of EDX to around 1 μm . However, this broader penetration is advantageous for analyzing thicker or bulk specimens, making SEM-EDX useful for surface and near-surface compositional analysis in a wide range of materials.^[542,549]

Together, TEM, SEM, and EDX provide a comprehensive suite of techniques for materials characterization, allowing detailed structural, morphological, and compositional analysis across various scales. These methods are indispensable in fields such as materials science, biology, and nanotechnology, offering unparalleled insight into the microstructural properties of materials.

2.4. X-RAY DIFFRACTION

X-ray diffraction (XRD) is a powerful analytical technique used to elucidate the crystallographic structure, chemical composition, and physical properties of materials. XRD exploits the interaction of X-rays with the periodic atomic structures of crystalline materials.^[550]

X-rays are high-energy electromagnetic waves with wavelengths from 10^{-3} and 10^1 nm, typically generated in laboratory equipment using sealed tubes and rotating anodes. In these devices, electrons are produced by heating a tungsten filament and then accelerated towards a target by a high voltage.^[550]

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When these high-energy electrons strike the target, they generate X-rays through two main processes: *Bremsstrahlung*, which emits a broad, continuous spectrum of X-ray photons as the electrons decelerate, and *characteristic X-ray emission*, which occurs when electrons from outer shells fill vacancies left by ejected inner-shell electrons, emitting photons with specific energies unique to the target material. The resulting X-ray output is a combination of a continuous spectrum and characteristic radiation.^[551]

XRD primarily uses the most intense characteristic radiation, known as $K\alpha$, and filters out other wavelengths using filters or monochromators, which selectively absorb unwanted radiation while allowing the $K\alpha$ radiation to pass. The choice of filter is based on the target material to ensure optimal radiation for analysis.^[550]

When a monochromatic X-ray beam strikes a crystalline sample, the atoms in the crystal lattice scatter the X-rays in specific directions. This scattering produces a diffraction pattern that, according to *Bragg's law*, reveals essential information about the material's interatomic spacings, lattice parameters, crystallite size, and crystal orientation. Bragg's law, the core principle behind XRD, describes the relationship between the wavelength of the incident X-rays (λ), the diffraction angle (θ), and the spacing between atomic planes in the crystal (d_{hkl}) using the equation:^[552]

$$n\lambda = 2d\sin\theta \quad (22)$$

where n is an integer representing the order of the diffraction peak. This equation is derived from the requirement for constructive interference of X-rays scattered by parallel planes of atoms in a crystal, as shown in **Figure 14**. Constructive interference occurs when the path difference between X-rays scattered from successive planes equals an integer multiple of the X-ray wavelength, resulting in a diffraction peak.

The XRD pattern produced consists of a series of peaks, each associated with different crystallographic planes within the material. The positions (2θ) of these peaks are used to determine lattice parameters, while their intensities reveal details about the atomic arrangement within the unit cell. Furthermore, the broadening of these peaks can provide insights into the crystallite size and strain in the sample, enabling phase identification and quantitative analysis of the crystal structure.^[553]

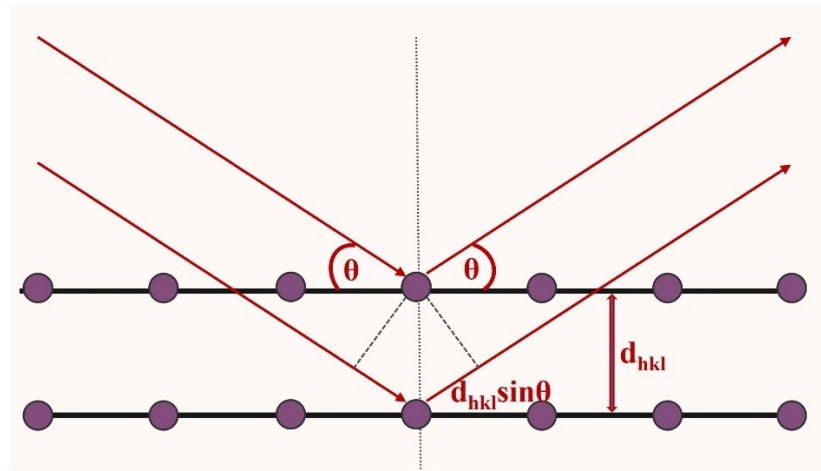


Figure 14: A schematic representation of Bragg diffraction occurring on a set of (hkl) lattice planes with an interplanar spacing of d_{hkl} . The Bragg condition is met at an angle θ when the path difference between the two reflected waves equals an integer multiple of the X-ray wavelength λ .

XRD is a standard method for phase identification in materials science. By comparing the measured diffraction pattern with reference patterns from databases such as the Powder Diffraction File (PDF), one can identify the crystalline phases present in a sample.^[554] This is particularly important in materials research, where phase purity and phase transitions play a critical role in determining material properties. Beyond phase identification, XRD is used to determine the detailed crystal structure of materials. By analyzing the positions and intensities of diffraction peaks, one can derive the unit cell dimensions, atomic positions, and symmetry elements of the crystal.^[555]

2.5. ELECTROCHEMICAL CHARACTERISATION

Electrochemical characterization techniques are fundamental tools in the study of material properties and the development of energy storage devices. In material science, particularly for supercapacitors and MSCs, these techniques provide critical insights into the charge storage mechanisms, efficiency, and stability of the materials and devices. Understanding these characteristics is crucial for optimizing performance, particularly in applications where high power density, rapid charge-discharge cycles, and long-term stability are required.

Recalling Section 1.4.3, where it was explained that supercapacitors are classified into two types: EDLCs and pseudocapacitors. EDLCs store charge electrostatically, typically using carbon-based materials that provide high surface areas for charge accumulation at the

electrode-electrolyte interface. In contrast, pseudocapacitors utilize faradaic processes, where charge storage involves reversible redox reactions within the electrode materials. This distinction is critical when tailoring electrochemical characterization techniques to these different types of supercapacitors, as each mechanism exhibits unique electrochemical signatures.

2.5.1. ELECTROCHEMICAL CELLS

In a typical electrochemical setup, a potential difference is applied between two electrodes that are immersed in an electrolyte. While electrons can travel externally between the electrodes, they cannot move through the electrolyte itself. Instead, ions in the electrolyte act as the charge carriers to close the circuit.^[556] Electrochemical characterization of energy storage devices, such as supercapacitors, often employs two distinct cell configurations: *two-electrode* and *three-electrode* systems, as depicted in **Figure 15**. Each configuration serves a specific purpose and provides different insights into the electrochemical behaviour of materials. Understanding the differences between these setups is crucial for correctly interpreting data and optimizing device performance.

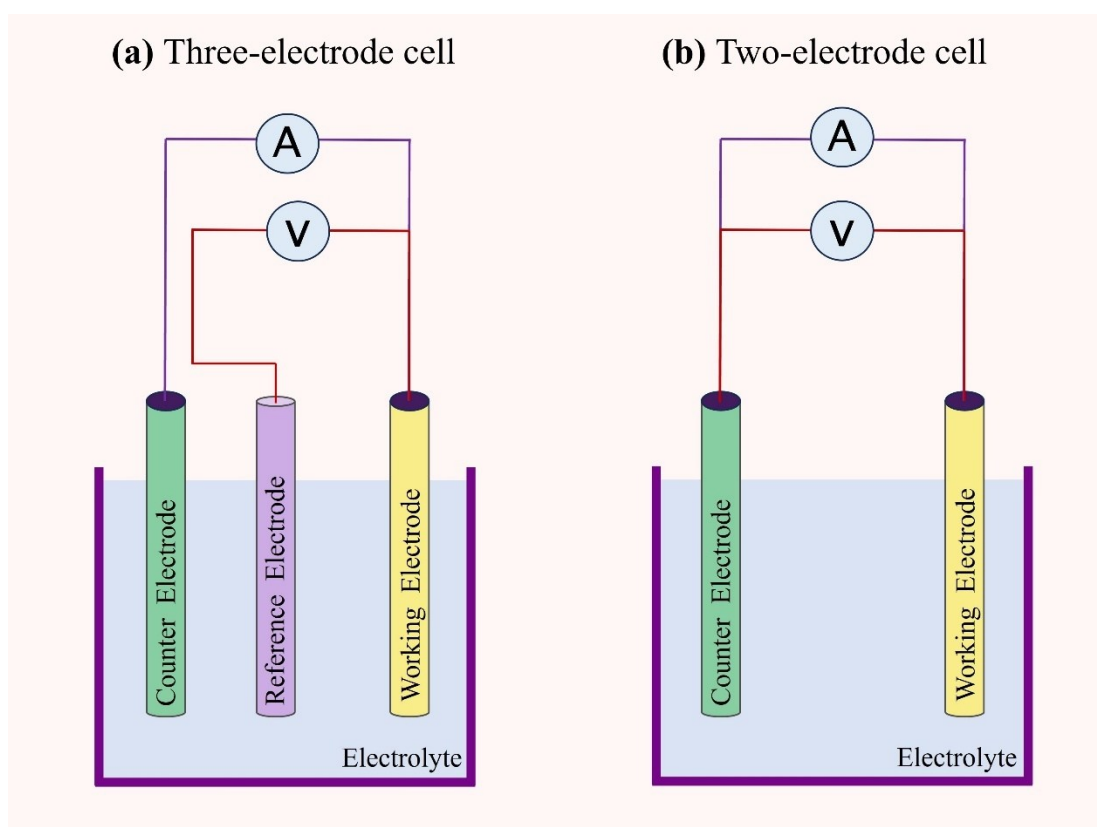


Figure 15: Schematic representation of electrochemical cell configurations: **(a)** three-electrode setup and **(b)** two-electrode setup. Adapted from Ref^[557].

Chapter 2: Deposition & Characterisation Techniques

Electrodes are fundamental components in electrochemical cells, each serving a specific function to facilitate controlled electrochemical reactions. The three primary types of electrodes: reference, working, and counter electrodes, are integral to obtaining precise and reliable measurements in electrochemical studies. *Working electrodes* are the sites where electrochemical reactions occur, providing a conductive surface for electron transfer between the electrode and the solution. When a potential is applied, the working electrode enables electron flow, generating a current proportional to the electrochemical activity. The material choice for working electrodes, typically platinum, gold, or glassy carbon, depends on the specific application, as they must be conductive, chemically inert, and capable of facilitating efficient electron transfer. Maintaining a clean and active surface is crucial, as surface contamination can significantly impact the kinetics of electron transfer and compromise data quality. *Counter electrodes* serve to complete the circuit by balancing the electron flow at the working electrode. Made from inert materials like platinum, graphite, stainless steel, gold, or silver, counter electrodes provide a source or sink for electrons without participating in the electrochemical reaction itself. They are designed to have a larger surface area than the working electrode to handle the current without affecting the working electrode's performance. The primary function of the counter electrode is to ensure a stable and consistent current flow, thus supporting accurate electrochemical measurement. *Reference electrodes* provide a stable and well-defined potential against which the working electrode's potential is measured, ensuring accuracy and consistency across different experiments. Their ability to decouple potential from current allows for precise potential control and comparison. Ideal reference electrodes are characterized by a stable and reproducible potential, non-polarizability, low solubility, and reversible behaviour as defined by the Nernst equation. Common reference electrodes for aqueous systems include the hydrogen electrode, silver/silver chloride (Ag/AgCl) electrode, and calomel (Hg/Hg₂Cl₂) electrode. Among these, the Ag/AgCl electrode is widely used due to its stability and ease of handling.^[558,559]

THREE-ELECTRODE CELLS

The three-electrode cell configuration (**Figure 15(a)**) is a fundamental setup used primarily to study the intrinsic electrochemical properties of individual electrode materials. It consists of all three: working, counter electrode, and reference electrodes. In a three-electrode system, the potential of the working electrode is measured against the reference electrode while the current flows between the working and counter electrodes. This setup

allows for precise control and measurement of the electrochemical reactions occurring at the working electrode surface. By isolating the working electrode from the counter electrode, the three-electrode configuration minimizes the influence of the counter electrode's behaviour on the measurements. This approach is particularly advantageous for studying the electrochemical properties of new materials, such as redox potentials, capacitance, and charge-transfer kinetics, providing a clear and accurate assessment of the electrode material's performance without interference from other cell components. In this setup, only half of the cell is studied, allowing researchers to accurately measure changes at the working electrode while eliminating any impacts from the counter electrode.^[241,560]

TWO-ELECTRODE CELLS

The two-electrode cell configuration (**Figure 15(b)**), in contrast, is designed to evaluate the complete performance of an electrochemical device under conditions that closely resemble practical applications. This setup includes only two electrodes: a positive (working) electrode and a negative (counter/reference) electrode. Unlike the three-electrode system, the two-electrode setup measures the total voltage across both electrodes, capturing the combined electrochemical behaviour of the entire cell, including contributions from both the electrodes and the electrolyte interface. In a two-electrode cell, the current and sense measurements are typically obtained using the current-carrying electrodes, where the current and sense leads are attached to the working electrode, and the counter and reference electrodes are shorted together at the other electrode. This configuration allows the voltage of the whole cell to be measured, which is crucial for analyzing the overall energy storage capability of the device.^[241,558,560]

In the context of supercapacitors, both configurations offer valuable insights. Three-electrode measurements allow for precise characterization of electrode materials, while two-electrode measurements provide comprehensive data on device performance and stability under operational conditions. Together, these configurations provide a robust framework for developing and optimizing next-generation energy storage devices.

2.5.2. ELECTROCHEMICAL CHARACTERISATION TECHNIQUES

To achieve a complete electrochemical characterization of supercapacitors, it is essential to utilize techniques such as cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS).^[177,561] These techniques allow

for evaluating important parameters of supercapacitors such as capacitance, ESR, energy and power densities, cycle life and rate performance.^[179]

CYCLIC VOLTAMMETRY (CV) is a versatile and widely used electrochemical technique that involves the linear sweeping of a potential between two limits while measuring the resulting current. This method is particularly useful for understanding the electrochemical processes occurring on the electrode surface during the charging and discharging of supercapacitors.^[562] The primary output of CV is a plot of current versus potential, known as a voltammogram, which provides detailed information on the electrochemical reactions occurring at the electrode surface, including distinguishing between faradaic and non-faradaic processes. The shape and features of the voltammogram can reveal key information about the kinetics and mechanisms of these reactions, as well as the capacitive behaviour of the materials, enabling the determination of the supercapacitor's capacitance, rate performance, power and energy densities, voltage window, and cycle life.^[170,563,564]

During CV analysis, a linearly changed electric potential is applied between the negative and positive electrodes in a two-electrode cell or to the working electrode with respect to a reference electrode in a three-electrode cell.^[565] The instantaneous current is recorded during both the cathodic and anodic sweeps, serving as a response signal to the applied potential.^[170] This current can be thought of as a response signal to the potential signal.^[566] This current data, plotted against the potential data, forms the voltammogram, which can be used to characterize the interactions between active materials and electrolyte ions.^[170,566]

CV provides critical insights into electrochemical systems. It identifies redox behaviour, including oxidation and reduction potentials, and assesses the reversibility of these processes. CV also reveals electrochemical kinetics, helping to determine rate constants and reaction mechanisms. Additionally, it measures diffusion coefficients and can be used for concentration analysis of chemical species. The technique also characterizes electrode surfaces, providing information on capacitance and adsorption, and evaluates the stability and reactivity of electroactive species over multiple cycles.^[567]

Moreover, CV is particularly useful for determining the potential window (operating voltage) of supercapacitor materials in a three-electrode system by gradually adjusting the reversal potential. This approach not only identifies the appropriate voltage range for

operation but also allows for the simultaneous evaluation of the reversibility of charge and discharge processes. Moreover, specific capacitance and energy performance of supercapacitor materials can be derived from the integration of CV curves. A similar method can be employed for entire supercapacitor devices to determine their total cell capacitance and quantify the stored electrical energy.^[568] CV can also be utilised to assess the cycle life of supercapacitors by performing repeated sweeps at a set scan rate, which evaluates the stability and durability of their electrochemical performance.^[170]

Typical CV outputs from the analysis of supercapacitors are shown in **Figure 16**. In supercapacitors, the CV response is directly related to the charge storage mechanism. For EDLCs, an ideal CV profile typically shows a rectangular shape, indicative of a purely capacitive process where the current response remains consistent across the potential range, reflecting rapid ion adsorption/desorption at the electrode surface.^[168,177,569]

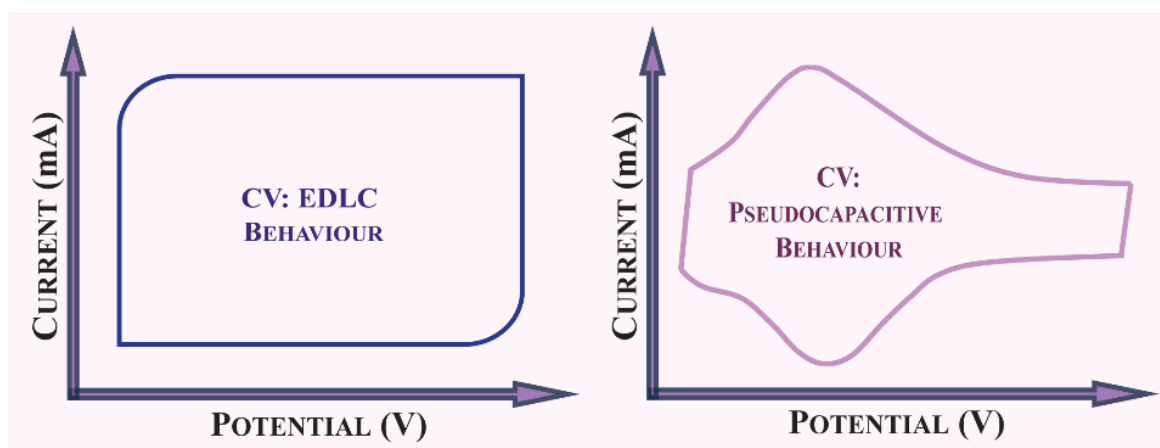


Figure 16: CV profiles for different supercapacitor mechanisms: **(left)** a rectangular CV curve characteristic of EDLCs, and **(right)** a CV curve with distinct redox peaks typical of pseudocapacitive behaviour. Adapted from Ref^[569].

In contrast, pseudocapacitors exhibit distinct redox peaks in their CV profiles, corresponding to faradaic reactions with reversible oxidation and reduction in the electrode materials. Ideally, the potential separation between these peaks should be minimal or nonexistent, indicating efficient and reversible redox processes. The position, shape, and area under these peaks offer insights into the redox kinetics, reversibility, and specific capacitance of the materials.^[168,177,569]

GALVANOSTATIC CHARGE-DISCHARGE (GCD) is a fundamental electrochemical technique widely used to evaluate the performance of energy storage devices. It involves

charging and discharging an electrode or device at a constant current while measuring the resulting voltage over time. The GCD technique provides critical insights into the capacitance, energy density, power density, and internal resistance of the system, making it an essential tool for characterizing and optimizing electrochemical energy storage materials.^[170]

In a GCD experiment, a constant current is applied to the electrochemical cell, causing the voltage to change over time as the device is charged and then discharged. The current is maintained at a fixed value throughout each phase, with the voltage response recorded to produce a charge-discharge curve. The shape and characteristics of this curve are directly related to the electrochemical properties of the device or material under investigation.^[565]

The specific capacitance can be calculated from the slope of the discharge curve, while the energy density is derived from the area under the discharge curve. Power density, on the other hand, depends on the rate of voltage change and the applied current density. Furthermore, ESR can be calculated from the immediate voltage drop (V_{drop}) that occurs following the reversal of current polarity, where a discontinuity appears in the triangular voltage profile.^[553] **Figure 17** shows typical GCD outputs from the analysis of supercapacitors.

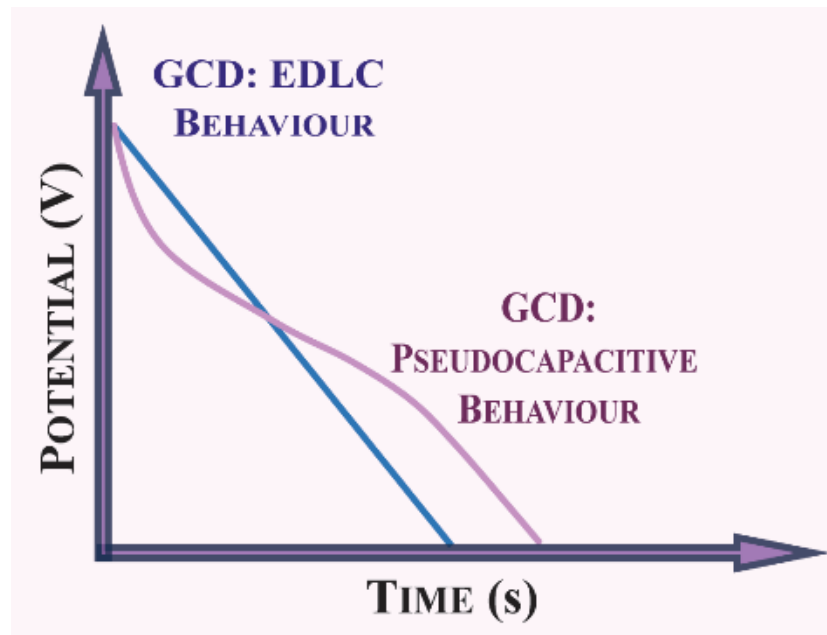


Figure 17: GCD profiles for different supercapacitor mechanisms: (blue) a linear response characteristic of EDLCs, and (purple) a non-linear response typical of pseudocapacitive behaviour. Adapted from Ref^[569].

In EDLCs, the ideal GCD curve exhibits a linear voltage-time relationship during both charging and discharging, reflecting a constant capacitance and low internal resistance. This linearity indicates that the energy is stored via electrostatic adsorption of ions at the electrode surface, with minimal resistive losses. For pseudocapacitors, the GCD curves are typically nonlinear due to the involvement of faradaic processes. The voltage profile may exhibit plateaus or changes in slope, corresponding to redox reactions at specific potentials that occur during cycling. The shape and features of the GCD curve can provide insights into the charge storage mechanisms, efficiency, and reversibility of the pseudocapacitive materials.^[168,177,569]

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS) is a powerful analytical technique used in electrochemistry to examine the impedance characteristics of materials and devices over a wide range of frequencies. EIS enables the measurement of both the current amplitude and phase shift in response to an applied alternating voltage, providing detailed insights into the electrochemical properties and processes occurring within a system.^[170,570]

Impedance, which is a measure of a system's ability to resist the flow of electrical current, is a key parameter in understanding the behaviour of electrochemical devices.^[570] To obtain EIS measurements, a small amplitude sinusoidal alternating voltage is typically applied across the device, and impedance data are collected at the open circuit potential while the system is in an equilibrated state.^[175,569] The impedance data from EIS are often represented graphically in a Nyquist plot, where the imaginary component of impedance, $-Z(f)''$, is plotted versus real component $Z(f)'$.^[569,571] These plots are typically displayed on a 1:1 square scale, facilitating clear visualization of impedance behaviour across different frequencies.^[569]

There are two states between which supercapacitors oscillate depending on the frequency. At low frequencies, both EDLCs and pseudocapacitors exhibit capacitive behaviour, shown by a sharp increase in the imaginary component of impedance ($-Z''$) on the Nyquist plot. This indicates efficient charge storage capabilities, with EDLCs displaying a near-vertical line due to pure capacitive ion adsorption at the electrode surface. Pseudocapacitors, however, may show deviations from this vertical line due to additional contributions from faradaic (redox) reactions, which involve electron transfer and add complexity to their capacitive behaviour.^[175,572] **Figure 18** effectively illustrates these behaviours.

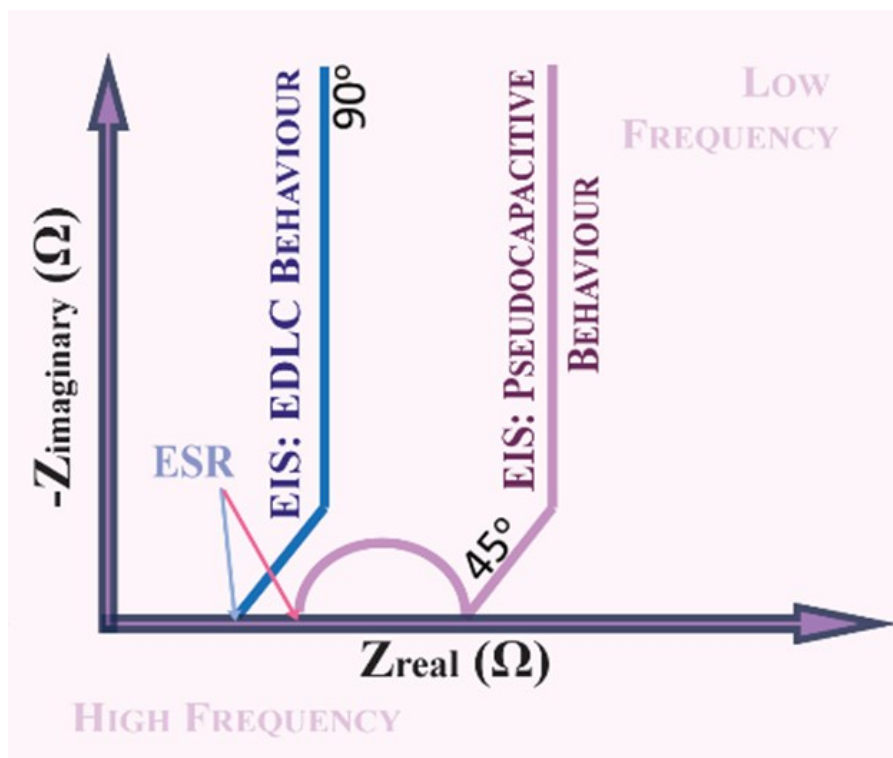


Figure 18: Typical Nyquist plot illustrating the typical electrochemical impedance behaviour of EDLCs (blue) and pseudocapacitors (purple). On this schematic, ESR, 45° and 90° lines are marked. Adapted from Ref^[569].

At high frequencies, the Nyquist plot reveals a resistance-dominated state where the impedance primarily reflects the conductivities of the active material and the electrolyte.^[175,572] EIS is commonly used to determine the ESR of supercapacitors, a critical parameter that affects the power density of these devices.^[564] As ESR decreases, the power density increases, which is due to the limiting effect the ESR has on the charging/discharging rates.^[179] In practice, the ESR can be determined by extrapolating the real axis of the Nyquist plot at very high frequencies; the intercept of the Nyquist plot with the x-axis represents the ESR.^[569,571,573]

Additionally, a semicircle may be observed at high frequencies, and it is crucial to identify the reason for its occurrence. It may result from surface functional groups or faradaic reactions in pseudocapacitive materials or interfacial impedance at the active material/current collector interface.^[569] For example, by using the diameter of the arc, the charge transfer resistance can be evaluated, considering the semicircle is caused by the presence of surface functional groups or from faradaic reactions.^[175] To identify which reason is valid, the impedance spectra may be recorded at different potentials, where

charge transfer resistance will change with potentials, while interfacial impedance will remain constant only with some changes in a low-frequency region.^[569]

Between the low and high-frequency regions, there is a resistance-capacitance state in which the effects of electrode porosity and thickness on ion migration rate could be observed. These effects also shift the plot towards more resistive values along the real axis.^[572] At intermediate frequencies, the linear part at an angle of 45° may be observed, which is a slope of the Nyquist plot known as the Warburg impedance. Warburg impedance is related to the ion-diffusion resistance and occurs due to the frequency dependence of ion diffusion in the electrolyte to the electrode interface.^[175,571,573]

Overall, EIS provides valuable insights into the internal dynamics of these energy storage devices, making it indispensable for both fundamental research and the development of advanced energy storage technologies.

3 AEROSOL JET PRINTED MXENE TEXTILES

AIMS & OBJECTIVES

This chapter aims to develop an optimised AJP strategy for depositing $\text{Ti}_3\text{C}_2\text{T}_x$ MXene onto textiles, ensuring uniform, conductive, and scalable coatings for e-textile applications.

The first objective is to synthesise and characterise an additive-free aqueous $\text{Ti}_3\text{C}_2\text{T}_x$ MXene ink, assessing its morphology, flake size, and stability using XRD, TEM, and EDX. The effect of ultrasonic atomisation on flake integrity post-printing will also be examined.

The second objective focuses on optimizing AJP parameters to achieve precise and reproducible MXene coatings. The impact of nozzle diameter, process speed, and gas flow rates on deposition uniformity and electrical conductivity will be investigated, alongside the role of substrate porosity and ink absorption. A mass loading-to-layer correlation will be established for controlled deposition.

The third objective is to evaluate the surface coverage, adhesion, and electrical performance of printed MXene films on cotton, polyester, and polycotton, using SEM, XRD, and resistance measurements. Alternative conductivity characterization methods will be explored to address textile-specific challenges.

The final objective is to provide a practical guide for researchers in troubleshooting AJP challenges, such as nozzle clogging, overspray, deposition instability, and mass quantification inaccuracies caused by textile hygroscopicity and porosity. A deposition rate monitoring strategy will be introduced as a real-time quality control measure to ensure consistent and scalable MXene deposition.

3.1. INTRODUCTION

The future of wearable technology is increasingly focused on fabrics that go beyond mere clothing. This emerging domain of e-textiles is at the forefront of technological innovation. However, a major challenge in realising this potential lies in integrating advanced, flexible electronics into soft, adaptable fabrics without compromising their essential qualities.

Textiles present an ideal platform for electronic integration, surpassing conventional bulky and rigid substrates due to their unique and highly advantageous properties. Their appeal stems from their inherent flexibility, deformability, and breathability, making them perfectly suited for wearable technologies that require both comfort and functionality. Textiles are not only durable and washable but also cost-effective, widely available, environmentally sustainable, and biodegradable. Moreover, their diverse porosity, which varies with fabric type, allows for effective thermal regulation, offering insulation in cold weather while facilitating the escape of heat and moisture in warmer conditions, thereby ensuring the breathability crucial for prolonged wear on human skin. From a user's perspective, textiles effortlessly conform to various body shapes and movements, providing unmatched comfort and freedom of movement.^[138,574–576]

Beyond their physical attributes, textiles are deeply embedded in human culture and daily life. For centuries, fabrics have played a central role in human existence, used in myriad forms to meet the needs of different body types, preferences, and environmental conditions. The transformation of textile production began with the Industrial Revolution, particularly following the invention of the steam engine in 1782, which shifted the industry from home-based craft to large-scale manufacturing. The 20th century further revolutionized textiles with the introduction of synthetic fibres and innovative dyes, expanding the possibilities for textile applications.^[576] This long-standing familiarity with textiles makes them an ideal medium for integrating advanced technologies in a manner that feels natural and unobtrusive, minimizing the disconnect often associated with modern technological innovations.

The construction of textiles begins with the fundamental building blocks: yarns, which are produced by spinning fibres into continuous strands. These fibres can be categorized into three main types: natural, synthetic, and blended.^[576]

Natural fibres, such as cotton, linen, wool, and silk, have been used for millennia due to their comfort, breathability, and aesthetic qualities. Each natural fibre offers unique characteristics suited to specific applications.^[576] Among these, cotton is particularly versatile and widely used, appreciated for its excellent mechanical properties, biocompatibility, and breathability. Its softness, moisture absorption, and natural porosity make it ideal for everyday wear, while its durability allows it to withstand frequent washing without significant wear.^[577] These characteristics also make cotton an excellent substrate for e-textiles, which integrate electronic components into fabrics. Cotton's good dyeability and printability facilitate the incorporation of conductive inks and coatings necessary for electronic functionality.^[578]

Cotton primarily consists of cellulose in the I β allomorph, a crystalline form that enhances its strength and durability. The cellulose structure features one primary hydroxyl group and two secondary hydroxyl groups per glucose unit, which improve its ability to absorb moisture and create opportunities for chemical bonding, which in turn enhances the adhesion of various materials through hydrogen and covalent bonds.^[578,579] Furthermore, cotton textiles are water-absorbing.^[580] This hydrophilicity allows for deeper penetration of adhesives and coatings when it absorbs moisture, enhancing bonding strength. Thus, cotton's unique combination of chemical reactivity and physical properties makes it suitable for both traditional textile applications and advanced e-textile innovations, balancing comfort, functionality, and durability.

Synthetic fibres, such as polyester, nylon, and viscose, are engineered materials designed to offer enhanced durability, elasticity, and resistance to environmental factors.^[576] Among synthetic fibres, polyester, primarily composed of PET, is a widely used synthetic material valued for its durability, strength, and versatility. It is known for its high tensile strength and resistance to stretching, shrinking, and abrasion, which make it suitable for various applications, from clothing to industrial textiles.^[581] These properties are advantageous for e-textile applications, as its strength and durability support the integration of electronic components.

Blended fabrics combine the properties of natural and synthetic fibres to create textiles that benefit from the strengths of both. One of the most popular combinations is polycotton, a blend of polyester and cotton, due to its balanced combination of the softness and breathability of cotton with the durability, wrinkle resistance, and quick-drying properties of polyester.^[582,583]

Fabrics, the finished products made from yarns, are typically produced by weaving or knitting, though non-woven manufacturing methods also exist. *Woven fabrics*, created by interlocking two sets of yarns – warp (lengthwise direction) and weft (widthwise direction) – at right angles, provide strength and stability, making them ideal for supporting intricate electronic circuits. The tight interlacing of yarns in woven fabrics ensures that electronic components remain securely embedded within the fabric even under mechanical stress, making these fabrics particularly suitable for applications requiring structural integrity and resistance to deformation. *Knitted fabrics*, on the other hand, are produced by interlinking loops of yarn, either from a single yarn (weft knitting) or multiple yarns (warp knitting). Known for their elasticity, knitted fabrics are perfect for applications that require flexibility and movement, such as sportswear or garments that must accommodate the dynamic movements of the human body. Their ability to stretch and recover shape ensures comfort while maintaining the functionality of embedded electronics.^[109,576]

However, transforming smart fabrics from concept to reality requires more than merely selecting an appropriate textile; it demands the development of advanced functional materials capable of imbuing these fabrics with electronic properties. In this context, nanomaterials have revolutionized the e-textile industry by providing the enhanced conductivity and multifunctionality needed to seamlessly integrate high-performance electronic components into fabrics. A particularly promising class of nanomaterials is MXenes, as discussed in detail in Section 1.5, with titanium carbide ($\text{Ti}_3\text{C}_2\text{T}_x$) standing out as an ideal candidate.

3.2. EXPERIMENTAL METHODS

3.2.1. SYNTHESIS OF $\text{Ti}_3\text{C}_2\text{T}_x$ MXENE INK

Additive-free aqueous $\text{Ti}_3\text{C}_2\text{T}_x$ MXene ink was synthesized from its parent Ti_3AlC_2 MAX phase via a MILD route using HCl/LiF .^[226,362] Concentrated hydrochloric acid (HCl , 45 mL, Sigma) was gradually added into a 40 mL vented PTFE bottle filled with deionized water (DI, 15 mL). To this resulting 9 M HCl solution, LiF powder (4.8 g, Sigma) was added, and the bottle was placed in a mineral oil bath, stirred at 400 rpm using a magnetic PTFE stirrer bar to ensure complete dissolution of LiF and stabilize the temperature. Over a 30-minute, small additions of Ti_3AlC_2 MAX phase powder (3 g, Carbon-Ukraine Ltd.) were carefully introduced into the vessel to prevent overheating. The solution was left to stir at 400 rpm and 35 °C for 24 hours to achieve etched, multilayer $\text{Ti}_3\text{C}_2\text{T}_x$ MXene. To

eliminate the etchant, the vessel's contents were evenly distributed into eight 50 mL centrifuge tubes and diluted to a total volume of 40 mL each using DI water. The dispersion underwent centrifugation at 5000 rpm for 5 minutes in a Thermo Scientific Heraeus Multifuge X1, with the supernatant discarded. This sedimentation process was repeated several times until the pH of the supernatant reached at least 6.5. To facilitate the delamination of the washed multilayer MXene, the tube was tightly sealed and vigorously shaken by hand and then vortex mixed for 30 minutes. Then, the dispersion underwent centrifugation at 1500 rpm for 30 minutes to sediment any multilayer MXene or unreacted MAX phase. The supernatant containing the delaminated MXene flakes was collected. This dispersion was then centrifuged at 5000 rpm for 1 hour to sediment the delaminated MXene, which was subsequently redispersed to a concentration of $\sim 30 \text{ mg mL}^{-1}$. Prepared additive-free aqueous $\text{Ti}_3\text{C}_2\text{T}_x$ MXene inks are stored in 5 mL glass vials, purged with nitrogen, and filled completely with ink before sealing to prevent oxygen entrapment.

3.2.2. CONCENTRATION DETERMINATION OF MXENE INK

The concentration of the synthesised $\text{Ti}_3\text{C}_2\text{T}_x$ MXene ink was determined by transferring 100 μL of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene dispersion to a small glass vial and diluting it with a 1:1 (v/v) ratio of DI water and absolute ethanol (Fisher). Filtration using a pre-weighed 0.25 μm pore nitrocellulose filter membrane (Millipore VSWP) and vacuum filtration flask followed this step. The vial and funnel sides were rinsed with an additional 1:1 DI water and absolute ethanol. After filtration, the membrane and MXene filtrate were dried overnight in a vacuum desiccator and then weighed to determine the final concentration.

3.2.3. TEXTILE SELECTION & PREPARATION

The textiles were selected based on several critical criteria: white colour to facilitate monitoring the quality of the printed patterns; optimal porosity to ensure that the spacing between yarns does not exceed the minimum size of the printed traces; hydrophilicity to promote strong adhesion of the ink to the surface, preventing peeling; no requirement for pre-treatment; and a consistent weave pattern in perpendicular directions. Furthermore, the selection prioritized fabrics of similar thickness to enable systematic study and comparison. The textiles' porosity, significantly higher than other flexible substrates, promotes a faster solvent evaporation rate. Three types of textiles were chosen: woven cotton (100%), polyester (100%), and polycotton (65% cotton, 35% polyester). Prior to

printing, the textiles were washed with DI water to remove dust and then laid flat to dry, minimizing wrinkles.

3.2.4. MICROSCOPY CHARACTERISATION

$\text{Ti}_3\text{C}_2\text{T}_x$ MXene ink was diluted to $5 \mu\text{g mL}^{-1}$ and drop-casted onto lacey carbon copper grids (Pelco, USA). The delaminated $\text{Ti}_3\text{C}_2\text{T}_x$ MXene flakes were then imaged with TEM (Titan, Thermo Fisher Scientific Inc.) at 300 kV. EDX mapping was conducted using the EDXS detector (Bruker QUANTAX XFlash® 6T-30 30mm²) of the (S)TEM and superimposed on HAADF images. TEM images were processed using Digital Micrograph (Gatan Inc, USA). At the same dilution, the ink was drop-cast onto lacey carbon TEM grids (Ted Pella) and imaged by Zeiss Ultra SEM fitted with a Gemini column, SE detector and ESB detector. Characterisation of the flakes was performed at 1.5 kV acceleration voltage using an energy selective backscattering detector with a retarding voltage of 975 V to enhance contrast. The lengths of 248 flakes from TEM and SEM imaging were calculated using ImageJ, and statistical methods were applied to determine the mean and standard deviation from these measurements. The morphology of AJP MX@Fabric electrodes was studied with SEM, operated at 5 kV acceleration voltage in SE2 mode. The optical characterisation was done using a digital microscope (Olympus DSX1000)

3.2.5. X-RAY DIFFRACTION CHARACTERISATION

The $\text{Ti}_3\text{C}_2\text{T}_x$ MXene filtered film, pristine fabrics (cotton C, polycotton PC, and polyester PR), and the printed fabrics (MX@C, MX@PC, and MX@PR) underwent XRD analysis using a Bruker D8 Discovery X-ray diffractometer, employing an unmonochromated copper source with detector-based K_β suppression. The characterization was conducted in $\theta/2\theta$ configuration scanning within the $5 - 70^\circ$ range at a rate of 2° per minute. The phase identification was accomplished by referencing the ICDD database PDF2019. D-spacing determination relied on Bragg's law, Equation 22, leveraging the $\text{Ti}_3\text{C}_2\text{T}_x$ (002) reflection.

3.2.6. ELECTRICAL RESISTANCE MEASUREMENTS

Square MX@Fabric (8 mm x 8 mm) samples were fabricated using the Optomec AJP 300 system, depositing additive-free $\text{Ti}_3\text{C}_2\text{T}_x$ (10 mg mL^{-1}) with 300 μm nozzle onto cotton (MX@C), polycotton (MX@PC) and polyester (MX@PR) fabrics. The printing was executed in a serpentine filling algorithm (SFA) at a process speed of 1 mm s^{-1} . The AJP sheath gas flow ranged from 50 to 55 SCCM, the atomiser gas flow from 20 to 35 SCCM,

and the atomiser current from 0.53 to 0.56 A. Electrical resistance was then measured using a Keithley 2400 SourceMeter in combination with a Signatone resistivity probing system equipped with a four-point probe head (SP4-4045TFJ). The probe head featured tungsten probe tips with a 40 mil (1016 μm) spacing, an applied pressure of 45 grams, and a tip radius of 5 mils (127 μm). A minimum of six measurements were taken at different locations across each printed film, and the mean resistance value and standard deviation were subsequently calculated.

Rectangular MX@Fabric (1 mm x 6 mm) samples were produced with Optomec AJP 300 system, depositing 10, 20, 30, 50 and 100 layers of additive-free $\text{Ti}_3\text{C}_2\text{T}_x$ (10 mg ml^{-1}) with 150 μm nozzle on cotton (MX@C). The printing was performed using SFA at a process speed of 2 mm s^{-1} . AJP sheath gas flow ranged from 50 to 55 SCCM, atomiser gas flow from 22 to 32 SCCM, and atomiser current from 0.53 to 0.58 A. Electrical resistance values were determined from cyclic voltammetry (CV) data collected using a Biologic VMP3 potentiostat under ambient conditions.

3.3. MXENE SYNTHESIS & CHARACTERISATION

$\text{Ti}_3\text{C}_2\text{T}_x$ MXene was the first MXene to be synthesized in 2011,^[301] and since its discovery, it has attracted substantial interest due to its distinctive combination of structural, electronic, and chemical properties, which makes it suitable for a variety of applications, from energy storage to biomedical devices. To date, over 70% of all research on MXenes has concentrated on $\text{Ti}_3\text{C}_2\text{T}_x$, highlighting its significance and versatility within this growing field of study.^[584] $\text{Ti}_3\text{C}_2\text{T}_x$ MXene exhibits a layered structure that is intricately derived from its Ti_3AlC_2 MAX phase precursor, typically via chemical etching with HF or HCL/LIF methods, that were previously introduced in Section 1.5. The hydrophilic nature^[303] and negative surface charge of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene flakes, due to the surface terminations (-O, -OH, and -F), facilitates their processing in aqueous and organic media to create stable, viscous, highly conductive, and electroactive colloidal inks. This process requires no surfactants, binders, additives, or harsh post-treatments, making MXenes particularly well-suited for direct use in various printing technologies.^[250,446] These surface terminations play a role in enhancing the adhesion of MXenes to fabric surfaces.^[449] Consequently, these properties make MXenes ideal for flexible, wearable, and e-textile applications.

However, the chemical stability of colloidal MXene solutions remains a critical factor in formulating high-performance functional inks. $\text{Ti}_3\text{C}_2\text{T}_x$ MXene is prone to oxidation, primarily when exposed to dissolved oxygen in water, which acts as the main oxidant. When oxidized, $\text{Ti}_3\text{C}_2\text{T}_x$ MXene transforms into TiO_2 and CO_2 .^[446,585,586] Although these degradation products are non-toxic to humans, they pose environmental concerns, especially in aquatic systems and soil. Thus, research into effective recycling methods post-device life cycle is essential to mitigate these impacts.^[587–589] Studies have demonstrated that oxidation can be significantly slowed, thereby extending the material's useful life by storing MXene solutions in hermetically sealed, argon-filled bottles at low temperatures (5 °C) with no light exposure.^[440] It has been reported that freezing aqueous dispersions at temperatures below –20 °C can preserve MXene flakes for up to two years.^[590] The rate of degradation was also shown to slow down with the addition of antioxidants such as sodium ascorbate.^[444] Furthermore, research indicates that dried MXene deposits degrade more slowly than colloidal solutions.^[216,345] For instance, a study on inkjet-printed devices using $\text{Ti}_3\text{C}_2\text{T}_x$ MXene inks showed that printed patterns maintained their integrity with only minimal oxidation after being stored under ambient conditions for six months. This was verified using XRD, Raman spectroscopy, X-ray photoelectron spectroscopy, and resistance measurements.^[106]

This chapter explores the synthesis and characterization of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene inks tailored for AJP onto textiles. Beginning with the minimally intensive layer delamination ‘MILD’ method synthesis, the chapter confirms the successful formation of MXene from the MAX phase through XRD. TEM is used to examine the flake structure, selected area electron diffraction (SAED) patterns, and elemental composition via EDX, alongside an estimate of flake size within the functional ink. The focus then shifts to the deposition of these MXene inks onto textiles using AJP, with detailed analyses through SEM and XRD to assess the morphology and structural integrity of the deposits. These findings provide critical insights into the behaviour of MXene on textile substrates, advancing the development of electronic textiles. The objective of this chapter is to demonstrate how, with the right materials and methods, $\text{Ti}_3\text{C}_2\text{T}_x$ MXene can transform everyday textiles into advanced, multifunctional fabrics, paving the way for the next generation of smart e-textiles.

3.3.1. $\text{Ti}_3\text{C}_2\text{T}_x$ MILD SYNTHESIS & SIZE SELECTION

All AJP samples in this study were fabricated using aqueous $\text{Ti}_3\text{C}_2\text{T}_x$ MXene ink without additives, binders, or surfactants synthesized via the MILD route using HCl/LiF .^[226,362]

With HCl/LiF methods (clay and MILD), etching and delamination happen in a single step. Solvated Li^+ ions aid the delamination of single- or few-layer flakes by intercalating between the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene layers, expanding the distance between them, and weakening the forces holding them together,^[323] schematically shown in **Figure 19**.

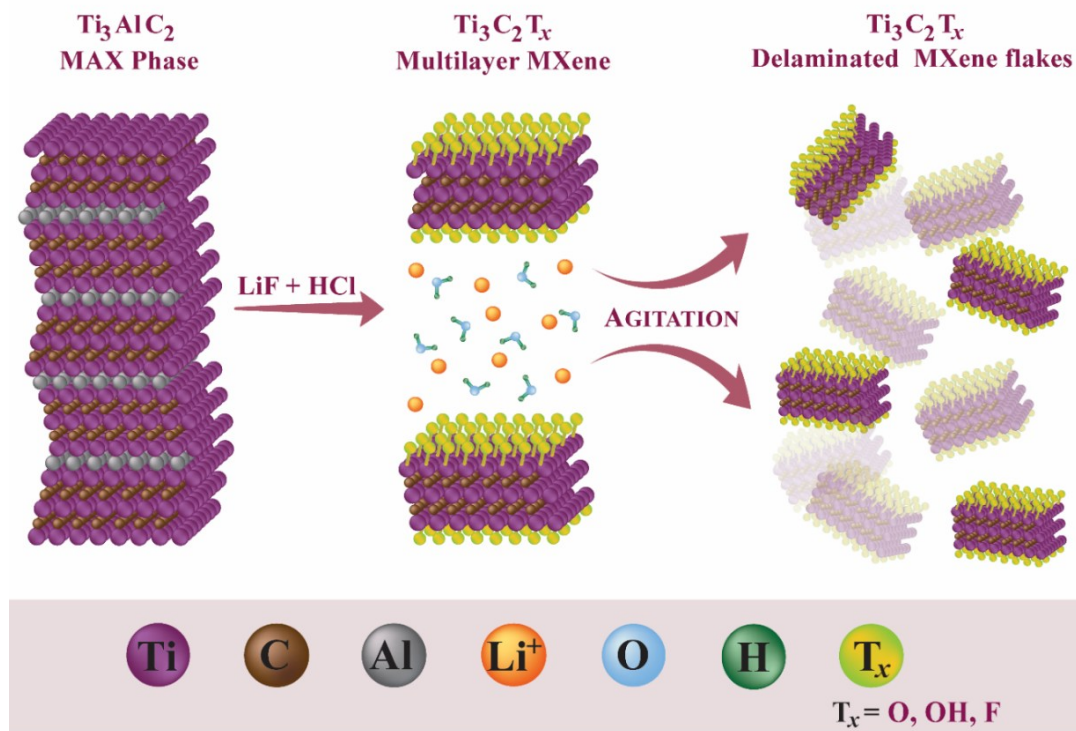


Figure 19: Etching and delamination processes for the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene synthesised through the MILD route. Adapted from Ref^[258].

This intercalation with Li^+ ions, therefore, makes the interlayer distance of HCl/LiF etched MXenes larger compared to the HF etched MXenes, which also allows for more pseudocapacitive redox sites and aids faster ion intercalation kinetics.^[226,591,592] Note that the difference between the above-mentioned "clay" and MILD methods lies in the concentration of etchants used, which results in the former method requiring sonication after delamination, which is optional for the latter. The resultant flakes after MILD etching are larger and have fewer defects.^[228,323,343,345,362] Research established that etching and delamination methods impact the chemical composition of the surface terminations in the resultant MXenes.^[216] The oxygen-to-fluoride ratio of terminations is affected by the concentration of HF (in HF etching), while with the HCl/LiF method, more oxygen than fluorine terminations may be achieved.^[323,344] HCl/LiF etched $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes were reported to exhibit much better electrochemical performance (up to $\sim 900 \text{ F cm}^{-3}$) than HF etched $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes (up to $\sim 530 \text{ F cm}^{-3}$).^[234,348,593] This difference in electrochemical

performance is related to the difference in surface chemistries, i.e., substituting fluorine-containing with oxygen-containing terminations increases gravimetric and volumetric capacitance.^[323] Therefore, the HCl/LiF route seems to be the most effective for energy storage applications, so it is predominantly used.^[216] In recent studies, the most commonly used MILD synthesis method employs a 12:1 molar ratio of LiF to Ti_3AlC_2 , equivalent to 1.6 g of LiF per 1 gram of Ti_3AlC_2 , which offers advantages in terms of yield, flake size, and electrical conductivity.^[343]

The reaction vessel used for etching is a polytetrafluoroethylene (PTFE) bottle. The reason for using a PTFE bottle rather than a glass beaker is because of in-situ HF production upon mixing the etching reagents. Fluoride anions can form strong bonds with silicon molecules, which will result in the etching of the glass.^[594] PTFE, on the other hand, is very non-reactive and highly resistant to most acids, including HF, and therefore is an ideal material to use for our etching method.^[595] While the production of HF occurs in situ during the etching process, strict safety precautions must be adhered to at all times. HF is an extremely hazardous chemical capable of causing severe chemical burns and systemic toxicity even at low concentrations. Therefore, all etching procedures must be conducted in a well-ventilated fume hood with appropriate personal protective equipment, including acid-resistant gloves, a lab coat, and eye protection. Additionally, it is crucial to have calcium gluconate gel and HEXAFLUORINE® eyewash readily available in the laboratory as an emergency treatment for potential HF exposure. Proper waste disposal protocols must also be followed to prevent environmental contamination and ensure the safety of laboratory personnel.^[596]

3.3.2. CHARACTERISATION OF SYNTHESISED $\text{Ti}_3\text{C}_2\text{T}_x$

To confirm the successful etching and conversion of Ti_3AlC_2 into $\text{Ti}_3\text{C}_2\text{T}_x$ MXene, XRD analysis was performed on both the Ti_3AlC_2 MAX phase and the synthesised $\text{Ti}_3\text{C}_2\text{T}_x$ MXene, as shown in **Figure 20**.

The XRD pattern of the Ti_3AlC_2 MAX phase (**Figure 20(a)**) contains all the reflections expected for its $\text{p}6_3/\text{mmc}$ space group, including prominent peaks at positions corresponding to the (002), (004), (101), (103), (104), (105) and (107) planes. The inset highlights a (002) peak recorded at $2\theta = 9.49^\circ$, which correlates with a c-lattice parameter of 18.6 Å, a value typical for Ti_3AlC_2 .^[329,597–599] This confirms the well-ordered, layered structure of the MAX phase.

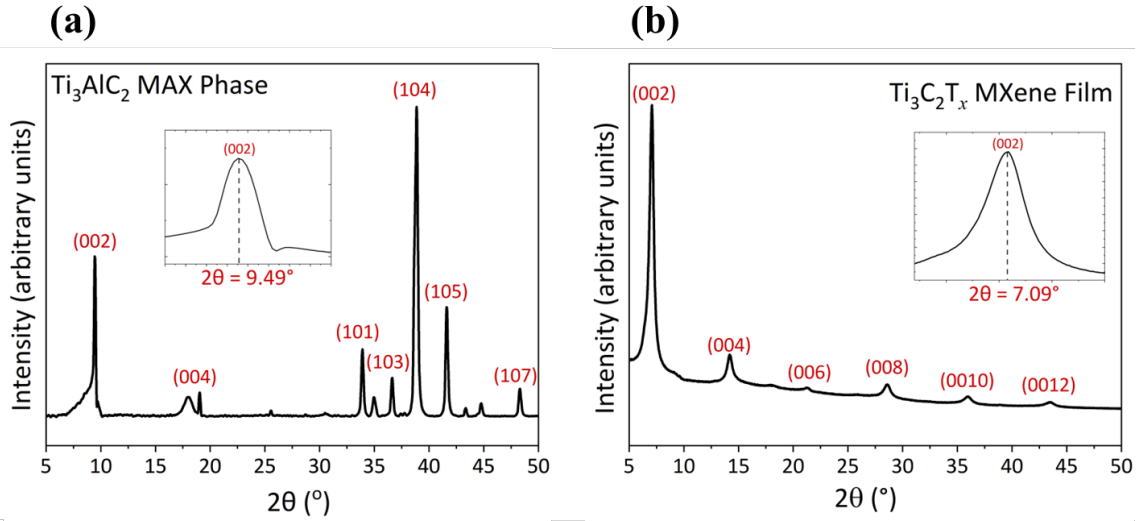


Figure 20: Crystallographic measurements of the MXene and its parent MAX phase.

(a) XRD of Ti_3AlC_2 MAX phase, with prominent reflections indexed.

(b) XRD of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene film, with prominent reflections indexed.

The insets provide a detailed view of the (002) peak position.

In contrast, the XRD pattern of the filtered $\text{Ti}_3\text{C}_2\text{T}_x$ MXene film (**Figure 20(b)**) shows a distinct change, characterised by the absence of a-lattice reflections and the exclusive presence of (00l) reflections. Notably, the MXene inherits the same hexagonal ($p6_3/mmc$) symmetry from its parent MAX precursor^[584] despite the absence of a-lattice reflections in the measured pattern. The absence of a-lattice reflections and the presence of exclusive (00l) reflections confirms the high purity of the $\text{Ti}_3\text{C}_2\text{T}_x$ film,^[329,600] further evidenced by the shift of the (002) peak to a lower angle at $2\theta = 7.09^\circ$, as shown in the inset. This downshift suggests an increase in the interlayer spacing, which is consistent with the removal of aluminium layers and the formation of a 2D MXene structure. The absence of a-lattice reflections and the exclusive presence of (00l) reflections are indicative of well-aligned MXene films derived from properly delaminated layers. The comparative analysis of the XRD patterns robustly verifies the effectiveness of the etching process and the formation of a high-purity $\text{Ti}_3\text{C}_2\text{T}_x$ MXene structure.

To evaluate the d-spacing of the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene layers, Bragg's law was applied using the (002) reflection at $2\theta = 7.09^\circ$, with an X-ray wavelength (λ) of 0.15406 nm, which corresponds to the $\text{CuK}\alpha$ radiation used in our XRD setup. Given the indexing convention for MXenes, the c-lattice parameter obtained from the (002) peak needs to be halved to determine the d-spacing between individual $\text{Ti}_3\text{C}_2\text{T}_x$ layers. For the filtered $\text{Ti}_3\text{C}_2\text{T}_x$ film, this calculation yields a d-spacing equal to 1.25 nm. To further analyze the structural characteristics, the interlayer spacing, which represents the region occupied by intercalated

water and ions, can be calculated by subtracting the d-spacing of dry, multilayer $\text{Ti}_3\text{C}_2\text{T}_x$ obtained from HF etching, measured at 0.94 nm.^[329] This results in an interlayer spacing of 0.31 nm.

The high purity and well-ordered structure of the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene make it an excellent candidate for use as ink in AJP processes. This structural integrity ensures that the intrinsic properties of the MXene are maintained, thereby enhancing its performance in subsequent energy storage applications.

Following the confirmation of the high purity and well-ordered structure of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene from the XRD analysis, the morphological characteristics of individual MXene flakes were further investigated. TEM provided a detailed visualization of the $\text{Ti}_3\text{C}_2\text{T}_x$ flakes, **Figure 21(a)**, elucidating their inherent structure. The image reveals a thin, transparent nanosheet with smooth edges and a uniform morphology, indicating successful exfoliation and delamination.

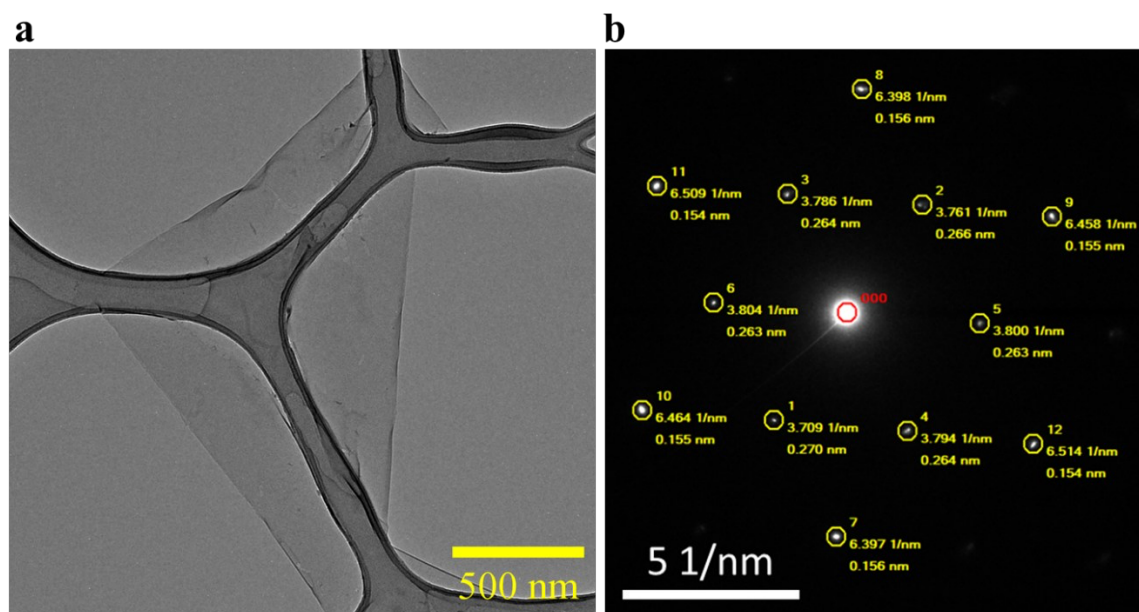


Figure 21: TEM characterisation of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene. **(a)** TEM image of $\text{Ti}_3\text{C}_2\text{T}_x$ flake. **(b)** The SAED image of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene along the [001] zone axis.

The SAED image of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene (**Figure 21(b)**) along the [001] zone axis displays distinct diffraction spots, indicating a highly ordered crystal structure with a characteristic hexagonal symmetry typical of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene.^[601] Moreover, the d-spacing values derived from the SAED pattern correspond closely with those obtained from the XRD analysis of the filtered $\text{Ti}_3\text{C}_2\text{T}_x$ MXene film. The agreement between these values reinforces the consistency and reliability of the structural characterization methods used. These d-spacing measurements also align with values reported in the literature.^[329,600]

EDX spectrum (**Figure 22(a)**) provides a comprehensive overview of the surface chemistry of the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene. The spectrum reveals distinct peaks corresponding to titanium (Ti) and carbon (C), which are the primary elements of the titanium carbide core structure of the MXene flakes. Additionally, significant peaks for oxygen (O) and fluorine (F) are evident, indicating the presence of typical surface terminations (T_x groups), such as O, OH, and F, which are commonly formed during the etching process. Notably, the spectrum also shows a chlorine (Cl) peak, which is expected given the MILD etching conditions that involve a high concentration of hydrochloric acid (HCl). This presence of Cl suggests that some Cl functionalization occurs on the MXene surface due to the etching process.

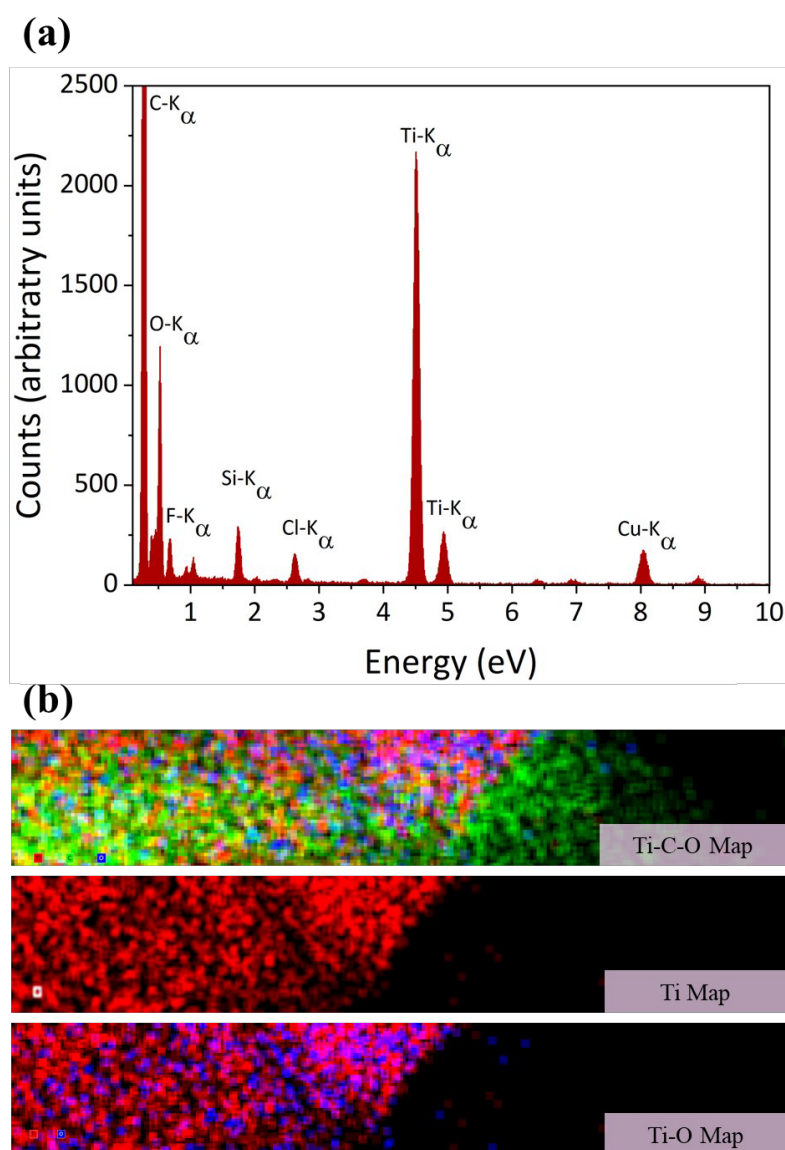


Figure 22: Elemental composition characterisation of the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene ink. (a) EDX analysis. (b) TEM elemental maps illustrating the distribution of titanium (Ti), carbon (C), and oxygen (O) in the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene ink.

The EDX mapping (**Figure 22(b)**) further corroborates the homogeneous distribution of Ti, C, O, and F across the MXene flakes. The elemental maps show a uniform spread of titanium (Ti) and carbon (C), confirming a consistent titanium carbide core throughout the flakes. The distribution of oxygen (O) and fluorine (F) indicates the uniformity of surface terminations, essential for maintaining MXene's chemical stability and functional properties. The absence of aluminium (Al) peaks in both the spectrum and the elemental maps confirms the complete removal of the “A” layer from the MAX phase, verifying the successful synthesis of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene. Overall, these EDX results provide clear evidence of the chemical composition and surface functionalization of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene, confirming the effectiveness of the etching process and the purity of the final material.

A comprehensive analysis of multiple TEM (**Figure 23**) and SEM (**Figure 24**) images was subsequently conducted to determine the flake size distribution within the $\text{Ti}_3\text{C}_2\text{T}_x$ ink.

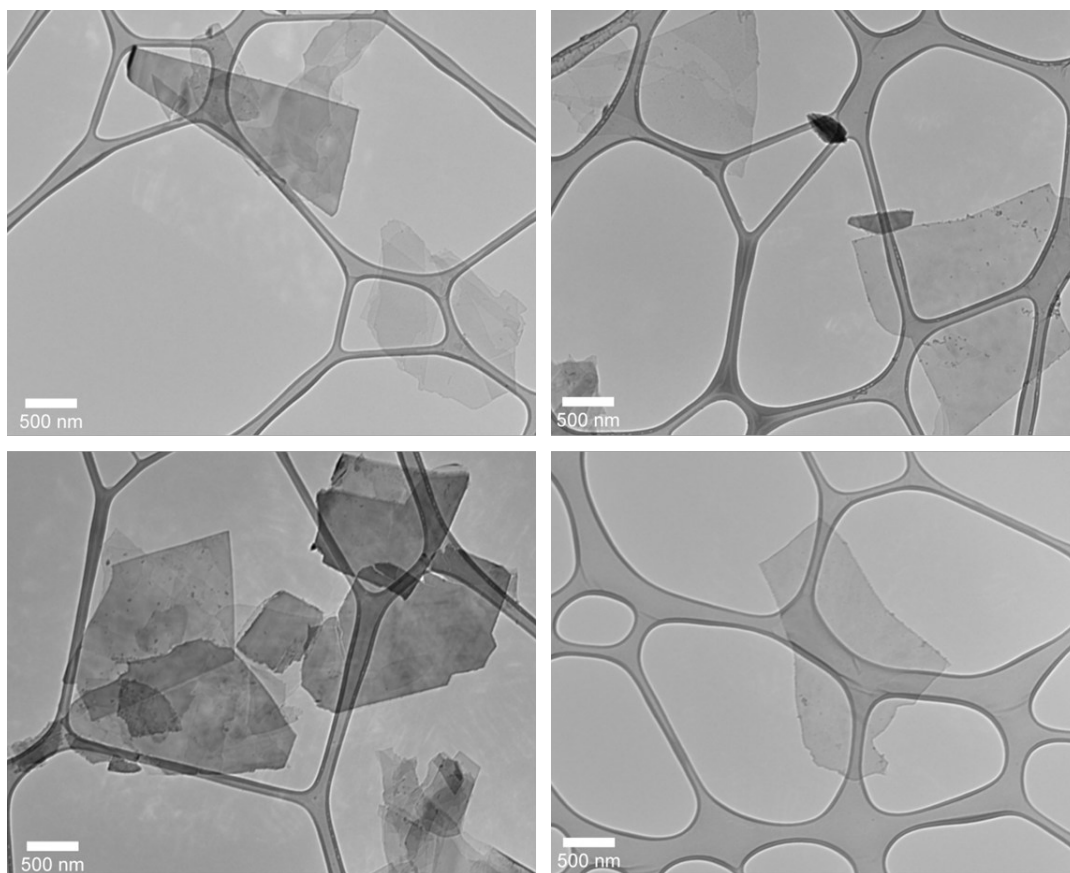


Figure 23: Representative TEM images of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene flakes.

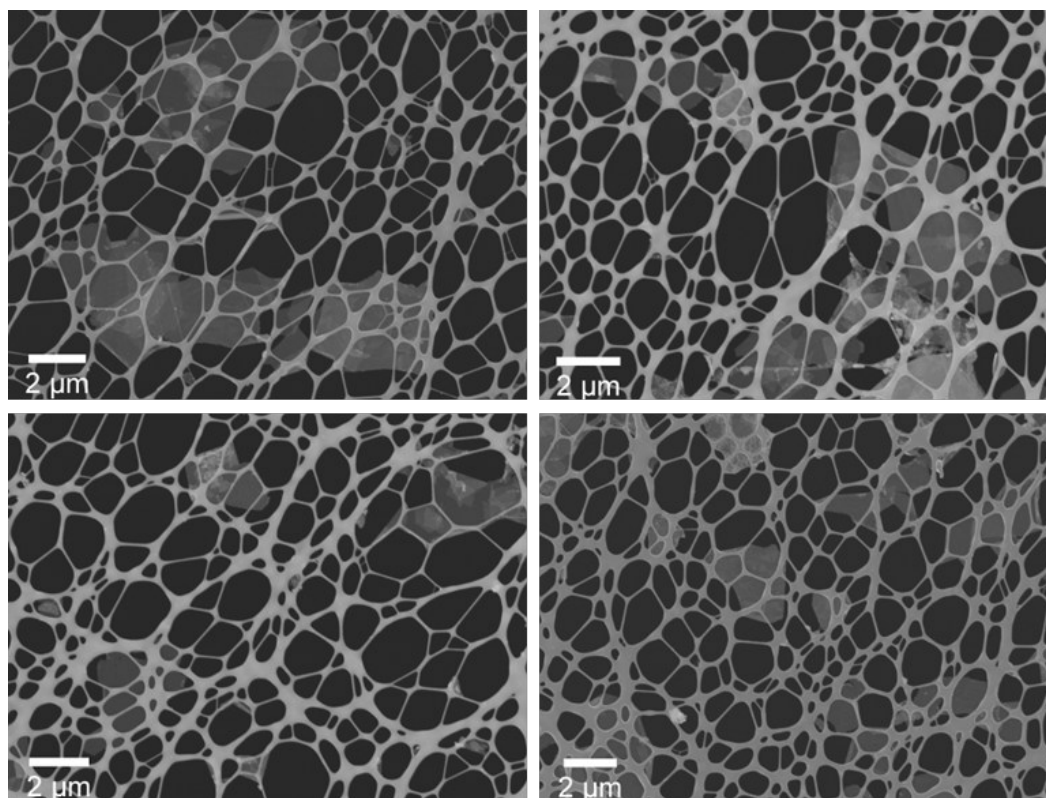


Figure 24: Representative SEM images of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene flakes.

The statistical evaluation, **Figure 25**, of these images revealed an average flake size of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene flakes in the ink to be (1584.2 ± 1.7) nm, showcasing the characteristic dimensions expected after the MILD synthesis.

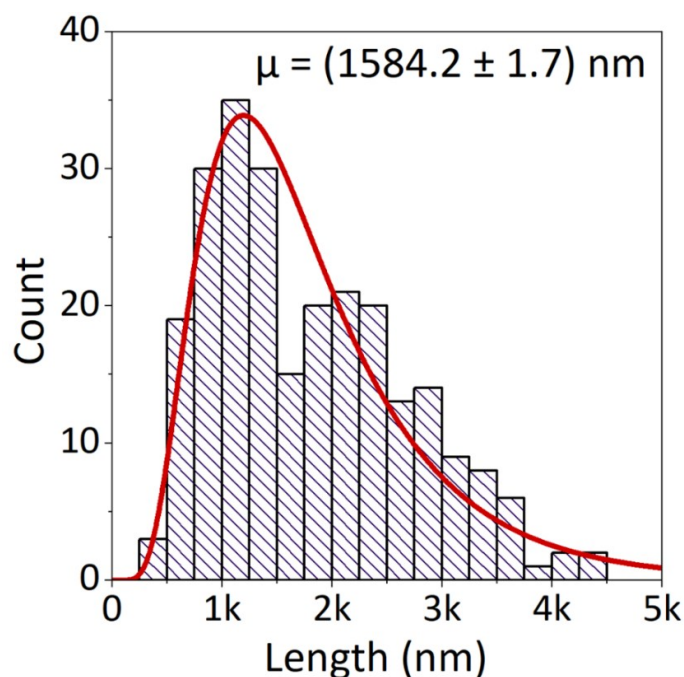


Figure 25: Size distribution histogram of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene flakes in the ink, determined through ImageJ analysis software across multiple TEM and SEM images. The Full Width at Half Maximum (FWHM) of the distribution is approximately 2100 nm.

Chapter 3: Aerosol Jet Printed MXene Textiles

Upon printing the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene ink with AJP, subsequent analysis of a singular MXene flake via TEM revealed an intriguing result. Recalling Section 2.2, AJP relies on the aerodynamically focused deposition of the aerosolised functional ink directed towards the substrates in a collimated beam.^[293,456] Achieving the desired deposition for TEM analysis presented a challenge, as observing a single MXene flake requires printing of an extremely dilute dispersion, making the deposition process quite difficult. Despite these challenges, the effort was successful, as evidenced by the observation of the isolated MXene flake shown in **Figure 26** and further imaging in **Figure S1 - S2**, Supplementary Information.

The observed $\text{Ti}_3\text{C}_2\text{T}_x$ MXene flake appeared crumpled and notably smaller in size compared to the original formulation. This alteration in the flake's morphology and size can be attributed to the effects of ultrasonic atomization during the printing process needed to create said aerosol, an integral part of the AJP process.

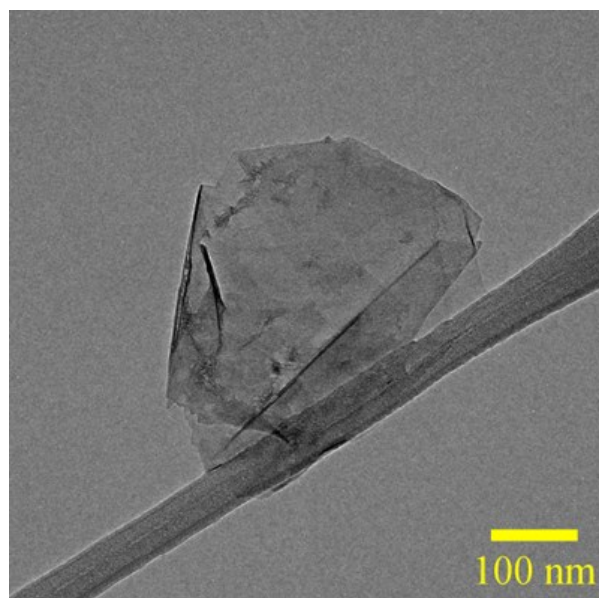


Figure 26: TEM image illustrating a crumpled $\text{Ti}_3\text{C}_2\text{T}_x$ MXene flake post ultrasonic atomization.

During ultrasonic atomization, the MXene flakes are subjected to high-frequency vibrations that cause mechanical disruption, leading to the observed crumpling and reduction in size. This deformation likely results from the mechanical stresses imparted during the aerosolization and subsequent deposition stages, highlighting the influence of the printing process on the physical characteristics of the MXene flakes. The characterization of this altered morphology sheds light on the impact of the printing technique on the physical properties of individual MXene flakes, offering valuable insights into their behaviour post-printing.

Similar morphological changes have been reported in a recent study, where MXene flakes undergo curling and alignment due to the confined environment within aerosol droplets during AJP. This curling has been attributed to the mechanical forces and microstructural modulation exerted by the droplets acting as microreactors. The study reported that this modified morphology was beneficial for supercapacitor applications. The curling of MXene flakes enhances their surface area and facilitates ion transport, which are crucial factors for improving the electrochemical performance of supercapacitors. The study concluded that controlling the microstructure of MXene flakes through such techniques can optimize their properties, making them more effective for energy storage applications such as supercapacitors.^[602]

The crumpling observed in our TEM analysis appears to be a comparable response to mechanical stress and confinement, suggesting that the printing conditions play a critical role in determining the final morphology of MXene flakes. Understanding these effects is essential for tailoring the structural properties of MXene-based materials for specific applications, highlighting the importance of optimizing printing techniques to control flake morphology and, consequently, material performance.

3.4. AEROSOL JET DEPOSITION OF $\text{Ti}_3\text{C}_2\text{T}_x$ MXENE INKS ON TEXTILES

This section explores the deposition of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene inks onto textile substrates using AJP to develop flexible and conductive materials. The samples in this study were fabricated using aqueous $\text{Ti}_3\text{C}_2\text{T}_x$ MXene ink without any additives, binders, or surfactants. Previous research by the Nicolosi Group identified that a concentration of 10 mg mL^{-1} is optimal for achieving well-atomized $\text{Ti}_3\text{C}_2\text{T}_x$ MXene ink using Optomec's ultrasonic atomizer, minimizing nozzle clogging during the printing process. Additionally, because solvents evaporate more rapidly from textile substrates than from other flexible materials, adjusting the platen temperature was essential to achieving the optimal evaporation rate.

Figure 27 shows the surface morphology of the AJP deposits on three distinct fabrics: cotton (C), polycotton (PC), and polyester (PR). “MX@” stands for “ $\text{Ti}_3\text{C}_2\text{T}_x$ MXene deposited on”, followed by the type of fabric - cotton, polycotton, or polyester. The SEM images reveal exceptional and uniform surface coverage of $\text{Ti}_3\text{C}_2\text{T}_x$ with minimal charging on the fibres, indicative of high electrical conductivity. A close-up scanning electron SEM

image of a cotton sample reveals distinct MXene flakes, confirming that AJP achieves a uniform and well-dispersed coating, crucial for the efficient performance of MSCs.

The observed uniform coverage and strong adhesion across different fabric types suggest that the MXene coatings could provide excellent electrical conductivity while maintaining the mechanical flexibility of the textile substrates. This dual functionality is particularly important for applications in wearable electronics and smart textiles, where both electrical performance and comfort are critical.

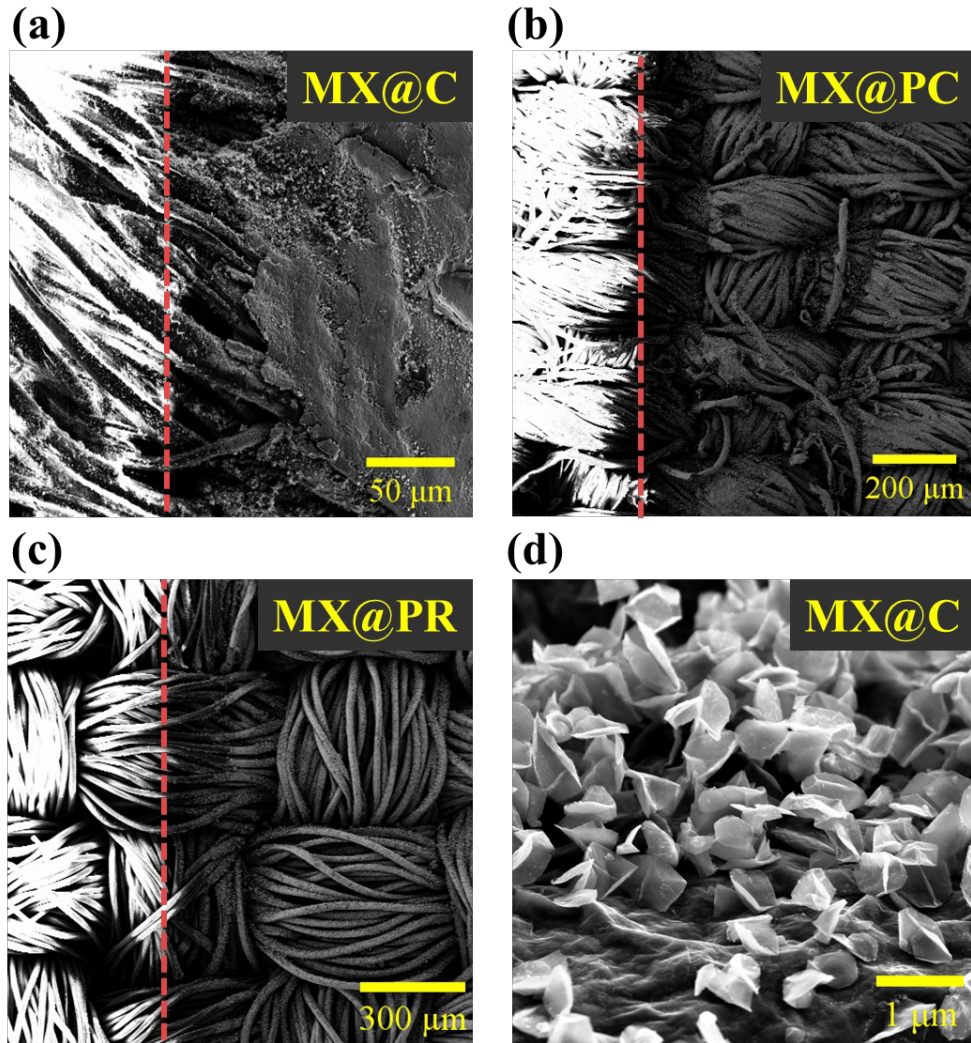


Figure 27: SEM images of $\text{Ti}_3\text{C}_2\text{T}_x$ deposits on (a) cotton (C), (b) polycotton (PC), (c) polyester (PR) through AJP. The dashed red line denotes the interface between the pristine (left) and printed (right) regions. Pristine substrates appear white because their insulating surfaces, uncoated prior to imaging, accumulate charge under the electron beam.

In contrast, the conductive MXene deposits appear darker, thereby enhancing fibre contrast. (d) Close-up view of the cotton surface, highlighting individual $\text{Ti}_3\text{C}_2\text{T}_x$ ink flakes on the fabric's surface.

A comprehensive array of XRD spectra, **Figure 28**, encompasses various critical compositions in this study. It illustrates distinct spectra: the XRD of the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene film, the pristine fabric samples (cotton, polycotton, and polyester), and the XRD patterns of MXene printed onto these respective fabrics.

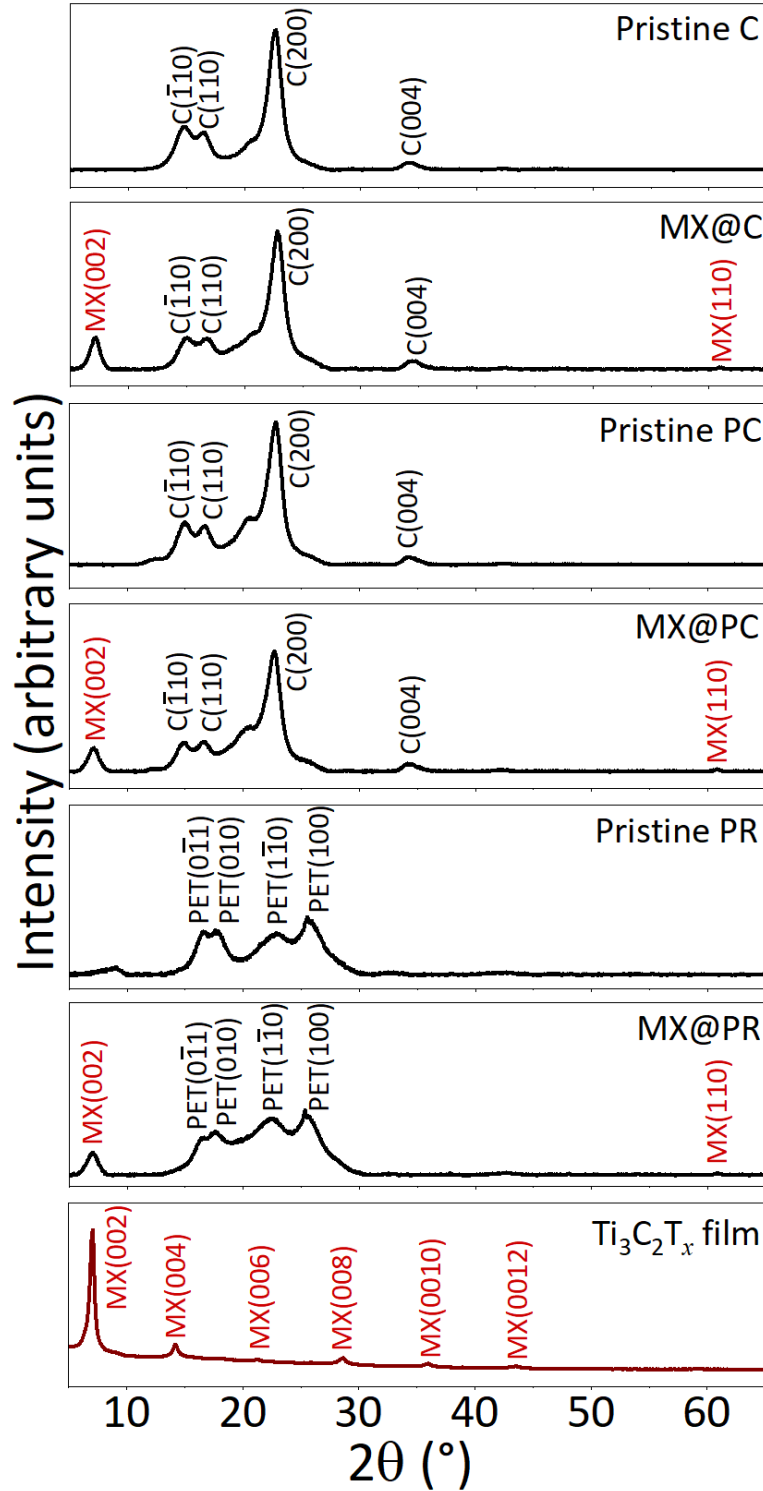


Figure 28: Comprehensive XRD spectra of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene film, pristine fabric samples (C, PC, PR), and MXene-printed fabrics (MX@C, MX@PC, MX@PR). The spectra reveal specific MXene-related peaks alongside characteristic fabric peaks.

Collectively, these spectra provide crucial insights into the crystalline nature, phase composition, and structural modifications induced by the MXene printing process on different fabric substrates. The comparative analysis among these spectra elucidates alterations in crystallinity and diffraction patterns resulting from the interaction between MXene and the diverse fabric matrices.

Distinct diffraction patterns were discernible for each pristine fabric substrate, showcasing characteristic peaks representative of their compositions identified. Cotton (C) exhibited peaks aligned with its cellulose-rich structure.^[579,603,604] These were denoted as C(hkl) reflections in **Figure 28** with accordance to Cellulose I β (C₆H₁₀O₅)_n monoclinic crystal system (PDF no. 00-056-1718), referenced in **Figure S3**, Supplementary Information.

Polyester (PR) displayed characteristic peaks closely related to (C₁₀H₈O₄)_n polyethylene terephthalate (PET).^[605] The reflections were assigned based on the PET triclinic crystal system (PDF no. 00-060-0989), denoted as PET(hkl) with an XRD pattern, referenced in **Figure S4**, Supplementary Information.

Polycotton (PC) is a combination fabric of cotton and polyester, and therefore, it should potentially present a combination of distinctive peaks from both materials, illustrating its blended composition. The characteristic peaks observed, however, closely resemble the results obtained for cotton with slightly decreased intensity, depicted in **Figure 28** and **Figure 29(a)**, and therefore also denoted as C(hkl) with accordance to Cellulose I β (C₆H₁₀O₅)_n monoclinic crystal system (PDF no. 00-056-1718), which agrees with the literature.^[606]

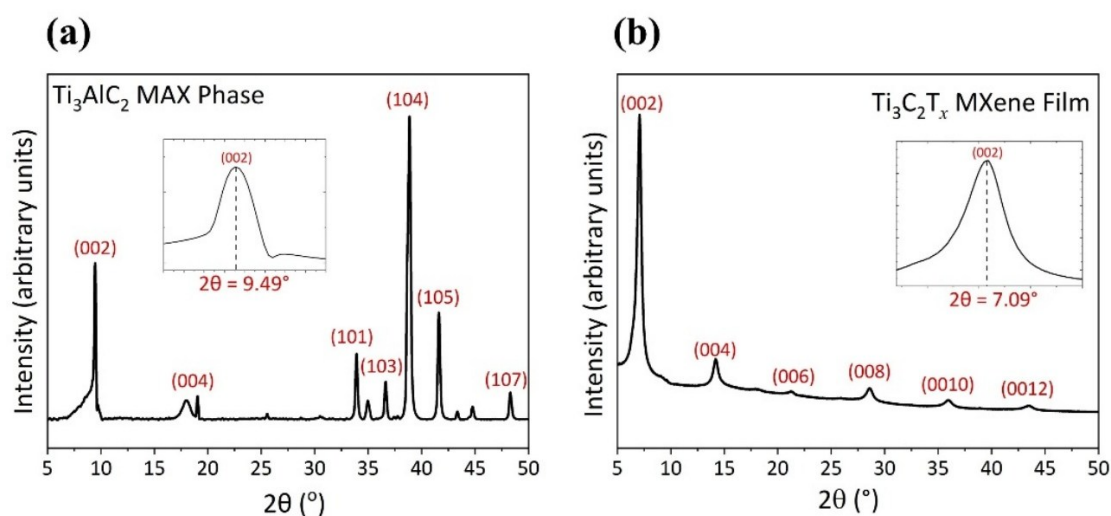


Figure 29: XRD analysis comparing the crystalline structures of (a) pristine cotton (C), polycotton (PC), and polyester (PR), and (b) printed fabrics MX@C (Ti₃C₂T_x on cotton), MX@PC (Ti₃C₂T_x on polycotton), and MX@PR (Ti₃C₂T_x on polyester).

Upon MXene integration, notable alterations in the XRD patterns of the printed samples (MX@C, MX@PR, MX@PC) were observed (**Figure 28**). Firstly, a prominent MXene-specific peak (002) emerged alongside fabric-specific peaks in all printed samples, validating the successful integration of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene onto fabrics. Secondly, small MXene-specific peaks at $2\theta = 60.86^\circ$ for MX@C and $2\theta = 60.72^\circ$ for both MX@PC and MX@PR corresponding to (110) reflection were detected by contrast to the MXene film, attributed to the alignment effect.^[607] This result agrees with the literature since $\text{Ti}_3\text{C}_2\text{T}_x$ MXene flakes randomly orient themselves on the fabric substrate during printing.^[106] This co-appearance of MXene-specific peaks alongside characteristic fabric peaks proves the effective surface functionalization of the fabrics with MXene, showcasing tailored material-fabric interactions.

The XRD spectra also reveal intriguing peak intensity and width changes between pristine fabrics and their printed counterparts **Figure S5**, Supplementary Information. These alterations in MX@C and MX@PC suggest potential variations in fabric crystallinity or altered orientation due to MXene integration.

However, it is vital to consider the influence of texturing. Texturing, the preferential alignment of crystallites within a material, might significantly contribute to these observed variations.^[608] Factors such as sample positioning or orientation during the analysis can notably affect texturing, thereby influencing peak characteristics in XRD spectra. Specifically, a decrease in intensity at $2\theta = 16.66^\circ$ in pristine polyester to $2\theta = 16.60^\circ$ in MX@PR suggests a texturing effect induced by $\text{Ti}_3\text{C}_2\text{T}_x$ integration, fostering a more ordered structure within the polyester fabric.

These observations highlight $\text{Ti}_3\text{C}_2\text{T}_x$ MXene's potential for tailored interactions with diverse fabric substrates, paving the way for multifunctional applications. The findings elucidate $\text{Ti}_3\text{C}_2\text{T}_x$ MXene's versatility as a functional material for fabric integration, emphasising its role in shaping tailored material-fabric interactions for advanced applications.

3.5. PROCESS OPTIMISATION & TROUBLESHOOTING IN AEROSOL JET PRINTING OF MXENE E-TEXTILES

Achieving high-quality, reproducible AJP deposits requires precise control of multiple interdependent parameters, especially when printing on textiles, which present inherent challenges due to their porosity, surface roughness, and mechanical flexibility. Unlike rigid substrates, textiles exhibit variable ink absorption rates and non-uniform surface topographies, necessitating careful optimisation of printing parameters to ensure uniform deposition, strong adhesion, and reliable electrical performance. This section outlines key process parameters, challenges, and troubleshooting strategies to support reproducible fabrication, serving as a comprehensive reference for researchers optimising AJP for textile-based applications.

3.5.1. NOZZLE SELECTION & PROCESS SPEED OPTIMISATION

In the preliminary work, the impact of nozzle diameter on film morphology and electrical properties was evaluated. Films were printed using two different nozzle diameters (150 μm and 300 μm) under identical process conditions, with a consistent number of printed layers (6L on each fabric). The results, as shown in **Figure 30 (a-c)**, demonstrated a clear increase in resistance for films printed with the 300 μm nozzle compared to those printed with the 150 μm nozzle across all textile substrates. This difference can be attributed to variations in the thickness of the printed lines, which is directly influenced by nozzle size. Previous studies have shown that, under fixed process parameters, line thickness decreases as nozzle diameter increases.^[500] Since the same volume of functional material is deposited in both cases, the 150 μm nozzle results in a more focused deposition, producing a thicker film with enhanced conductivity, whereas the 300 μm nozzle distributes the ink over a wider area, leading to a thinner film with higher resistance. Given that resistance is inversely proportional to the cross-sectional area, this explains why films printed with the 150 μm nozzle exhibited significantly lower resistance than those printed with the 300 μm nozzle under identical conditions. Based on these findings, the 150 μm nozzle was selected for all subsequent depositions.

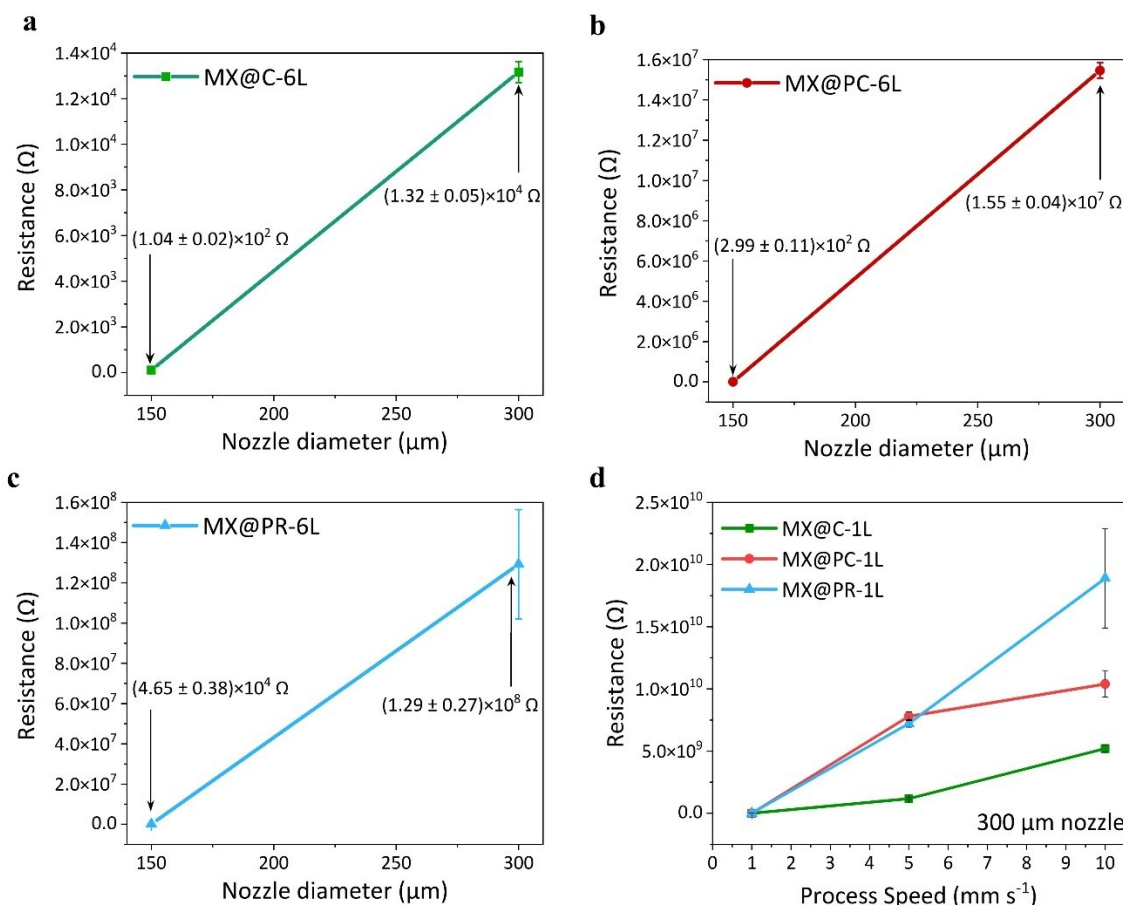


Figure 30: Preliminary evaluation of nozzle diameter and process speed on the electrical resistance of AJP MXene films on textiles. **(a-c)** Resistance comparison for films printed with 150 μm and 300 μm nozzles at six printed layers (6L) on cotton (MX@C-6L), polycotton (MX@PC-6L), and polyester (MX@PR-6L). **(d)** Effect of process speed on resistance for 1-layer (1L) printed films using a 300 μm nozzle on textile substrates.

Another critical parameter influencing deposition quality is process speed, which directly affects mass loading and film uniformity. As shown in **Figure 30(d)**, a clear positive correlation between process speed and resistance was observed, where lower process speeds resulted in significantly lower resistance across all textile substrates. The process speed directly influences the quantity of material deposited at a specific location on the substrate: as the speed increases, the amount of material deposited per unit length decreases, leading to thinner films with higher resistance.

CHALLENGE #1: RESISTANCE MEASUREMENTS ON TEXTILES

A key challenge in characterising AJP MXene textiles was the unreliability of four-point probe resistance measurements due to the porous, fibrous, and flexible nature of textile

substrates. Unlike rigid surfaces, textiles exhibit variable topographies and inconsistent probe contact, leading to high measurement variability. Even slight differences in probe pressure or positioning can significantly affect readings, making it difficult to obtain a representative resistance value.

Moreover, the four-point probe method assumes a continuous, homogeneously conductive layer, a condition rarely met in printed textiles, where ink penetration, fibre exposure, and substrate interactions vary. This inconsistency further skews resistance values, making direct comparisons between samples challenging. Textile porosity distorts current distribution, causing non-uniform charge transport that further compromises measurement accuracy. Another limitation is the large sample size ($\sim 1 \text{ cm}^2$) required for accurate four-point probe measurements, which significantly increases printing time. At slow AJP process speeds, producing multiple large-area samples for statistical validation becomes impractical, presenting a bottleneck in high-throughput characterization.

SOLUTION #1: To overcome these limitations, an alternative approach was adopted by evaluating the electrical resistance of AJP MXene films using cyclic voltammetry (CV). By printing a rectangular sample, which acts as a conductor, the CV output provides an I - V response, from which resistance can be determined using Ohm's law. This method offers a more reliable and scalable approach for assessing conductivity, as it eliminates inconsistencies associated with probe contact and substrate porosity, ensuring a more representative evaluation of the printed films' electrical performance. Additionally, because this approach does not require large-area samples, it significantly minimises AJP fabrication time, making it a more efficient method for evaluating the electrical properties of printed films.

The electrical performance of the printed MXene films was first evaluated by measuring the resistance as a function of the number of AJP layers, as shown in **Figure 31**. A significant reduction in resistance was observed with an increasing number of printed layers, a trend attributable to the progressive accumulation of material, which enhances film thickness and improves interflake connectivity. As additional layers are deposited, the percolation network of conductive $\text{Ti}_3\text{C}_2\text{T}_x$ MXene nanosheets becomes more interconnected, reducing the sheet resistance and enhancing charge transport pathways. This trend confirms that resistance can be systematically controlled by adjusting the number of printed layers, a critical consideration for tailoring the electrical properties of e-textile energy storage devices.

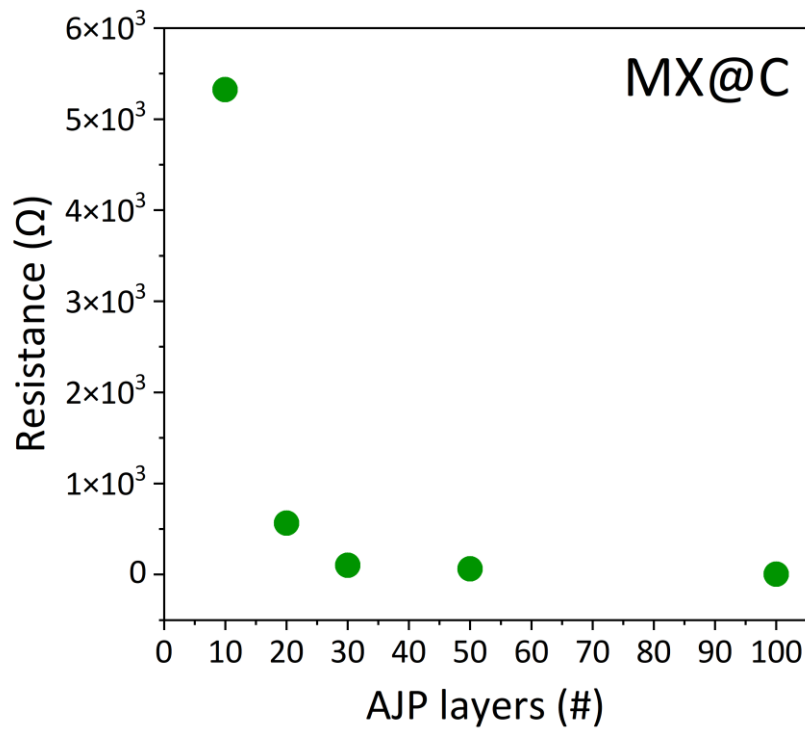


Figure 31: Relationship between resistance and the number of AJP layers for $(1 \times 6) \text{ mm}^2$ sample on cotton.

3.5.2. AEROSOL JET PRINTING OPTIMISATION

While AJP enables precise, conformal deposition of MXene inks onto textiles, several challenges must be addressed to ensure reproducibility and high-quality prints. These include nozzle clogging, overspray, and contamination within the ink transport system, all of which can significantly impact deposition consistency.

CHALLENGE #2: NOZZLE CLOGGING

Nozzle clogging in AJP occurs due to ink instability, particle agglomeration, or solvent evaporation at the nozzle tip. This leads to erratic material flow, reduced deposition accuracy, and frequent interruptions in the printing process. Additionally, when the AJP shutter is closed while the machine is on, ink continues to be delivered to the nozzle, leading to rapid buildup and clogging.

SOLUTION #2.1: Before each print, the nozzle tip must be cleaned and sonicated for at least 30 minutes in hydrogen peroxide, acetone, or isopropanol. Hydrogen peroxide is the most effective for removing any residual deposits. Ensuring a clean nozzle before printing significantly reduces clogging risks and improves deposition consistency.

SOLUTION #2.2: If the nozzle is not cleaned after printing, any residual ink dries inside the tip, making it much harder to remove before the next session. Cleaning the nozzle after every sample ensures that ink does not accumulate and solidify.

SOLUTION #2.3: In cases where dried ink obstructs the nozzle, acupuncture needles can be used to physically clear the clog from inside the tip.

SOLUTION #2.4: Ensuring that the ink is properly dispersed and stable is critical. MXene inks have the advantage of not requiring additives, but other nanoparticle-based inks often do. Before printing, the ink should be sonicated and checked for sedimentation.

SOLUTION #2.5: When the AJP is on but not actively printing, the shutter should be kept open to allow continuous flow through the nozzle.

CHALLENGE #3: OVERSPRAY

Overspray in AJP occurs when fine aerosolised droplets deviate from the intended deposition path, leading to blurred features, unintended material accumulation, and reduced print resolution. This phenomenon arises primarily due to improper focusing of the aerosol stream, suboptimal gas flow ratios, or excessive ink deposition. Minimizing overspray is particularly critical when defining fine features, such as interdigitated electrodes (IDEs) for energy storage or sensing applications. Excessive overspray can lead to unintended material spread, causing adjacent electrode fingers to merge and potentially short-circuit the device.

SOLUTION #3.1: Achieving precise beam collimation in AJP is essential for mitigating overspray and ensuring well-defined deposition. This requires careful tuning of the sheath gas and carrier (atomizer) gas flows, as AJP relies on aerodynamic focusing to direct aerosolized ink droplets accurately onto the substrate. The sheath gas flow confines and narrows the aerosol stream, preventing excessive droplet dispersion and reducing overspray. Insufficient sheath gas leads to a poorly focused beam, causing blurred edges and reduced print resolution, whereas excessive sheath gas can overly constrict the aerosol, reducing deposition efficiency. Similarly, carrier gas flow regulates droplet transport to the deposition head. A well-balanced sheath-to-carrier gas ratio ensures that droplets follow a controlled trajectory, minimizing unintended lateral spread while

maintaining uniformity in deposition. Optimizing these gas flows prevents ink diffusion beyond the intended area, enhancing print precision and reproducibility.

SOLUTION #3.2: Optimizing process speed is an effective strategy for mitigating overspray in AJP. Higher speeds reduce dwell time, limiting ink accumulation and minimizing lateral ink spread, which helps maintain sharp, well-defined features. However, process speed must be carefully balanced—excessive speed can result in insufficient material deposition, while too slow a speed can lead to ink pooling and further spreading. Adjusting the speed to match the ink properties and substrate characteristics ensures precise deposition, reducing overspray while maintaining print resolution and uniformity.

SOLUTION #3.3: Optimizing the nozzle-to-substrate distance (standoff height) helps minimise unintended ink diffusion, ensuring precise and controlled deposition. A lower standoff height enhances accuracy by reducing aerosol dispersion and improving feature definition.

SOLUTION #3.4: Ensuring stable ink formulation is crucial for mitigating overspray in AJP. Optimising viscosity and solvent composition ensures controlled droplet formation and precise deposition. To prevent ink concentration fluctuations, carrier gas humidification via a bubbler can be used during printing, counteracting solvent evaporation during transport.

CHALLENGE #4: DEPOSITION INSTABILITY & SAMPLE DAMAGE

In AJP, aerosolised ink is continuously transported through mist tubing to the nozzle, and without proper maintenance, residual ink can accumulate within the tubing and nozzle system. Over time, these deposits may dislodge unexpectedly, leading to uncontrolled droplet ejection onto the substrate. This contamination disrupts pattern precision, affects print uniformity, and compromises overall deposition quality. Additionally, inconsistencies in ink flow can cause sudden fluctuations in deposition rates, further impacting film morphology.

SOLUTION #4.1: Mist tubing should be routinely cleaned using a Nitrogen gas gun to remove residual ink buildup. If thorough cleaning is not possible, the tubing should be

replaced to maintain optimal ink flow. Importantly, mist tubing should be replaced for each different ink formulation to prevent cross-contamination and ensure stable deposition.

SOLUTION #4.2: Proper nozzle-to-substrate distance is crucial to avoid both sample damage and nozzle contamination.

CHALLENGE #5: OPTIMISATION OF SHEATH & ATOMISER GAS FLOWS

Precise control of sheath and atomizer gas flows is essential for uniform, high-resolution AJP deposition. The sheath gas collimates the aerosol stream, directing ink droplets toward the substrate, while the atomizer gas transports aerosolized ink from the mist generator to the nozzle. Their balance, defined by the focusing ratio (FR), governs beam collimation, deposition resolution, and pattern fidelity. High sheath gas constricts the stream, leading to under-deposition and accelerated solvent evaporation, while low flow causes droplet dispersion and overspray. Similarly, an unbalanced atomizer gas flow affects droplet transport, with excessive flow causing deposition inconsistencies and insufficient flow reducing material delivery.

SOLUTION #5.1: Maintaining an optimal focusing ratio (~ 2) is crucial to ensuring a well-collimated beam, preventing both excessive spreading and over-constriction.

SOLUTION #5.2: Continuous monitoring of gas flow parameters can help identify fluctuations in deposition and prevent issues such as material under-deposition or overspray. Implementing process control strategies can help maintain optimal conditions throughout printing.

CHALLENGE #6: REPRODUCIBILITY OF AJP

Achieving reproducibility in AJP is essential for ensuring the consistent and scalable fabrication of MXene-coated textiles. Variability in deposition parameters, such as ink properties, gas flow stability, and substrate interactions, can lead to inconsistencies in mass loading and film morphology, directly impacting electrical performance. A key factor in evaluating reproducibility is the accurate measurement of deposited mass, which presents significant challenges when working with textile substrates.

Initial attempts at mass quantification involved pre-weighing the fabric, printing the MXene film, drying it in a vacuum oven, and re-weighing the sample to determine the

deposited mass by subtraction. However, this approach proved highly unreliable due to the hygroscopic nature of textiles, which readily absorb ambient moisture upon exposure to air, causing continuous weight fluctuations. Furthermore, textile porosity introduced material loss, as some of the deposited MXene penetrated the fabric structure or was lost through open pores, further complicating accurate mass determination.

SOLUTION #6.1: To accurately assess mass loading, MXene films were printed as (2 mm x 2 mm) squares on Celgard 3501 polymer membranes, a non-porous, peelable substrate that allowed for easy removal of the printed samples. After drying in a vacuum oven (~24 hours), the films were weighed, providing stable and reproducible mass readings. This method eliminated inconsistencies associated with porous substrates, ensuring precise quantification of deposited material. The results revealed a strong linear correlation ($R^2 = 0.98896$) between mass loading and the number of AJP passes (Figure 32), demonstrating the predictability and scalability of the deposition process (**Figure 32**). This linearity demonstrates that mass loading can be reliably controlled by adjusting the number of printing passes, ensuring uniform deposition across multiple samples.

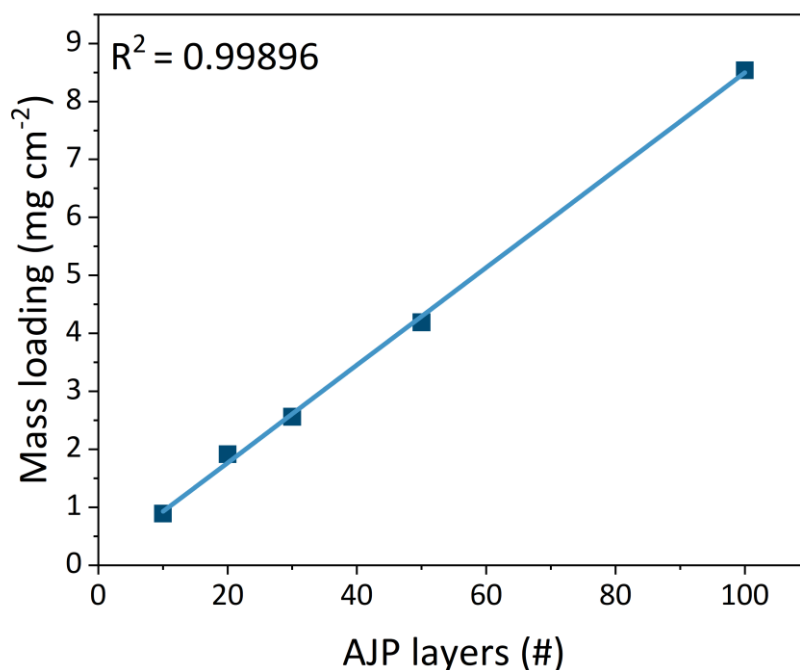


Figure 32: Linear correlation between mass loading and the number of AJP-deposited layers ($R^2 = 0.98896$), demonstrating the precision, consistency, and reproducibility of the deposition process.

SOLUTION #6.2: To enhance reproducibility in AJP, deposition rate monitoring can serve as a practical method for ensuring consistent mass loading. A reference sample of known dimensions is printed on a pre-weighed glass slide or Celgard 3501 peelable substrate under identical conditions as the target sample. By measuring the deposited mass on this reference and normalizing it to the printing duration, a deposition rate (mg/s) can be established. This allows for better control over deposition consistency across multiple samples without the inaccuracies associated with direct textile weighing due to porosity and moisture absorption.

Beyond mass estimation, this method also helps regulate deposition rate throughout the printing process by accounting for variations that may occur due to ink evaporation, fluctuations in atomizer performance, or environmental conditions such as humidity. While it does not fully eliminate the impact of ink penetration into textile pores, tracking deposition over time allows for process adjustments, improving overall reliability and scalability in MXene e-textile fabrication.

3.6. CONCLUSIONS

This chapter has systematically explored the AJP of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene inks onto textile substrates, addressing key challenges in process optimisation, deposition reproducibility, and material characterisation. Through rigorous synthesis and characterisation, the structural integrity and high purity of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene were confirmed. XRD analysis validated the successful transformation from the Ti_3AlC_2 MAX phase to a layered $\text{Ti}_3\text{C}_2\text{T}_x$ structure, with a characteristic shift in the (002) peak indicative of increased interlayer spacing due to aluminium removal. TEM and SAED further revealed the well-defined 2D morphology, while EDX confirmed a homogeneous elemental distribution, verifying complete etching and the absence of residual aluminium.

The integration of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene into textile substrates via AJP was comprehensively evaluated, demonstrating excellent surface coverage and strong adhesion across cotton, polycotton, and polyester fabrics. SEM analysis revealed the formation of uniform MXene coatings, while XRD spectra of the printed textiles exhibited both MXene-specific peaks and fabric-characteristic reflections, confirming the successful incorporation of the conductive material into the textile matrix. Subtle peak shifts in the XRD patterns suggested potential crystallinity modifications upon MXene deposition, highlighting the strong interaction between the printed material and the underlying textile structure.

A key aspect of this study was the systematic optimization of AJP parameters, including nozzle selection, process speed, and gas flow regulation, to achieve high-resolution, reproducible, and conductive MXene deposits. The results showed that smaller nozzles (150 μm) improved conductivity by enhancing deposition focus and interflake connectivity, while larger nozzles (300 μm) led to higher resistance due to increased dispersion and thinner films. Similarly, slower process speeds produced thicker films with lower resistance, whereas higher speeds resulted in thinner, higher-resistance deposits. These findings underscore the importance of fine-tuning deposition conditions to optimize electrical and morphological properties for e-textile applications.

Several technical challenges inherent to AJP of MXene textiles were systematically analyzed, with targeted troubleshooting strategies implemented to enhance deposition precision and long-term reproducibility. Among these, nozzle clogging was identified as a recurring issue due to ink aggregation and solvent evaporation at the nozzle tip. This was mitigated through pre-printing sonication, post-printing cleaning, and maintaining continuous ink flow to prevent residual buildup. Overspray, a critical concern when defining fine-featured structures such as IDD, was controlled by precise adjustment of sheath and atomizer gas flows, process speed modulation, and optimized nozzle standoff height. The need for accurate mass loading quantification was also addressed by developing alternative deposition monitoring techniques, ensuring consistent and scalable material deposition despite textile-specific challenges such as substrate porosity and moisture absorption.

To overcome the inherent limitations of direct mass measurement on textiles, a controlled mass quantification strategy was introduced using Celgard 3501 polymer membranes, a non-porous, peelable substrate that allowed for precise mass determination. The results revealed a strong linear correlation ($R^2 = 0.98896$) between mass loading and the number of printed layers, confirming the predictability and reproducibility of AJP. Furthermore, an additional process control method was proposed, involving deposition rate monitoring by printing reference samples on pre-weighed glass slides or peelable substrates under identical conditions as the main samples. This approach will allow for real-time assessment of deposition uniformity, providing an additional quality control mechanism to mitigate variations arising from environmental fluctuations or ink instability.

This chapter has demonstrated that AJP is a robust, scalable, and highly precise fabrication technique for integrating $\text{Ti}_3\text{C}_2\text{T}_x$ MXene into textile substrates, offering a viable pathway

for the development of high-performance e-textiles. By systematically addressing deposition challenges and refining process parameters, this work establishes a comprehensive framework for achieving reproducible, high-resolution MXene coatings on flexible substrates. These findings reinforce the potential of AJP as a leading fabrication approach for next-generation wearable electronics, energy storage devices, and smart textile applications.

3.7. ACKNOWLEDGEMENTS

I want to express my gratitude to *Dr Dahnan Spurling* for his essential assistance in synthesizing the MXene functional inks and for their SEM and XRD characterizations. I thank *Dr Oskar Ronan* for his expertise in the TEM characterization of the MXene ink, and I want to acknowledge both *Dr Sergio Pinilla* and *Dr David Caffrey* for their indispensable support in the XRD characterization of the printed samples.

4 AEROSOL JET PRINTED MXENE TEXTILE ELECTRODES

AIMS & OBJECTIVES

This chapter aims to investigate the electrochemical performance of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene-based textile electrodes fabricated via AJP, with a focus on their suitability for wearable energy storage applications.

By systematically varying the number of printed MXene layers (10, 20, 30, 50, and 100 layers) on different textile substrates (cotton, polycotton, and polyester), the study seeks to evaluate the impact of mass loading on key electrochemical parameters, including areal capacitance, equivalent series resistance (ESR), rate performance, and cycling stability.

The primary objective is to assess the feasibility of using AJP to create a uniform, conductive, and mechanically stable textile-based electrodes that demonstrate high pseudocapacitive charge storage, low internal resistance, and robust long-term cycling stability.

Through cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS), this work aims to provide a comprehensive characterisation of the charge storage behaviour, ion diffusion properties, and capacitive retention of MXene-printed textile electrodes.

The insights gained from this work will serve as a foundation for the subsequent development of MXene-based microsupercapacitors (MSCs), helping to optimise printing parameters, electrode architectures, and electrochemical performance for future textile-integrated energy storage solutions.

4.1. INTRODUCTION

One of the key challenges in advancing e-textiles, as discussed in Chapter 1, is the development of reliable and sustainable power supplies that can be seamlessly integrated into fabrics without sacrificing comfort or flexibility.^[110,139,140] The search for flexible, high-performance energy storage solutions has led researchers to explore the remarkable potential of MXenes. $\text{Ti}_3\text{C}_2\text{T}_x$ MXene, in particular, has attracted significant attention due to its unique combination of properties that make it exceptionally well-suited for energy storage applications. Its capabilities extend to e-textiles, offering the possibility of transforming everyday fabrics into advanced, energy-storing materials perfectly suited for wearable technology.^[397,398]

$\text{Ti}_3\text{C}_2\text{T}_x$ MXene stands out for its exceptional metallic conductivity ($\sim 24,000 \text{ S cm}^{-1}$),^[302] which arises from the free electrons in its transition metal carbide backbone.^[609] This high conductivity enables $\text{Ti}_3\text{C}_2\text{T}_x$ MXene to serve a dual role in supercapacitor applications, acting both as an active electrode material, facilitating efficient charge storage, and as a current collector, ensuring rapid electron transport.^[106,250] The unique layered structure $\text{Ti}_3\text{C}_2\text{T}_x$ further enhances its effectiveness in energy storage applications by providing a high surface area that allows for rapid ion intercalation, enabling ions to easily penetrate and diffuse through the material. This layered configuration not only facilitates the quick and reversible insertion and extraction of ions but also maximizes the exposure of redox-active sites within the layers, thereby enhancing the material's ability to undergo redox reactions. Additionally, the ability of titanium atoms within the $\text{Ti}_3\text{C}_2\text{T}_x$ matrix to adopt multiple oxidation states significantly improves charge transfer dynamics, thereby enhancing the performance of MXenes as supercapacitor electrodes.^[216]

In H_2SO_4 , electrolyte, $\text{Ti}_3\text{C}_2\text{T}_x$ MXene exhibits a pseudocapacitive charge storage mechanism, where variations in electrode potential closely correlate with changes in the oxidation state of titanium, accompanied by the protonation of oxygen functional groups.^[235] Under these conditions, $\text{Ti}_3\text{C}_2\text{T}_x$ demonstrates impressive volumetric capacitances, achieving $\sim 900 \text{ F cm}^{-3}$ with clay electrodes,^[226] and $\sim 1500 \text{ F cm}^{-3}$ with hydrogel electrodes.^[235] It also displays excellent capacitive performance at high charge/discharge rates and maintains stability over 10,000 cycles, which is critical for long-term applications.^[244,610] The hydrophilic nature of $\text{Ti}_3\text{C}_2\text{T}_x$ flakes, attributed to surface terminations ($-\text{O}$, $-\text{OH}$, and $-\text{F}$), enables easy processing in aqueous media. This

property allows formulating stable, viscous, highly conductive, and electroactive colloidal inks without requiring surfactants, binders, additives, or post-treatment.

Ti₃C₂T_x MXene also offers excellent mechanical attributes that make it particularly suitable for wearable electronics and e-textile applications. Recent studies revealed that 40-nm-thick Ti₃C₂T_x nanosheets have a tensile strength of approximately 670 MPa and Young's modulus ranging from 80 to 100 GPa perpendicular to the basal plane.^[611] The mechanical properties of these nanosheets largely depend on the cohesion, bonding, and interfacial interactions among MXene nanoflakes. While the flexibility of MXenes decreases with increased layer thickness, the thinnest layers remain highly elastic, with Young's modulus of up to 502 GPa.^[612] This elasticity and flexibility are crucial for wearable electronics, as they enable the material to withstand dynamic movement without compromising performance. Additionally, MXenes can be combined with polymers to create composites that are both flexible and durable, further enhancing their suitability for smart textiles and wearable technology applications.^[427] These mechanical properties, coupled with its unique electrical and electrochemical characteristics, make Ti₃C₂T_x MXene an ideal material for flexible and durable energy storage systems integrated into wearable technology.

Recent studies have demonstrated the superior electrochemical performance of Ti₃C₂T_x MXenes compared to other electrode materials.^[377] For example, Ti₃C₂T_x MXene-based conductive electrodes in high-energy, solid-state bendable supercapacitors have shown significantly better performance than traditional carbon-based electrodes, such as activated carbon and rGO, by providing greater energy storage capacity.^[613] This indicates that Ti₃C₂T_x MXene-based negative electrodes could serve as a more effective alternative to carbon-based materials for boosting the electrochemical capacity of supercapacitors.^[235,614] These properties highlight the potential of Ti₃C₂T_x MXenes as a novel material for creating high-performance, durable smart textiles for a wide range of advanced applications.

This chapter focuses on the use of AJP to fabricate Ti₃C₂T_x MXene-based electrodes directly onto textile substrates. AJP is a cutting-edge technique that allows for the precise deposition of functional inks onto complex surfaces, making it particularly well-suited for applications involving flexible and non-planar materials like textiles. The ability to control the deposition process at a microscale level ensures that the MXene ink is applied uniformly, creating a continuous, conductive layer that adheres well to the fabric.

Building upon the detailed theoretical framework of AJP presented in Section 2.2, this chapter applies this technique to the fabrication of MXene-textile electrodes. The process begins with the preparation of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene ink, optimized for AJP, followed by the systematic deposition onto various textile substrates. The resulting electrodes are then subjected to a rigorous three-electrode electrochemical characterization, where key performance metrics such as capacitance, charge-discharge behaviour, and cycling stability are meticulously evaluated. These tests are crucial for determining the practical viability of MXene-based textile electrodes in real-world applications, particularly in wearable devices that demand both high performance and durability.

4.2. EXPERIMENTAL METHODS

4.2.1. SYNTHESIS OF $\text{Ti}_3\text{C}_2\text{T}_x$ MXENE

$\text{Ti}_3\text{C}_2\text{T}_x$ ink was formulated via the MILD synthesis route detailed in Section 3.2.1.

4.2.2. AEROSOL JET PRINTING OF MX@TEXTILE ELECTRODES

The MX@Fabric electrodes (2 mm x 2 mm) were produced utilizing the Optomec AJP 300 system, depositing 10, 20, 30, 50, and 100 layers on cotton (MX@C), polycotton (MX@PC), and polyester (MX@PR). The additive-free aqueous $\text{Ti}_3\text{C}_2\text{T}_x$ MXene ink was diluted with deionized water to a concentration of 10 mg mL^{-1} , optimizing performance for efficient atomization with Optomec's UA, ensuring consistent and reproducible results while minimizing nozzle clogging. Each print iteration involved 1 mL of the diluted ink, with the ultrasonic atomiser (UA) temperature controlled at 10°C and an atomization current set at approximately 0.55 A.

Employing a $150 \mu\text{m}$ diameter nozzle, carrier gas flow rates ranged from 25 - 35 SCCM, and sheath gas flow rates were maintained between 50 - 60 SCCM. Slight adjustments in flow rates were necessary due to daily variations in ambient conditions (temperature, pressure, humidity). Platen temperature at 50°C ensured optimal solvent evaporation, facilitating the formation of dried conductive deposits. Consistent mass loading was maintained by keeping all machine parameters and total print time constant. The printing was performed using a SFA. The details are summarised in **Table 1**.

Table 1: Summary of process parameters used for AJP fabrication of MX@Fabric electrodes.

Process Parameters	MX@Fabric Electrodes
Nozzle diameter (D_n)	150 μm
Functional ink	Additive-free aqueous $\text{Ti}_3\text{C}_2\text{T}_x$ MXene
Ink concentration	10 mg ml^{-1}
Fabric substrate(s)	Cotton (C) Polycotton (PC) Polyester (PR)
Sheath gas flow (f_s)	50 – 60 SCCM
Atomiser gas flow (f_a)	25 – 35 SCCM
Atomiser current	0.53 – 0.58 A
Process speed	2 mm s^{-1}
Chiller temperature	5 – 10 $^{\circ}\text{C}$
Platen temperature	50 $^{\circ}\text{C}$

Various essential factors were monitored for stable deposition. To maintain consistent mass loading, carrier gas moisturising via a bubbler was needed within a single printing session. The ink concentration within the atomiser gradually increased during atomisation, emphasising the need to avoid highly concentrated ink, which could compromise the process's long-term stability. During printing, periodic checks and adjustments were made to ensure stable deposition, such as modifying sheath and atomiser gas flow parameters if fluctuations appeared. Maintaining nozzle cleanliness (via sonication and N_2 gun), tubing clearance (with N_2 gun), and re-adjusting gas flow parameters were imperative to prevent significant ink drop issues that could damage the sample.

4.2.3. ELECTROCHEMICAL CHARACTERISATION

The MX@Fabric electrodes were studied by utilising a Biologic VMP3 potentiostat in ambient conditions in a three-electrode Swagelok cell (PFA420-3) with 3 M H_2SO_4 aqueous electrolyte. The MX@Fabric electrode is compressed on the glassy carbon current collector and used as the working electrode since it demonstrates a remarkable overpotential for hydrogen evolution reaction.^[235,591,615] The overcapacitive activated

carbon (YP-50, Kuraray, Japan) is used as the counter electrode, and Ag/AgCl in 3.5 M KCl as the reference electrode. Celgard 3501 membrane, located between the MX@Fabric electrode and over-capacitive activated carbon, is used as a separator. The 3 M H₂SO₄ (0.5 mL) aqueous electrolyte is placed into the cell through the top insertion nut and tightly sealed with the parafilm. Before collecting electrochemical data, the MX@Fabric electrodes were initially precycled at 5 mV s⁻¹ for 100 cycles. CV measurements were recorded in the potential window of -0.65 V - 0.2 V (vs Ag/AgCl) from 5 mV s⁻¹ to 1000 mV s⁻¹ scan rates. GCD tests were recorded at current densities from 0.01 A cm⁻² to 0.5 A cm⁻² in the potential window from -0.65 V to 0.2 V (vs Ag/AgCl). EIS was recorded in the 10 mHz to 1000 kHz frequency range under a potential amplitude of 10 mV under 0.2 V applied potential on the working electrode. The long-term cycling stability of MX@C-10L, MX@PC-10L, and MX@PR-10L was investigated with 10,000 CV cycles at 100 mV s⁻¹ scan rate post-pre-cycling.

The ESR was calculated from the immediate voltage drop (V_{drop}) observed in GCD curves that occurred following the reversal of current polarity as:^[553]

$$R_{ESR} = \frac{V_{drop}}{2I} \quad (23)$$

The areal capacitance of MX@Fabric electrodes was obtained by integrating current with respect to time on the discharge portion of the CV curve and dividing it by the scan rate and voltage window, as shown in **Equation 24**:

$$C_D = \frac{\int_0^t i dV}{v \Delta V} \quad (24)$$

where C_D is a discharge capacitance, i is the instantaneous current at the potential of V , v signifies the scan rate (V s⁻¹), and ΔV depicts the potential window (V). The areal capacitance, C_A (mF cm⁻²), was then calculated by normalising the obtained discharge capacitance with the AJP MX@Fabric electrode surface area.

The charge storage kinetics of MX@Fabric electrodes were studied using a relationship between peak current and the scan rate, governed by the power-law relationship:

$$i_p = i_{capacitive} + i_{diffusion} = av^b \quad (25)$$

where i_p is the peak current, which is the sum of surface-controlled ($i_{\text{capacitive}}$) and diffusion-controlled ($i_{\text{diffusion}}$) current contributions; v is scan rate, and a and b are adjustable parameters.

The logarithm of both sides:

$$\log(i_p) = \log(a) + b \log(v) \quad (26)$$

yields a log-log plot of current against scan rate, giving slope b , a measure of charge storage kinetics, which depends on potential, scan rate, and charge storage mechanism.^[569] A slope of 1 ($i_p \propto v$) indicates the capacitive/pseudocapacitive charging with fast ion diffusion, while 0.5 ($i_p \propto v^{1/2}$) suggests a diffusion-limited behaviour.^[226,244,569] Pseudocapacitive materials are expected to yield $i_p \propto v$ linear responses.^[569]

4.3. AEROSOL JET PRINTING OF MX@TEXTILE ELECTRODES

The design and fabrication of the electrodes (**Figure 33**) leveraged advanced AJP technology to achieve precise and uniform deposition of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene ink onto various textile substrates, including cotton, polycotton and polyester. To explore the influence of layer thickness on electrode performance, a series of printing protocols were implemented, producing electrodes with 10, 20, 30, 50, and 100 layers on each fabric type. Hence the name of the samples is MX@Fabric-#L, where 'MX' represents $\text{Ti}_3\text{C}_2\text{T}_x$ MXene ink, '@C' stands for cotton, '@PC' for polycotton, '@PR' for polyester, and '#L' indicates the number of printed layers (10, 20, 30, 50, 100).

This systematic layering approach was enabled by the precision of AJP, which allowed for the controlled deposition of $\text{Ti}_3\text{C}_2\text{T}_x$ aqueous MXene ink (at a concentration of 10 mg ml⁻¹) through a fine 150 μm nozzle. Each layer adhered seamlessly to the previous one, demonstrating the effectiveness of AJP in creating high-quality, multilayered structures.

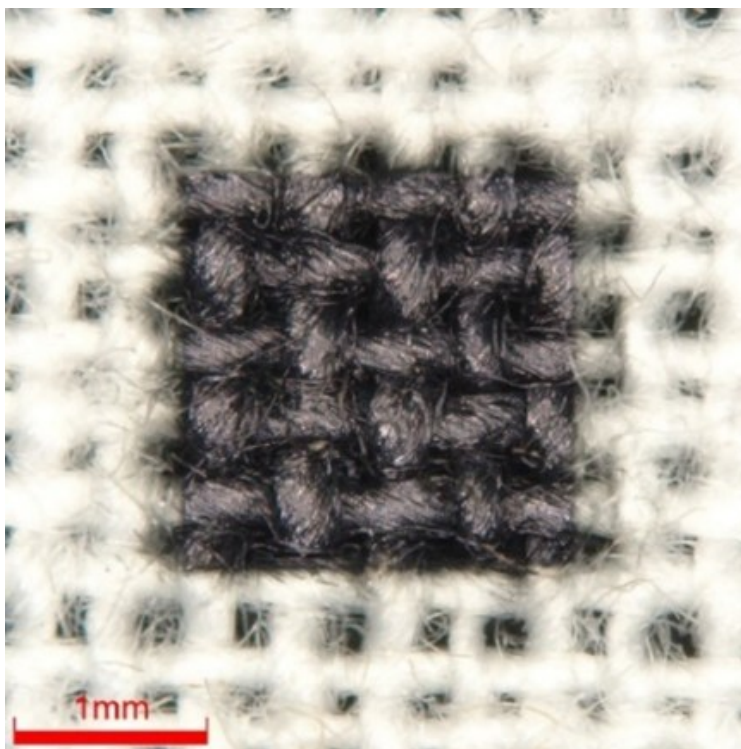


Figure 33: Representative digital microscope image of $\text{Ti}_3\text{C}_2\text{T}_x$ MX@Fabric-#L electrode.

The rationale behind selecting a range of 10 to 100 layers was informed by prior studies on $\text{Ti}_3\text{C}_2\text{T}_x$ -based supercapacitors, which have shown that increasing the mass loading of the electrode material can significantly enhance areal capacitance.^[370,569,616,617] The AJP process was finely tuned to deposit the first 10 layers continuously, ensuring a uniform foundation. For electrodes requiring greater thicknesses (20, 30, 50, 100 layers), additional sets of 10 layers were sequentially printed on top of the initial layers. This method not only highlights the versatility of AJP in fabricating multilayered electrodes but also offers insights into optimising electrode thickness for enhanced electrochemical performance.

4.4. ELECTROCHEMICAL CHARACTERISATION OF MX@TEXTILE ELECTRODES

The electrochemical performance of the AJP MX@Fabric-#L electrodes was rigorously evaluated using three-electrode Swagelok cells (**Figure 34**) with a 3 M H_2SO_4 electrolyte. This setup was employed to examine the suitability of AJP textile-based electrodes for energy storage applications.

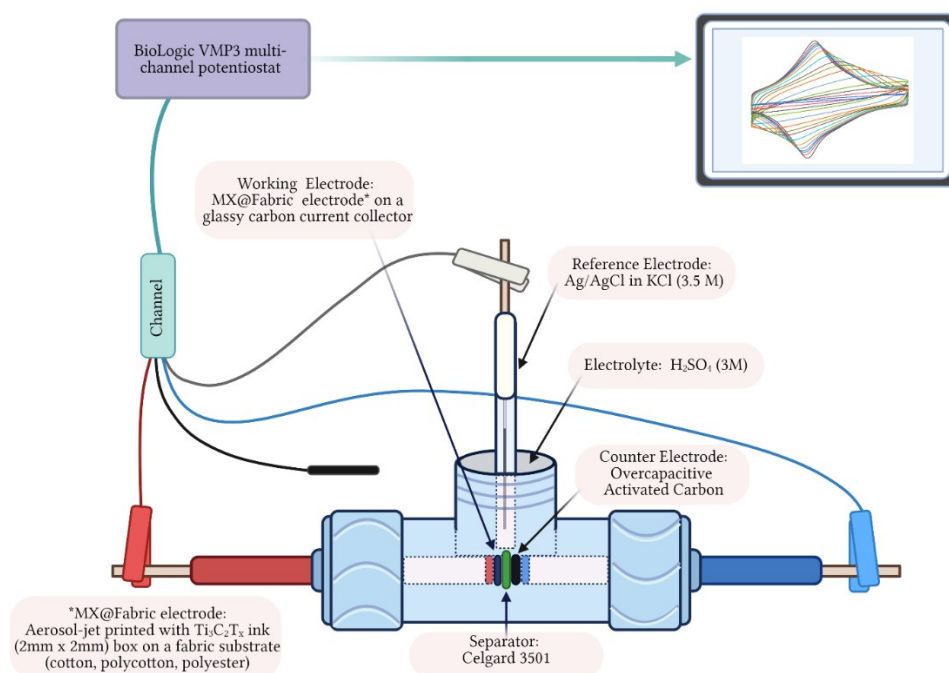


Figure 34: Swagelok cell setup employed for electrochemical characterisation of MX@Fabric-#L electrodes. The three-electrode configuration and a 3 M H₂SO₄ electrolyte were utilised to systematically study the electrodes' electrochemical performance.

The charge storage mechanism of Ti₃C₂T_x in 1 M H₂SO₄ is pseudocapacitive, characterised by a nearly linear correlation between the electrode potential and the oxidation state of titanium atoms within the MXene structure. As the electrode potential changes, titanium undergoes reversible redox transitions (e.g., Ti³⁺ to Ti⁴⁺), directly impacting the charge storage capacity. Concurrently, the acidic environment of the H₂SO₄ electrolyte facilitates the protonation and deprotonation of oxygen functional groups (such as -O and -OH) present on the MXene surface. Thus, the combination of titanium redox activity and functional group protonation underpins the pseudocapacitive nature of Ti₃C₂T_x MXene in acidic electrolytes, enabling efficient and high-capacity energy storage.^[235,618] Previous studies showed that using 3 M H₂SO₄ instead of 1 M H₂SO₄ results in larger capacitance and superior rate performance of electrodes, possibly related to the higher conductivity of the former.^[235] A 3 M H₂SO₄ solution provides a greater number of protons (H⁺), which lowers electrolyte resistance, enabling faster ion transport and more efficient charge transfer during electrochemical cycling. Additionally, the increased proton concentration promotes more extensive protonation and deprotonation of oxygen-containing functional groups on the MXene surface, further enhancing pseudocapacitive contributions to overall capacitance through reversible redox reactions.

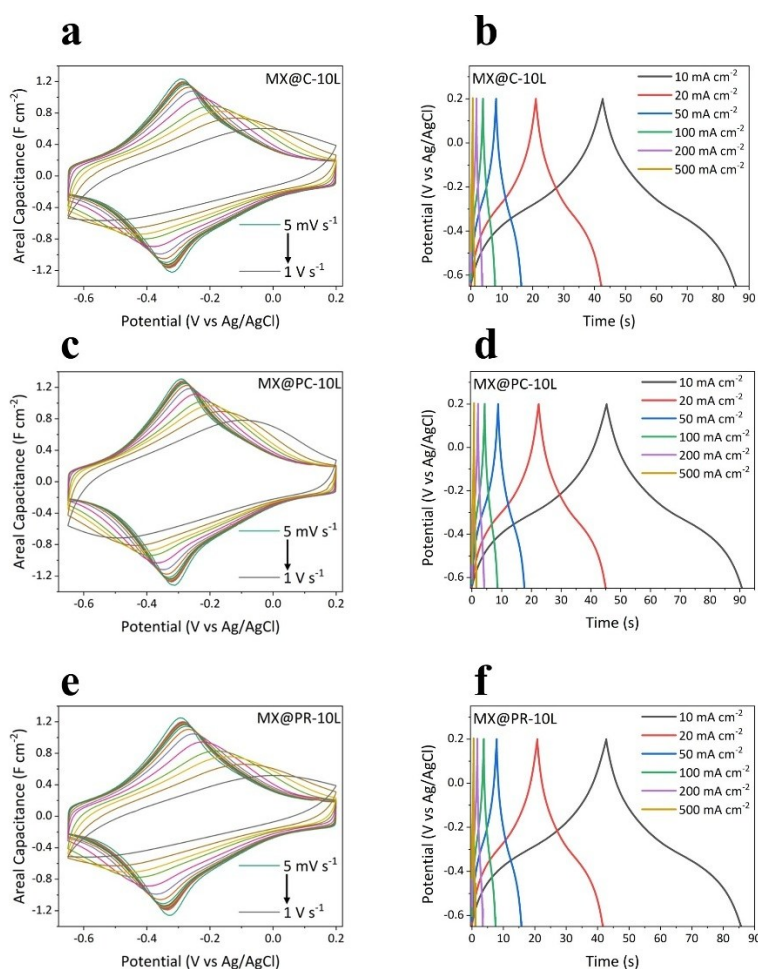


Figure 35: Electrochemical characterisation of AJP MX@Fabric electrodes, highlighting: **(a, c, e)** MX@C-10L, MX@PC-10L, and MX@PR-10L electrodes' CVs at 5, 10, 11, 12, 13, 15, 16, 20, 30, 50, 100, 200, 300, 500, and 1000 mV s^{-1} scan rates; and **(b, d, f)** GCD plots of MX@C-10L, MX@PC-10L, and MX@PR-10L electrodes at 10, 20, 50, 100, 200, and 500 mA cm^{-2} current densities.

The CV results for MX@C-10L, MX@PC-10L, and MX@PR-10L electrodes, depicted in **Figure 35(a, c, e)**, respectively, display characteristic cathodic and anodic peaks of $\text{Ti}_3\text{C}_2\text{T}_x$, indicating the presence and reversibility of redox processes. The stable operating voltage window for $\text{Ti}_3\text{C}_2\text{T}_x$ electrodes ranges from -0.6 V to 0.2 V, with a pair of redox peaks observed around -0.3 V versus the Ag/AgCl reference electrode. This is an indicator of pseudocapacitive behaviour, meaning that changes in electrode potential can be almost linearly correlated to the changes in the oxidation state of titanium, which in turn is accompanied by protonation of oxygen functional groups^[235,618], which is further supported by the small cathodic and anodic peak potential separation. The consistent behaviour across various electrodes with different layer counts – 10, 20, 30, 50, and 100 AJP layers – on cotton, polycotton, and polyester (**Figure S6**, Supplementary Information) demonstrates the robust electrochemical activity of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene deposits.

Complementing the CV analysis, galvanostatic charge/discharge (GCD) tests, illustrated by the comparative GCD plots of MX@C-10L, MX@PC-10L, and MX@PR-10L at different current densities, as shown in **Figure 35(b, d, f)** respectively, further confirm the redox activity and its reversibility through symmetrical and non-linear profiles. Such results indicate efficient charge storage and release mechanisms within the electrodes. This high reversibility is crucial for the MSC's long-term stability and performance. The non-linear GCD curves align well with the CV data, reinforcing the pseudocapacitive behaviour, efficient charge transfer and minimal resistive losses of the AJP electrodes. GCDs also exhibit a systematic trend with an increasing number of printed layers (**Figure 36**), maintaining the symmetry at current densities from 10 mA cm^{-2} up to 500 mA cm^{-2} . This observation aligns with the exceptional rate performance and the capacitance retention exhibited by these electrodes.

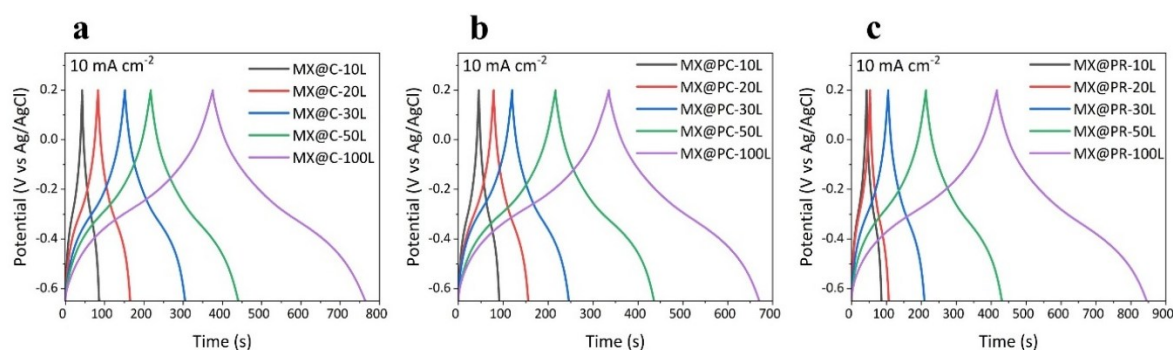


Figure 36: Comparison of GCD curves of MX@Fabric electrodes with 10, 20, 30, 50, and 100 printed layers at 10 mA cm^{-2} current density highlighting (a) cotton – MX@C, (b) polycotton – MX@PC and (c) polyester – MX@PR.

The GCDs of MX@C-10L, MX@PC-10L, and MX@PR-10L electrodes exhibit significant similarity at 10 mA cm^{-2} , all exhibiting small IR drops of 3.4 mV, 3.2 mV, and 7.1 mV, respectively, calculated according to **Equation 23**. This outcome aligns with the CV data, again affirming the suitability of cotton, polycotton, and polyester for wearable AJP MSC applications.

Comparative CV analysis at 5 mV s^{-1} for MX@C-10L, MX@PC-10L, and MX@PR-10L electrodes display substantial congruence, **Figure 37(a)**, underscoring the suitability of cotton, polycotton, and polyester for wearable AJP MSC applications. This result also emphasises the versatility of AJP, indicating the potential to employ the same techniques while extending them to other fabric variants.

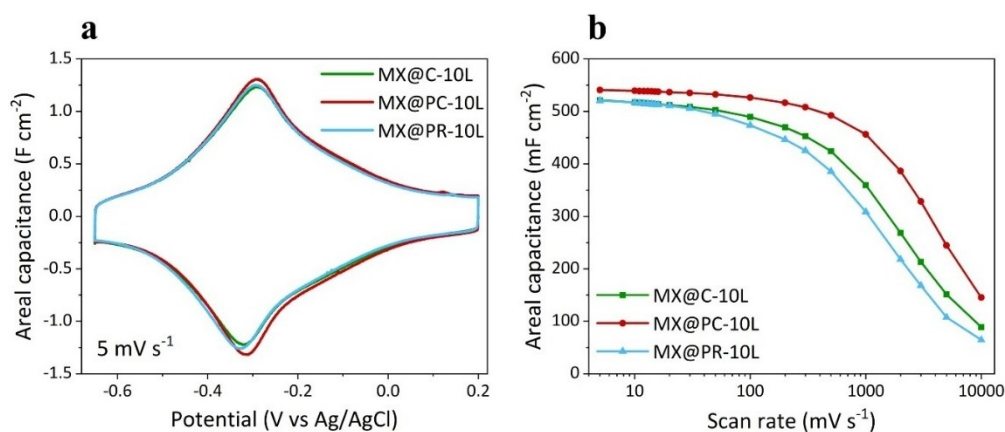


Figure 37: Comparative CV analysis AJP MX@Fabric electrodes. **(a)** Comparative CVs of the MX@C-10L, MX@PC-10L, and MX@PR-10L electrodes at 5 mV s⁻¹ scan rate. **(b)** Rate performance comparison of MX@C-10L, MX@PC-10L, and MX@PR-10L electrodes represented in areal capacitance.

The areal capacitance is a crucial metric for understanding the charge storage performance of the printed electrodes.^[258] According to **Equation 24**, MX@C-10L, MX@PC-10L, and MX@PR-10L electrodes attained areal capacitances of 521.26 mF cm⁻², 540.89 mF cm⁻², and 520.52 mF cm⁻² at 5 mV s⁻¹ respectively, also demonstrating high-rate performance (**Figure 37(b)**). Notably, MX@PC-10L exhibits a slightly higher capacitance than both MX@C-10L and MX@PR-10L at 5 mV s⁻¹. This small but consistent advantage persists at intermediate scan rates, underscoring the favourable ion-transport environment provided by the polycotton substrate. Cotton fibres likely enhance porosity and electrolyte uptake, while polyester fibres supply mechanical robustness, collectively improving the electrode's electrical conductivity and effective surface area more than single-fibre fabrics could achieve.

Furthermore, in line with expectations, the areal capacitance exhibited a consistent rise with an increasing number of AJ printed layers across all three fabric variants. Taking the MX@C electrode as a representative example, the corresponding areal capacitances at 5 mV s⁻¹ were 521.26 mF cm⁻², 990.68 mF cm⁻², 1809.96 mF cm⁻², 2597.85 mF cm⁻², and 4387.06 mF cm⁻² for 10, 20, 30, 50, and 100 printed layers, respectively.

Notably, **Figure 38** and **Figure S10**, Supplementary Information, provide evidence of a systematic elevation in rate performance as the number of printed layers increases. This observation suggests that the additional layers facilitate more efficient charge storage by providing more active sites, better electrical conductivity and optimized charge transport pathways. Similar results of high capacitance and rate performance were also previously

reported on MXene-coated cotton yarns, highlighting the robustness of MXene films for flexible textile-based applications.^[90]

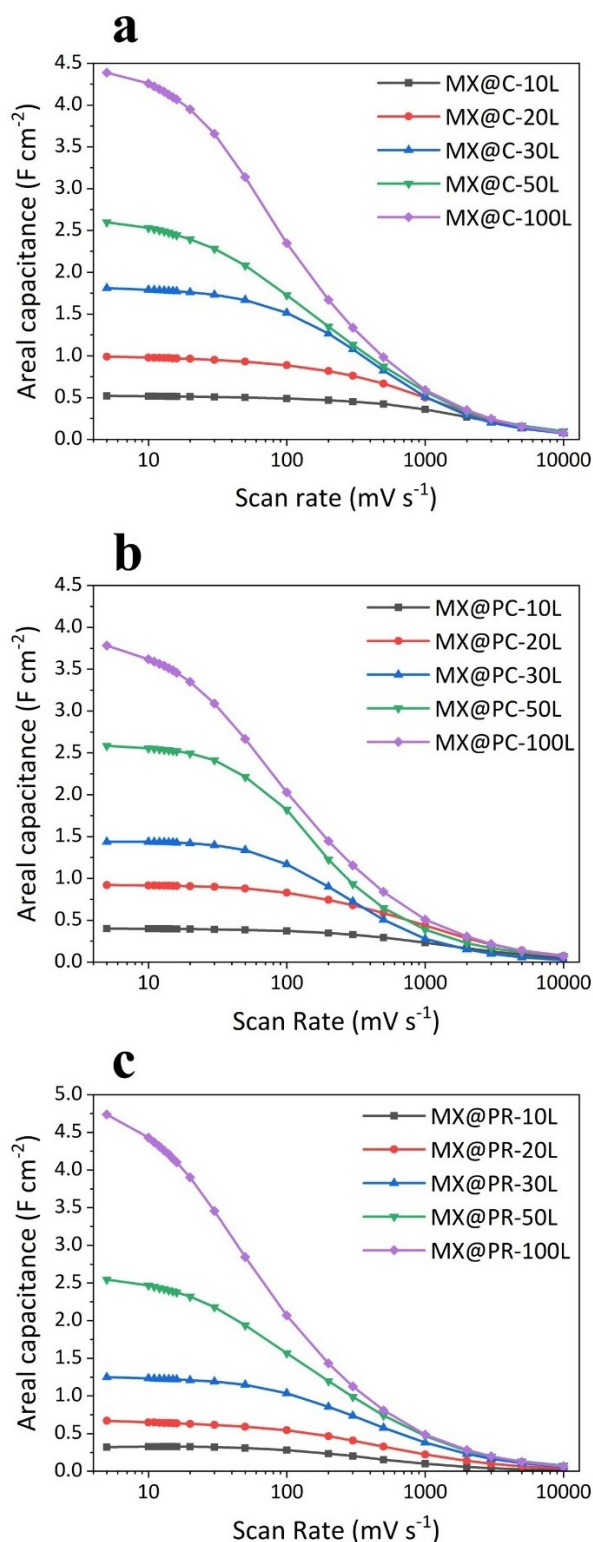


Figure 38: Rate performance of MX@Fabric electrodes with 10, 20, 30, 50, 100 printed layers on (a) cotton – MX@C, (b) polycotton – MX@PC, and (c) polyester – MX@PR.

It, however, was noted that the areal capacitance of our MX@Fabric electrodes reduces at high scan rates, attributed to diffusion-limited ionic transport. A similar phenomenon was

previously observed in thick planar MXene electrodes that exhibited decreased performance at high rates due to limited accessibility of electrochemically active sites.^[226]

Consistent capacitance retention, exemplified by electrodes at 10L AJP loading (**Figure 39**), highlights the stability and robustness of AJP $\text{Ti}_3\text{C}_2\text{T}_x$ MXene prints.

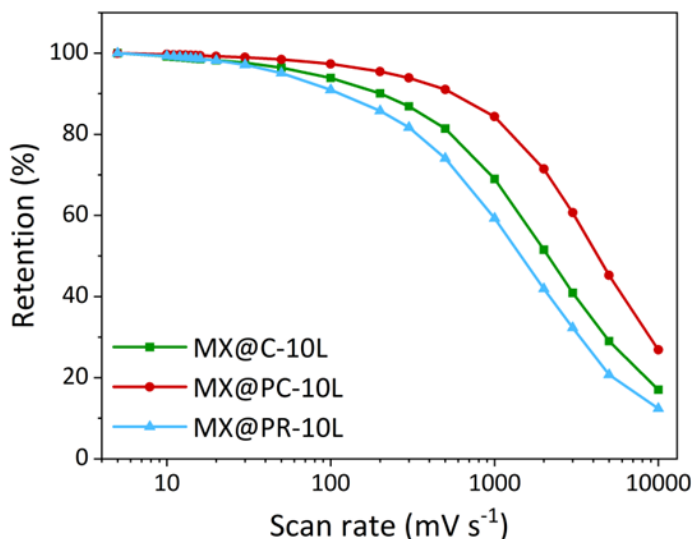


Figure 39: Comparison of areal capacitance retention for MX@C-10L, MX@PC-10L, and MX@PR-10L electrodes.

Areal capacitance retention with increasing scan rate for MX@C-10L, MX@PC-10L, and MX@PR-10L electrodes is depicted in **Figure 39**. All three electrodes show excellent stability at moderate scan rates, but MX@PC-10L demonstrates the most pronounced retention of ~90+% capacitance up to 500 mV s^{-1} . In contrast, MX@C-10L retains the same high fraction only up to 200 mV s^{-1} , and MX@PR-10L shows notable decay beyond 100 mV s^{-1} . The reduction of areal capacitance at higher scan rates likely stems from diffusion-limited ionic transport. The superior retention profile of MX@PC-10L likely arises from the dual-fibre architecture of polycotton, which promotes more efficient electrolyte infiltration and preserves a greater proportion of active sites at high scan rates. A comparison of areal capacitance retention for MX@C, MX@PC, and MX@PR at other AJP loadings is shown in **Figure S11**, Supplementary Information.

The high-rate performance of these electrodes was further confirmed by the small ESR determined using EIS, **Figure 40**, by finding the point intercept of the Nyquist plot with the x-axis.^[569,571–573,619] The correlation between ESR values and the IR drop obtained from GCD analysis should be direct, i.e. higher ESR should give a larger IR drop during charge-discharge cycles.

MX@PC-10L electrode exhibited the smallest ESR at $0.068 \Omega \text{ cm}^2$ and the smallest resistance of $0.16 \Omega \text{ cm}^2$, determined from GCD analysis at 0.8 mA current. In contrast, the MX@PR-10L electrode displayed the largest ESR at $0.12 \Omega \text{ cm}^2$ and the largest resistance of $0.36 \Omega \text{ cm}^2$. MX@C-10L electrode had an intermediate ESR of $0.09 \Omega \text{ cm}^2$ and a resistance of $0.17 \Omega \text{ cm}^2$.

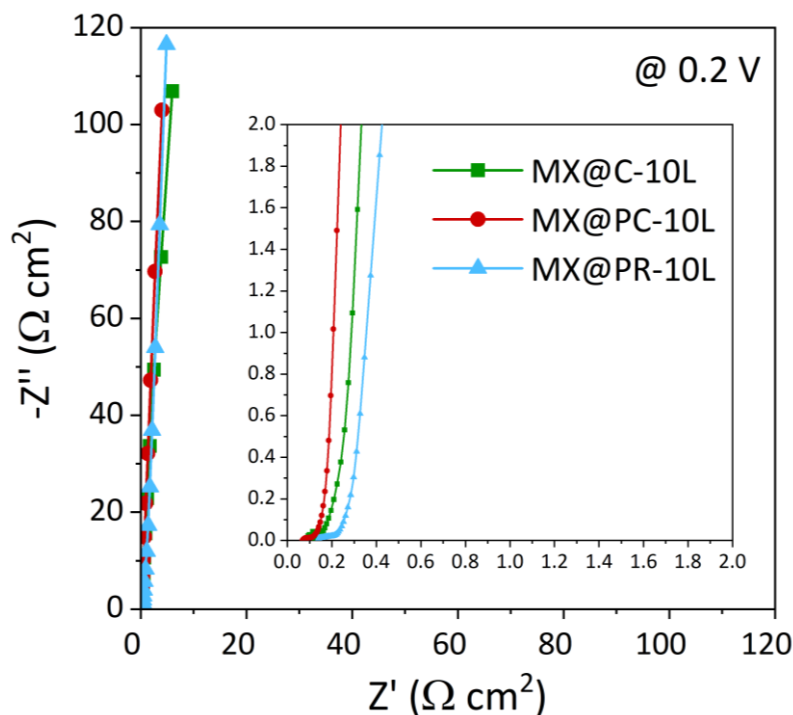


Figure 40: EIS Nyquist plots of MX@C-10L, MX@PC-10L, and MX@PR-10L electrodes recorded at 0.2 V. EIS was performed in the 10 mHz to 1000 kHz frequency range under a potential amplitude of 10 mV and analysed at 0.2 V applied potential on the working electrode.

These differences in ESR values can be attributed to the inherent properties of the substrates used. For example, previous studies also observed a higher ESR of carbon-coated polyester samples compared to carbon-coated cotton samples, attributing these differences to the structure, porosity and mass of the fibres, which may impact the distance of the ion transport to the active material through the fabric.^[620] The cotton-like properties of polycotton, evidenced with XRD, **Figure 28**, including higher porosity and favourable fibre arrangement, facilitate better electrolyte infiltration and ion transport, leading to more uniform electron pathways and the lowest ESR. In contrast, MX@PR-10L exhibits the highest ESR due to polyester's less porous and denser structure, which impedes ion transport and increases resistance. MX@C-10L has an intermediate ESR, reflecting the properties of pure cotton fibres, which are porous and conducive to ion transport but less

uniform and efficient than polycotton. The nearly identical IR drops of MX@C-10L and MX@PC-10L reflect their similar ESR values and confirm the compositional similarity indicated by XRD analysis.

The overall low ESR values indicate efficient electron transport and minimal resistive losses within the electrodes, contributing to their excellent electrochemical performance. EIS curves show a distinct rise of the imaginary impedance component (near-vertical line, almost parallel to $-Z''$ axis) at the low-frequency region, indicating the capacitive behaviour and fast ion diffusion. Nevertheless, the polycotton-based electrode's overall impedance curve is shifted toward lower real impedance values (Z'), reinforcing its enhanced electronic and ionic conductivity relative to the cotton- and polyester-only samples. These results are consistent with the high rate performance of these electrodes and the differences observed among them earlier.

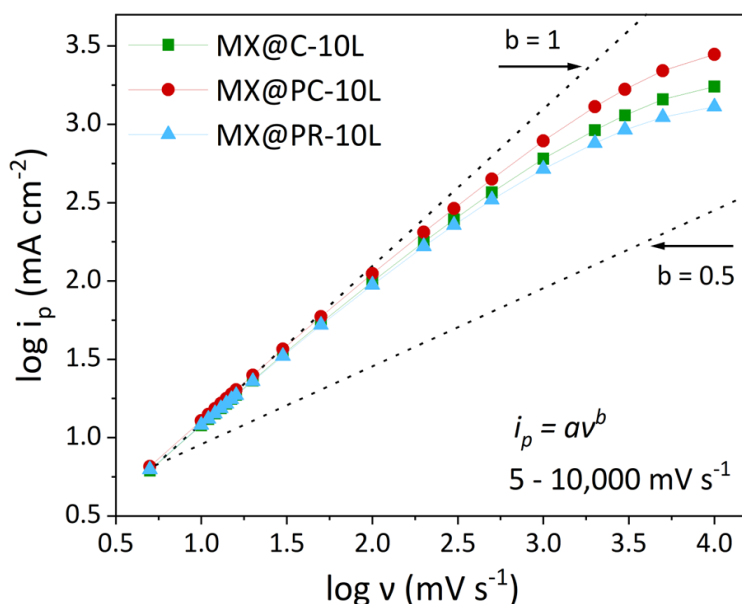


Figure 41: Analysis of the charge storage kinetics via b -values of MX@C-10L, MX@PC-10L, MX@PR-10L electrodes. The dashed line with a slope $b=1$ indicates the ideal capacitive/pseudocapacitive charging mechanism and fast ion diffusion.

The charge-storage kinetics of MX@Fabric electrodes was evaluated by the dependence of the peak current (i_p) on the scan rate (v) according to the relationship: $i_p = av^b$, where a and b are variables^[569] to evaluate their capacitive performance. The b -values are extracted from the slope of the $\log(i_p)$ versus the $\log(v)$ line (Equation 25 - 26).

For MX@C-10L, MX@PC-10L, and MX@PR-10L electrodes (Figure 41), b -values were up to ~ 0.94 from 5 mV s^{-1} to 20 mV s^{-1} , persisting at ~ 0.9 up to 1000 mV s^{-1} . This

proximity to the ideal $b = 1$ suggests a dominant capacitive charge storage mechanism, consistent with their robust high-rate performance. A similar analysis was achieved by comparing electrodes at 10, 20, 30, 50, and 100 printed layers, **Figure S12 – S13**, Supplementary Information.

The long-term stability of electrodes was investigated with 10,000 CV cycles after all the tests mentioned above, meaning that the electrodes were precycled before recording this data.

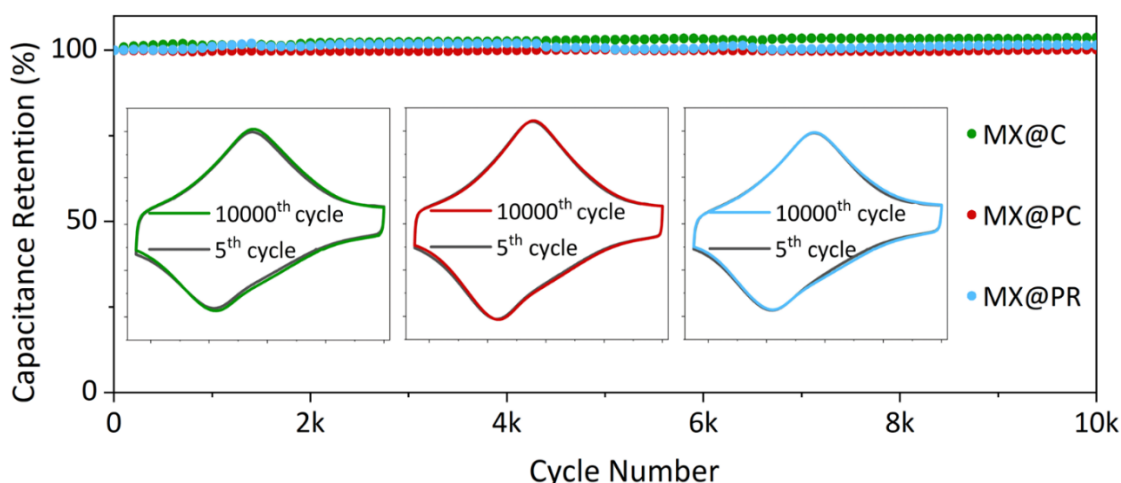


Figure 42: Cycling stability study of MX@C-10L, MX@PC-10L, MX@PR-10L electrodes by CV long-term cycling for 10,000 cycles at 100 mV s^{-1} .

MX@C-10L, MX@PC-10L, and MX@PR-10L electrodes exhibit outstanding long-term stability, with $\sim 100\%$ areal capacitance retention over each cycle (**Figure 42**), with an inset depicting the comparison at the 5th and 10,000th cycles. After 10,000 cycles, MX@C-10L, MX@PC-10L, and MX@PR-10L retained $\sim 103.7\%$, $\sim 100.3\%$, and $\sim 101.5\%$ of their initial areal capacitances, respectively, highlighting their exceptional cycling stability. These results underscore the robustness and durability of the MX@Fabric electrodes, demonstrating their potential for long-term use in practical applications.

4.5. CONCLUSIONS

This chapter explored the fabrication and characterisation of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene-based textile electrodes using AJP, with a focus on developing flexible, high-performance energy storage solutions for wearable electronics. The integration of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene inks onto various textile substrates, such as cotton, polycotton, and polyester, demonstrated the feasibility of creating functional textile electrodes with excellent electrochemical

properties and mechanical flexibility. By depositing 10, 20, 30, 50, and 100 MXene layers, the work showed how both mass loading and fibre composition influence electrochemical properties such as areal capacitance, ESR, and cycling stability. At a scan rate of 5 mV s^{-1} , the MX@PC-10L electrode reached $540.89 \text{ mF cm}^{-2}$, outperforming the MX@C-10L and MX@PR-10L counterparts with $521.26 \text{ mF cm}^{-2}$ and $520.52 \text{ mF cm}^{-2}$, respectively. Systematically increasing the number of printed layers boosted areal capacitance across all fabrics; for instance, MX@C rose from $521.26 \text{ mF cm}^{-2}$ at 10 layers to $4387.06 \text{ mF cm}^{-2}$ at 100 layers.

EIS indicated that polycotton-based electrodes exhibited notably lower ESR, likely due to cotton's porosity enhancing electrolyte uptake and polyester's mechanical stability. This synergy was particularly evident in MX@PC-10L, which retained over 90 % of its low-scan-rate capacitance at 500 mV s^{-1} . Moreover, all electrodes demonstrated strong pseudocapacitive behaviour and remarkable cycling stability, maintaining or surpassing their initial capacitance after 10,000 cycles at 100 mV s^{-1} . Such robust performance across different substrates underscores $\text{Ti}_3\text{C}_2\text{T}_x$ MXene's high ion-diffusion rate, efficient charge transport, and mechanical resilience - crucial features for wearable electronic applications.

AJP proved instrumental in depositing uniform, well-adhered MXene coatings on diverse textile substrates. The findings of this chapter lay a solid foundation for the development of MXene-based textile electrodes, offering valuable insights into optimising printing parameters and electrode design for advanced applications. The results underscore the potential of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene as a superior material for flexible and durable energy storage systems integrated into wearable technology. The work presented here not only advances the understanding of MXene's behaviour on textile substrates but also sets the stage for future research into the fabrication of AJP textile MSCs, which will be explored in subsequent Chapter 6.

4.6. ACKNOWLEDGEMENTS

I want to acknowledge *Dr Dafnan Spurling* for synthesising the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene inks used in the printing of the MX@Fabric-#L electrodes and *Dr Ke Li* for providing comprehensive training in the electrochemical and data analysis of the printed electrodes.

5 WASHABILITY STUDY OF AEROSOL JET PRINTED MXENE TEXTILE ELECTRODES

AIMS & OBJECTIVES

Washability remains a critical challenge for the development of e-textiles. This study seeks to systematically investigate the impact of repeated laundering on the structural integrity and electrochemical performance of AJP $\text{Ti}_3\text{C}_2\text{T}_x$ MXene-based textile electrodes. By extending the evaluation up to 100 wash cycles, the research seeks to provide a comprehensive understanding of MXene's resilience under real-world washing conditions, addressing the current gap in the literature regarding the washability of printed MXene-based e-textiles.

To achieve this, the study aims to fabricate and characterise MXene-based textile electrodes with controlled layer thicknesses using AJP, ensuring uniform deposition and strong adhesion. Electrodes with 10 and 50 printed layers will be examined to assess the effect of mass loading on washability and electrochemical retention. Washability testing will follow the ISO 105-C06 A1M standard, providing a rigorous evaluation of mechanical and electrochemical durability under standardised laundering conditions. Extending the investigation to 100 cycles will offer insights into the long-term stability of MXene-based e-textiles beyond conventional washability studies.

The study also aims to analyse morphological changes using SEM and digital microscopy to assess material detachment, surface degradation, and substrate wear across different

washing stages. Electrochemical performance will be evaluated through CV, GCD and EIS to correlate structural modifications with functional degradation.

The findings from this study will provide essential insights into optimising material formulations, printing parameters, and protective strategies to enhance the washability and durability of MXene-based textile electrodes, ultimately contributing to the development of more robust and practical e-textile energy storage solutions.

5.1. INTRODUCTION

As the field of wearable technology advances, the integration of electronic components into textiles has emerged as a key innovation, transforming fabrics into sophisticated platforms for a variety of applications. However, transitioning from concept to practical use requires overcoming several critical challenges, with washability being one of the most significant. The durability of textile-based electronics under repeated washing is crucial, as these materials must endure the rigours of regular laundering without compromising their functionality or structural integrity. Washability in wearable electronics is not just a desirable feature but a fundamental requirement. The mechanical forces, chemical exposures, and thermal fluctuations inherent in the washing process pose significant threats to the delicate electronic components within textiles. These elements must withstand not only everyday wear and tear but also the harsh conditions of regular washing, maintaining their integrity and performance across multiple cycles. The success of smart textiles in real-world applications depends on their ability to meet this challenge. Despite the recognition that washability is a critical hurdle for e-textiles, research in this area remains limited. Moreover, the studies that do exist often employ varied and non-standardized testing methods, making it difficult to draw consistent conclusions or establish best practices. This variability in testing approaches – ranging from the use of standard textile washing protocols to more improvised methods – further complicates the ability to reliably assess and compare the washability of different e-textile products.^[144,151]

A critical aspect of washability in e-textiles is the influence of Sinner's factors: time, temperature, mechanical action, and chemistry/biology, which together determine the outcomes of the washing process. While these factors are essential for achieving cleanliness, they can also introduce secondary effects such as mechanical degradation, loss of conductivity, and changes in appearance, all of which can compromise the functionality of e-textiles. Additionally, repeated washing can lead to various failure modes, including

changes in electrical properties^[104] (e.g., loss of conductivity, increase in resistance, change in capacitance), functionality^[621] (e.g., either one of the components or the whole e-textile stops working), physical integrity^[146] (e.g., delamination, loss of components), characteristics^[622] (e.g., ranges), and the overall aesthetic quality^[623] of the textile (e.g., pilling, fuzzing, shrinkage).^[144,151]

The integration of conductive materials into textiles presents unique challenges as they are susceptible to mechanical degradation, loss of conductivity, and changes in surface morphology when subjected to repeated washing. These challenges are compounded by the complex interactions between the textile substrate, the conductive coating, and the harsh conditions of laundering, which include mechanical agitation, exposure to detergents, and thermal fluctuations. Existing research has highlighted various failure modes in e-textiles related to washing.^[144] These issues are exacerbated by the diverse range of materials and fabrication methods used in e-textile production, which result in significant disparities in durability and performance after laundering.^[144]

A comprehensive overview of the factors influencing the washability of e-textiles emphasizes the importance of material selection, protective coatings, and washing parameters. For example, silver-based conductive inks often exhibit cracks after just a few wash cycles, with the mechanical stresses causing the ink to flake off, leading to increased resistance.^[624] Similarly, graphene composites applied to textiles can suffer partial loss of material and entanglement of the underlying fibres, primarily due to the collisions and mechanical forces experienced during washing.^[625]

Additionally, differences in the formulation and thickness of metal-based conductive coatings can significantly influence the severity of washing-induced damage, further contributing to variability in washability outcomes.^[626] Furthermore, different substrates, such as cotton, polyester, and nylon, interact uniquely with conductive coatings, affecting the degree of mechanical wear and overall durability of the e-textile. For instance, absorbent materials like cotton provide better adhesion for conductive inks, leading to improved washability, while less absorbent substrates like polyester are more prone to degradation during washing.^[144,627]

Protective layers have been shown to significantly enhance the washability of e-textiles by shielding conductive components from direct exposure to the washing environment. The effectiveness of these layers, however, varies depending on their material properties and the specific washing conditions.^[144] For example, thermoplastic polyurethane (TPU) is

widely used as a protective coating due to its ability to prevent mechanical abrasion and chemical attacks on the underlying conductive materials. Research has demonstrated that TPU coatings can effectively slow the rise in resistance that typically results from repeated washing, transitioning from an exponential increase to a more manageable linear one.^[146] This protective effect has been observed in various applications, such as printed conductive structures and embroidered tracks.^[624,628] Nevertheless, TPU is not without its challenges. The mismatch in thermal expansion coefficients between the TPU coating and the underlying conductive layer can lead to cracks under thermal stress during washing, compromising the overall durability of the e-textile.^[629] Additionally, while TPU generally offers better protection than some alternatives like silicone,^[630] its effectiveness can be influenced by factors such as coating thickness and the specific materials involved. For instance, in some cases, thicker^[631] or double-layered^[632] TPU coatings have been found to provide superior protection, while in others, alternative strategies such as increasing encapsulation stiffness^[633] may be required to achieve the desired level of durability.^[144]

Moreover, the washability of e-textiles is influenced by the design and layout of the integrated electronic components. Weak points, such as transitions between conductive tracks and contact pads, are particularly vulnerable to mechanical stresses during washing. These areas often experience cracks and breakages, which can lead to a loss of functionality. The research highlights the importance of optimizing the mechanical robustness of these transition zones to improve the overall durability of e-textiles.^[144,146]

The assessment of washability in e-textiles is further complicated by the lack of standardized testing methods. The absence of universal testing protocols means that different studies often employ varied methodologies, making it difficult to compare results across different products. This variability can lead to inconsistencies in how washability is reported, with some e-textiles being labelled as washable despite exhibiting significant degradation after washing. This underscores the urgent need for standardised testing practices that would allow for more reliable comparisons and evaluations of e-textile washability.^[151]

Building on the promising electrochemical properties demonstrated in Chapter 4, this chapter focuses on the washability of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene-based textile electrodes, specifically examining how these electrodes perform both electrochemically and morphologically after being subjected to an extensive number of wash cycles. Typically, studies focus on a limited number of wash cycles, which may not fully capture the long-term durability of

Chapter 5: Washability Study of Aerosol Jet Printed MXene Textile Electrodes e-textiles. In contrast, the present study extends the investigation to up to 100 wash cycles, providing an extensive evaluation that pushes the boundaries of current research. Although e-textiles in real-world scenarios may not typically undergo this many wash cycles, testing to this extent allows for a thorough assessment of the material's durability under more extreme conditions.

5.2. EXPERIMENTAL METHODS

5.2.1. SYNTHESIS OF $\text{Ti}_3\text{C}_2\text{T}_x$ MXENE

$\text{Ti}_3\text{C}_2\text{T}_x$ ink was formulated via the MILD synthesis route detailed in Section 3.2.1.

5.2.2. AEROSOL JET PRINTING OF MX@TEXTILE ELECTRODES

MX@C-10L and MX@C-50L electrodes in the washability study were fabricated in the same manner as the ones detailed in Section 4.2.2.

5.2.3. WASHING PROCEDURE OF MX@TEXTILE ELECTRODES

The washability study of MX@Fabric electrodes was performed on washing fastness tester SKYLINE, which has a cup capacity of 550 mL / 1200 ml; spin speed of $40 \pm 2 \text{ r min}^{-1}$; time control range of 99.9 min, and time control error $< \pm 5 \text{ s}$. The temperature control of the tester ranges from 0 – 100 °C with temperature control error $< \pm 2 \text{ °C}$.

The washability analysis was carried out according to the International Standards Organization (ISO) standard ISO 105-C06 test A1M for textile colour fastness^[634] with wash cycles (45 minutes each) and rinse cycles (twice, one minute each), both at the temperature of 40 °C, followed by air drying. Neither chlorine nor sodium perborate was used because there was no need for pH adjustment or souring treatment with acetic acid reagent. The wash solution was prepared by dissolving 600 mg of ECE Phosphate detergent in 150 ml of water.

Ten steel balls per test accelerated the washing process, mimicking the wear from multiple washes. Each cycle with steel balls equated to five cycles without. The study covered 1, 2,

5, 10, 12, 14, 16, and 20 wash cycles, simulating 5, 10, 25, 50, 60, 70, 80, and 100 cycles per ISO standard A1M Table 4.^[634]

5.2.4. MICROSCOPY ANALYSIS OF MX@TEXTILE ELECTRODES

The optical characterisation of MX@Fabric electrodes was done using a digital microscope (Olympus DSX1000). SEM imaging was performed using a Zeiss Ultra Plus microscope equipped with a Gemini column, SE detector, and ESB detector. The microscope operated at a typical acceleration voltage of 5 kV in SE2 mode.

5.2.5. ELECTROCHEMICAL CHARACTERISATION

The electrochemical characterisation, including CV, GCD, and EIS of MX@C-10L and MX@C-50L electrodes, was performed in the same manner as detailed in Section 4.2.3.

5.3. WASHABILITY OF MX@TEXTILE ELECTRODES

A washability study is an integral part of developing wearable e-textile technology that helps to evaluate the resilience and longevity of integrated textile-based electronic components. The rigorous washability analysis was conducted on a specialised washability tester, **Figure 43**. The ISO standard 105-C06 test A1M was followed to test MX@C-10L-#W and MX@C-50L-#W electrodes to evaluate their resilience to real-world laundering processes, where #W indicates the number of wash cycles performed.



Figure 43: Washing fastness tester SKYLINE.

5.4. CHARACTERISATION OF MX@TEXTILE ELECTRODES

Figure 44(a) depicts MX@C-10L-0W, the surface morphology achieved through the precision of AJP. Remarkably, the attainment of uniform coverage becomes evident with a mere deposition of 10 printed layers, consistently validating earlier research. This striking uniformity in surface coverage underscores the meticulous mastery inherent to AJ printing techniques and reflects the electrode's unblemished structural integrity in its pristine, unwashed state. Similarly, an MX@C-50L in its unwashed state, shown in **Figure 44(b)**, reveals a uniform coverage with a film noticeably thicker than its MX@C-10L counterpart.

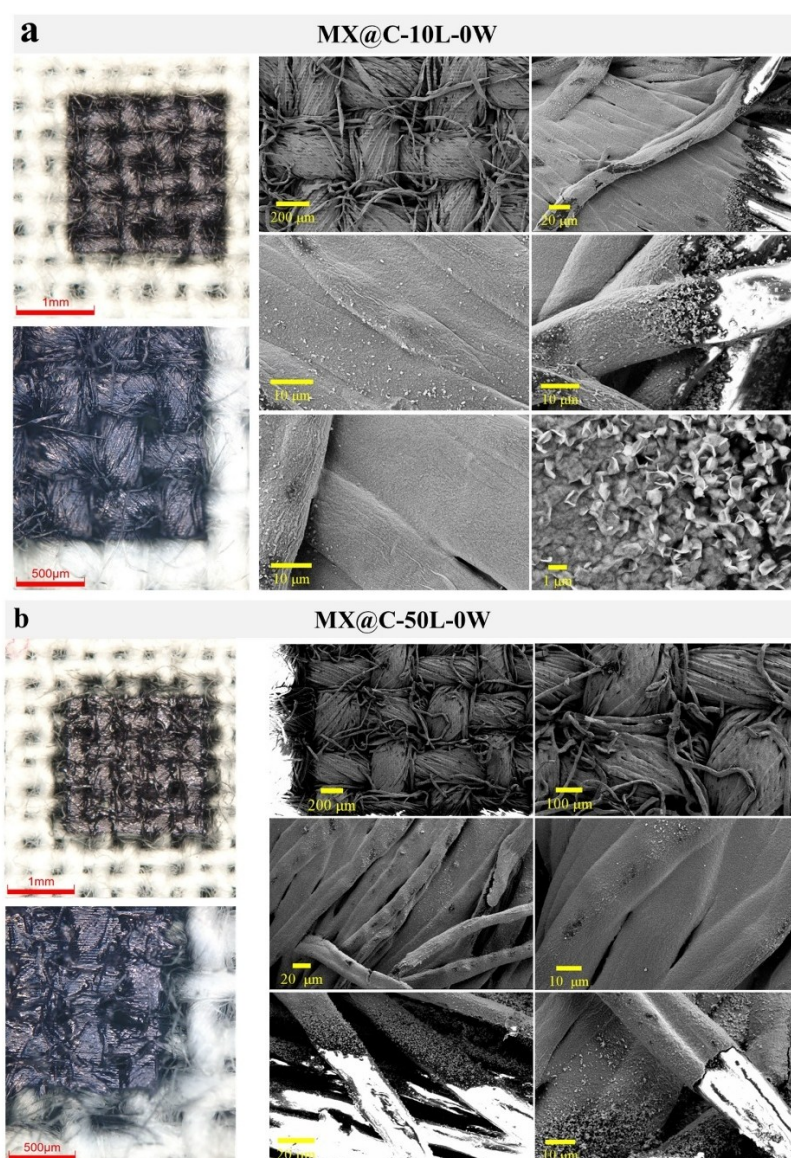


Figure 44: Surface characterisation of unwashed electrodes showcasing digital microscope images revealing surface morphology at different magnifications (left) and SEM images showcasing surface coverage (right):

(a) MX@C-10L-0W, (b) MX@C-50L-0W.

The surface coverage and structural integrity of the MX@C-10L-#W and MX@C-50L-#W electrodes exemplified at the unwashed state and after 5 and 60 washes, respectively (**Figure 45(a-c, g-i)**).

Post-washing, MX@C-10L-5W still shows uniform coverage (**Figure 45(b)**), with subtle fibre damage observed in the SEM inset. MX@C-50L-5W (**Figure 45(h)**) also appears uniform; however, it is less shiny and thinner than the unwashed state, with some detergent particles, possibly due to incomplete rinsing. A less shiny and thick film compared to the unwashed state may suggest that some top printed layers were removed during washing. Despite minor damage, both samples exhibit resilience, maintaining good coverage after five wash cycles.

After sixty washes, a reduction in material integrity can be observed in both MX@C-10L-60W (**Figure 45(c)**) and MX@C-50L-60W (**Figure 45(i)**). Some fibres appear distressed, likely due to prolonged washing and the use of steel balls. Correspondingly, SEM imaging accentuates substantial damage, notably in areas subject to heightened mechanical strain from the steel balls. These findings persist as the study progresses to 100 wash cycles (**Figure S14 - S16**, Supplementary Information), affirming a consistent and substantial structural impact on the materials due to persistent and rigorous washing conditions. The heightened mechanical stress, especially from including steel balls, exacerbates the observable damage, indicating a vulnerability shared by MX@C-10L and MX@C-50L under prolonged laundering scenarios.

Electrochemical performances of MX@C-10L-#W and MX@C-50L-#W electrodes were evaluated using three-electrode Swagelok cells. The resulting CVs (**Figure 45(d, j)** and **Figure S17 – S18**, Supplementary Information) consistently reveal well-defined cathodic and anodic peaks with small potential separation, characteristic of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene, located at approximately -0.3 V versus Ag/AgCl reference electrode at a scan rate of 5 mV s^{-1} . The MX@C-10L electrodes, after 0W, 5W, and 60W cycles, demonstrate areal capacitances of 409.15 mF cm^{-2} , 343.00 mF cm^{-2} , and 277.41 mF cm^{-2} at 5 mV s^{-1} , respectively. Similarly, the MX@C-50L electrodes attained 2.23 F cm^{-2} , 1.65 F cm^{-2} , and 1.23 F cm^{-2} at 5 mV s^{-1} , respectively. Even after 100 wash cycles, the MX@C electrodes exhibit consistent electrochemical performance, with MX@C-10L retaining an areal capacitance of 164.83 mF cm^{-2} and MX@C-50L retaining 0.68 F cm^{-2} . These results underscore their enduring stability and remarkable resilience, even under prolonged and rigorous washing conditions.

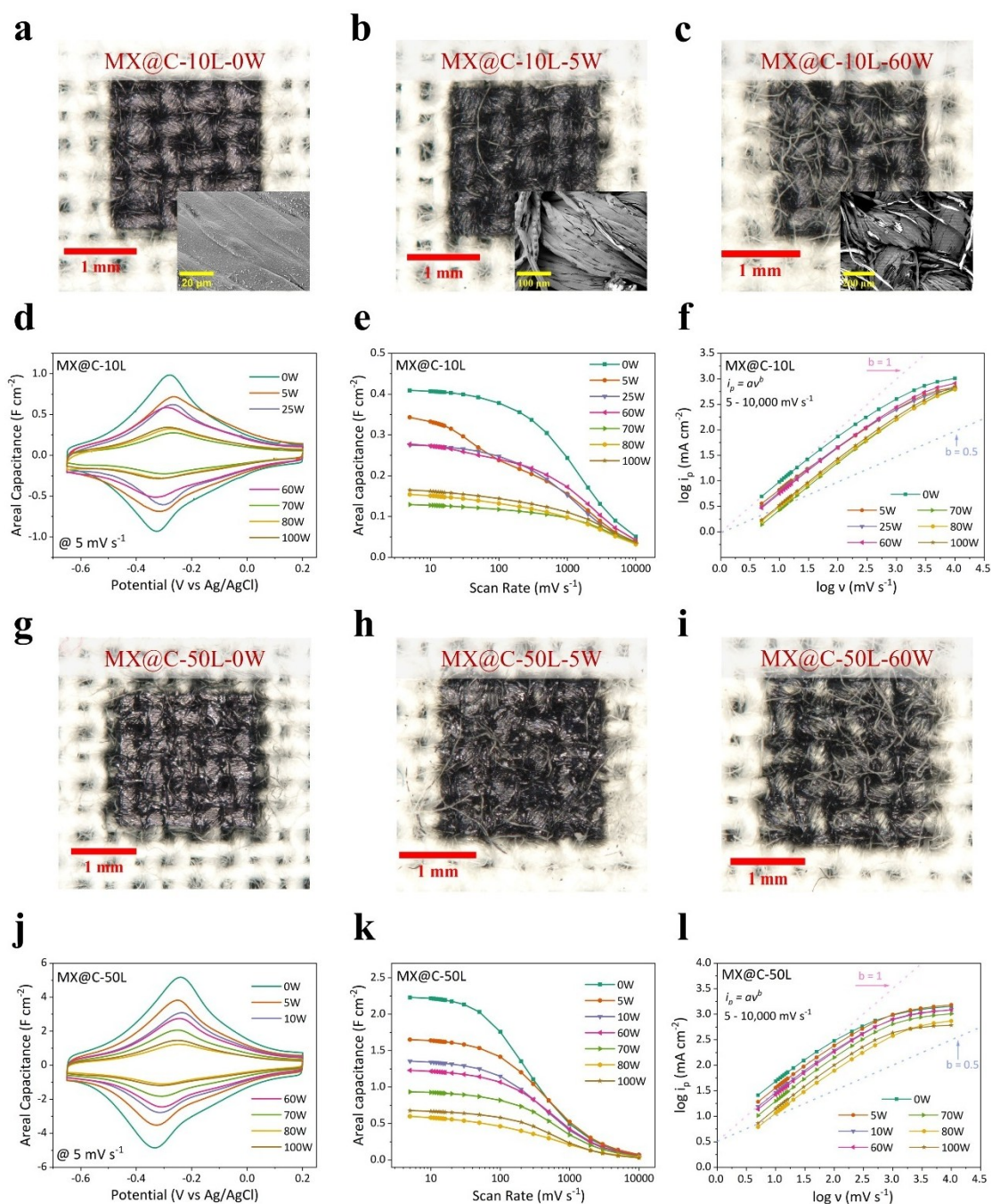


Figure 45: Washability study (following ISO 105-C06 test A1M) of MX@C electrodes via microscopy and electrochemical analysis. **(a-c, g-i)** Microscopic images illustrate structural changes in AJP MX@C-10L and MX@C-50L electrodes over varying wash cycles. **(d, j)** CVs showing well-defined cathodic and anodic peaks for MX@C-10L-#W and MX@C-50L-#W electrodes at 5 mV s⁻¹ scan rate over varying wash cycles. **(e, k)** Rate performance trends outlining the capacitance changes of MX@C-10L and MX@C-50L electrodes over multiple wash cycles. **(f, l)** Charge storage kinetics analysis of MX@C-10L-#W and MX@C-50L-#W electrodes across diverse wash stages through b-values. The dashed line with a slope $b = 1$ indicates the ideal capacitive/pseudocapacitive charging mechanism and fast ion diffusion.

The rate performance trend for MX@C-10L over multiple wash cycles unveils an initial decline stabilising around 70, 80, and 100 washes (**Figure 45(e)**). For MX@C-50L (**Figure 45(k)**), there is a notable drop in capacitance from the unwashed state to 5 washes, likely due to the removal of top printed layers. Subsequent changes in capacitance are gradual, with minimal variations at 80 and 100 wash cycles, suggesting a saturation point where further washes have limited impact. Charge storage kinetics, analyzed through b -values, show values of ~ 0.9 up to 100 mV s^{-1} for the MX@C-10L electrode (**Figure 45(f)**) and ~ 0.8 up to 100 mV s^{-1} for the MX@C-50L electrode (**Figure 45(l)**) across all wash stages, suggesting a dominant capacitive charge storage mechanism, and reaffirming the consistent and reliable electrochemical behaviour across diverse wash cycles.

5.5. CONCLUSIONS

The washability of e-textiles is a crucial factor in their practical application, as repeated laundering can lead to structural degradation, loss of conductivity, and diminished electrochemical performance. This study systematically evaluated the durability of AJP $\text{Ti}_3\text{C}_2\text{T}_x$ MXene-based textile electrodes under extensive washing conditions, addressing a major gap in the literature. By subjecting MXene-printed textile electrodes to up to 100 wash cycles, this research provides a thorough assessment of their resilience, far exceeding the frequency of laundering typically encountered in real-world scenarios.

As a thought experiment, the following could be considered. The frequency of laundering clothing varies significantly and is contingent upon multiple determinants, including individual practices, garment types, lifestyle, and prescribed care guidelines. As a conservative approximation, articles of clothing worn regularly may undergo laundering every 2 to 3 wears, resulting in an estimated 30 to 50 washing cycles per year when worn on a weekly basis within a standardised laundry routine. However, it is imperative to underscore the substantial variance in these statistics attributable to individual preferences, regional climates, fabric attributes, and diverse lifestyle elements. While e-textiles in practical use are unlikely to endure 100 cycles within a short timeframe, this extended evaluation serves as an accelerated stress test, offering valuable insights into long-term degradation trends.

Microscopy analysis revealed that surface degradation became increasingly pronounced beyond 60 wash cycles, with observable material loss, fibre damage, and structural changes in the printed MXene layers. SEM and digital microscopy images showed initial

uniform coverage at MX@C-0W and minor surface roughness after 5 cycles, with more pronounced fibre distress by 60 washes. After 100 cycles, while noticeable wear was present, the MXene coatings remained adhered to the textile substrates, demonstrating strong mechanical resilience despite the aggressive washing conditions.

The electrochemical analysis further reinforced this durability. CV measurements consistently displayed well-defined redox peaks characteristic of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene, even after extensive laundering. The electrodes maintained their pseudocapacitive charge storage behaviour, with capacitance declining gradually but stabilising beyond 70 wash cycles. The areal capacitance of MX@C-10L electrodes decreased from $409.15 \text{ mF cm}^{-2}$ in the unwashed state to $164.83 \text{ mF cm}^{-2}$ after 100 cycles, while MX@C-50L exhibited a reduction from 2.23 F cm^{-2} to 0.68 F cm^{-2} . This gradual decline suggests that mechanical wear affects electrode performance, but the electrodes remain electroactive.

The rate performance trends indicate that capacitance loss is more significant in early wash cycles, particularly for higher mass loadings. This is likely due to the removal of top layers, which reduces active material availability. However, once a stable structure is established, further washing has a diminished effect. Charge storage kinetics analysis, through b -values, consistently indicated a predominantly capacitive charge storage mechanism, affirming that despite surface degradation, the fundamental electrochemical behaviour of the electrodes remained intact.

The controlled washing procedure, adhering to the ISO 105-C06 A1M standard, ensured that the study accurately simulated real-world laundering conditions, incorporating standardised detergent use, temperature control, and mechanical agitation. The use of steel balls to accelerate wear further validated the robustness of MXene coatings under high-stress conditions, emphasising their mechanical integrity relative to conventional printed e-textile materials. These findings underscore the suitability of MXene-printed electrodes for wearable energy storage applications, demonstrating their ability to endure prolonged washing while maintaining structural and electrochemical integrity.

5.6. ACKNOWLEDGEMENTS

I want to acknowledge *Dr Tian Carey* for performing the washing of the printed electrodes, which significantly contributed to our understanding of the resilience of MXene-based e-textiles to laundering processes.

6 AEROSOL JET PRINTED MXENE TEXTILE MICROSUPERCAPACITORS

AIMS & OBJECTIVES

The primary aim of this chapter is to develop and evaluate AJP $\text{Ti}_3\text{C}_2\text{T}_x$ MXene-based textile microsupercapacitors (MSCs) for wearable electronics, addressing the need for flexible, high-performance, and durable energy storage solutions. The study focuses on optimising the AJP process to fabricate symmetric interdigitated MSCs, ensuring uniform deposition, strong adhesion, and high electrochemical performance.

The primary objective is to fabricate MXene-based MSCs with controlled layer thicknesses (15, 20, and 30 layers) using AJP, optimizing deposition parameters to ensure uniformity, prevent short-circuiting, and maintain structural integrity. This will be followed by a comprehensive electrochemical characterization, assessing capacitance, energy density, and power density to evaluate the performance and efficiency of the MSCs.

The second objective is to evaluate the electrochemical performance and capacitance retention of the MSCs under mechanical deformation by conducting bending tests at various angles. Given that e-textiles are designed for wearable applications, it is essential to assess their stability and durability under real-world conditions, ensuring that repeated bending does not compromise their functionality.

The third objective is to explore tandem MSC configurations by designing series and parallel connections to optimise energy and power output for different applications. This includes testing the performance of the tandem MSC device by integrating it with an LED

to evaluate its practical functionality and feasibility for powering wearable electronic devices.

By achieving these objectives, this study aims to advance the development of durable, high-performance MXene-based MSCs and establish AJP as a reliable method for scalable and flexible energy storage in wearable electronics. It seeks to optimize fabrication processes, improve device stability, and expand the practical applications of textile-integrated MSCs for next-generation e-textiles.

6.1. INTRODUCTION

As the boundaries between technology and the fabric of our daily lives continue to blur, wearable electronics are rapidly transforming how we interact with the world around us. Nevertheless, despite the remarkable advancements in this field, a critical challenge remains: how do we seamlessly integrate energy storage into the very textiles that we wear without sacrificing comfort, flexibility, or durability? Traditional batteries, with their bulky and rigid structures, are not well-suited for this task.^[110,139,140] This has led to a pressing need for innovative solutions that can power the future of electronic textiles. MSCs, with their high power density, rapid charge and discharge capabilities, long cycle life, and mechanical robustness, offer a promising solution to these limitations.^[139–143,179] What sets these devices apart is their ability to maintain flexibility and mechanical integrity even under conditions of bending or folding, making them particularly well-suited for integration into e-textiles.

The planar architecture of MSCs is essential in achieving a balance between high functionality and the specific demands of wearable technology, allowing for efficient power delivery without sacrificing flexibility or durability.^[199,265] As discussed in Section 2.1, printing technologies facilitate the seamless integration of MSCs in a planar IDD configuration into fabrics, preserving their flexibility and comfort. This makes them ideal candidates for the development of next-generation e-textiles.^[635]

In recent years, considerable progress has been made in developing flexible and printed MSCs for e-textiles, which are essential for advancing wearable electronics. One notable example involves using a laser-scribing masking technique combined with electroless deposition to fabricate interdigitated MSCs directly onto textile substrates such as polyester and nylon. This approach begins with the creation of conductive patterns using a laser-scribed mask and the deposition of nickel (Ni), followed by the application of rGO as

the active material. The result is an all-solid-state MSC with high flexibility and impressive electrochemical performance, achieving an areal capacitance of 8.19 mF cm^{-2} and retaining 91% of its capacitance after 10,000 cycles. These MSCs also demonstrate strong mechanical durability, maintaining functionality even when subjected to bending and twisting.^[636]

Another example demonstrated the fabrication of flexible in-plane MSCs directly on cotton using a thermal-initiated cross-linking polymer, IJP-assisted electroless copper deposition, and extrusion printing of activated carbon inks. This method preserved the MSCs' porous structure and ensured efficient electron transfer, achieving areal capacitance of 8.8 mF cm^{-2} and a long cycle life of over 6000 cycles. The MSCs demonstrated excellent mechanical flexibility, withstanding more than 2000 bending cycles at 90° , and were effectively integrated with conductive textiles to power wearable LED devices.^[637]

A very recent example involves the use of a green, water-based conductive ink made from acidified CNTs and MnO_2 to create MSCs on stretchable cotton/spandex fabric through screen printing. This method enables the formation of microelectrodes directly on the textile, combining the benefits of EDLC and pseudocapacitance to enhance electrochemical performance. The resulting MSCs exhibit a high area capacitance of 8.479 mF cm^{-2} at 10 mV s^{-1} scan rate and achieve an energy density of $0.132 \text{ mWh cm}^{-2}$ at a power density of 0.176 mW cm^{-2} . Additionally, these devices maintain excellent capacitance retention under various mechanical deformations, such as stretching, folding, bending, and friction.

Recent progress in printed MSCs for e-textiles has shown the potential of using MXene-based inks. A study developed an innovative approach utilizing additive-free, aqueous $\text{Ti}_3\text{C}_2\text{T}_x$ MXene inks tailored for thermal IJP on textiles. The initial layer used small flake MXene ink ($\sim 350 \text{ nm}$) to enhance ion access, while a second layer with larger flake MXene improved conductivity and removed the need for additional current collectors. These textile-based MSCs achieved a specific capacitance of up to 294 mF cm^{-2} , demonstrated excellent cycling stability over 10,000 cycles, and delivered high energy and power densities of $12.36 - 4.46 \text{ } \mu\text{Wh cm}^{-2}$ and $0.16 - 0.58 \text{ mW cm}^{-2}$, respectively.^[106]

In another example, an IJP symmetrical current collector-free $\text{Ti}_3\text{C}_2\text{T}_x$ MXene MSC was developed on TPU-coated cotton fabric. IJP and UV-curable electrolyte was also formulated, which, after UV polymerization, resulted in a thin, soft gel polymer electrolyte layer on the electrode surface. This fully printed device achieved an areal capacitance of

0.89 mF cm⁻² averaging over 2000 cycles, and demonstrated robust performance under mechanical deformation. Finally, an array of IJP MSCs demonstrated their feasibility as textile-based energy storage and micro-power sources, successfully powering a blue LED for several seconds.^[451]

The integration of MSCs into textiles holds significant promise for advancing wearable technology. Building on the progress made in printed MXene MSCs for textiles, where innovative techniques have demonstrated the potential of these materials for flexible energy storage, this chapter delves into a pioneering approach that takes this technology to the next level. In previous chapters, the groundwork was established by showcasing the successful deposition of MXene onto textile substrates using AJP, fabricating electrodes that were both highly efficient and washable.

This chapter extends that foundational work, advancing the research to the fabrication and rigorous evaluation of fully functional MSCs. The focus is on optimising the AJP process to fabricate symmetric IDD designs that meet the demands of wearable applications, with a detailed analysis of their capacitance, energy density, power density, and mechanical flexibility. However, flexibility is not just about bending; it is about adaptability. That is why this chapter also explores how AJP can be utilised to create tandem MSC structures in various configurations, such as series and parallel connections, tailoring their energy and power outputs to meet a wide range of applications. By optimising fabrication processes with the introduction of AJP and demonstrating the practical applications of MXene-based MSCs, this research lays the groundwork for the next generation of wearable electronics.

6.2. EXPERIMENTAL METHODS

6.2.1. SYNTHESIS OF Ti₃C₂T_x MXENE

Ti₃C₂T_x ink was formulated via the MILD synthesis route detailed in Section 3.2.1.

6.2.2. AEROSOL JET PRINTING OF MX@TEXTILE MICROSUPERCAPACITORS

The MX@C-#L IDD patterns were designed in AutoCAD software with four finger electrodes (3.85 mm length, 0.5 mm width) separated by 0.5 mm interfinger gaps, along with two contact electrodes (0.5 mm length, 3.5 mm width) and two contact

pads (2 mm length, 0.5 mm width). The IDD patterns were printed (Optomec AJP 300) on cotton fabric using the SFA in a layer-by-layer manner with a 150 μm nozzle. $\text{Ti}_3\text{C}_2\text{T}_x$ MXene ink (10 mg ml^{-1}) was used as both an active component and a current collector in the MSC. The systematic printing involved 15, 20, and 30 layers, each printed continuously and subsequently building layers on top of each other.

Table 2: Summary of process parameters used for AJP fabrication of MX@Fabric MSCs.

Process Parameters	MX@C MSCs
Nozzle	150 μm
Functional ink	Additive-free aqueous $\text{Ti}_3\text{C}_2\text{T}_x$
Ink concentration	10 mg ml^{-1}
Sheath gas flow	50 – 60 SCCM
Fabric substrate(s)	Cotton (C)
Atomiser gas flow	25 – 35 SCCM
Atomiser current	0.53 – 0.58 A
Process speed	1 mm s^{-1}
Chiller temperature	5 – 10 $^{\circ}\text{C}$
Platen temperature	off

Similar to the case of printing MX@Fabric electrodes, several critical factors were closely monitored to ensure stable deposition. Firstly, to ensure consistent mass loading the carrier gas was moisturized through a bubbler within each printing session. Secondly, periodic checks and adjustments were made throughout the printing process to ensure stability, including modifying sheath and atomizer gas flow parameters if any fluctuations were detected. It was essential to keep the nozzle clean (using sonication and an N_2 gun), clear the tubing (with an N_2 gun), and readjust gas flow parameters to prevent significant ink drop issues that could potentially damage the MSC samples.

6.2.3. MICROSCOPY EVALUATION OF MX@TEXTILE MICROSUPERCAPACITORS

The optical characterisation of MX@C IDDs was achieved using a digital microscope (Olympus DSX1000).

6.2.4. SYNTHESIS OF H₂SO₄ GEL ELECTROLYTE

1 g of polyvinyl alcohol (PVA, with MW: 89.000-98.000, 99+ % hydrolysed) (Sigma-Aldrich) was dissolved in 8 ml of DI water at 85°C for 2 hours to form a clear solution. After cooling to room temperature, a mixture of 3 g concentrated H₂SO₄ and 2 ml DI water was added and stirred for 1 hour.

6.2.5. MX@TEXTILE MICROSUPERCAPACITOR ASSEMBLY

Silver conductive paint (RS Pro) was coated onto the contact pads of each electrode to assemble a MSC device. Silver wires (0.1 mm) were inserted into the wet paint, allowed to dry in a vacuum desiccator for 30 minutes, and insulated with silicone varnish or transparent nail polish. Next, 3 M PVA/H₂SO₄ gel electrolyte was dropcasted onto the active area of each device, followed by 10 minutes of vacuum desiccation to ensure optimal electrolyte contact by removing trapped air within the active surface area.

6.2.6. ELECTROCHEMICAL CHARACTERISATION

The assembled MX@Fabric MSCs were connected with alligator clips to Biologic VMP3 potentiostat and subjected to electrochemical assessment in a two-electrode setup. The CV measurements were recorded from 2 to 50 mV s⁻¹ scan rates within a 0.5 V voltage window, which is optimal to avoid the oxidation of Ti₃C₂T_x MXene.^[370,617] The GCD tests were conducted at current densities from 0.5 mA cm⁻² to 4 mA cm⁻².

The bending capabilities of the MX@Fabric MSC were evaluated with CV tests performed at 0°, 45°, 90°, 135°, and 180° angles at a 10 mV s⁻¹ scan rate (on the precycled sample).

A series of four symmetric MX@Fabric MSCs were fabricated to illuminate an LED. This tandem device was cycled gradually to reach a voltage of 2.4 V before the connection to the LED circuit.

6.2.7. CAPACITANCE CALCULATIONS

The areal capacitance calculation of MX@Fabric MSC (mF cm⁻²) was obtained by integrating the discharge part of the CV curves ($\int idV$) with respect to time for the device:

$$C_A = \frac{\int idV}{vA\Delta V} \quad (27)$$

where C_A is an areal discharge capacitance, i is the current (mA) at the potential of V , v is the scan rate (mV s^{-1}), A is the geometrical footprint active area (includes finger electrodes and interspace regions) of the device (cm^2), and ΔV depicts the potential window (V).

6.2.8. ENERGY & POWER DENSITIES CALCULATIONS

The areal energy density ($\mu\text{Wh cm}^{-2}$) and power density (mW cm^{-2}) of the MX@Fabric MSC were determined using discharge scans derived from the GCD curves, using Equation 28 and Equation 29, respectively:

$$E_{MSC} = \frac{i}{A} \times \left(\int_0^{t_{max}} V dt \right) \quad (28)$$

$$P_{MSC} = \frac{E_{MSC}}{\Delta t} \quad (29)$$

where i is the current, A is the active area of MX@C MSC (including electrodes and interfinger gaps), t_{max} is the maximum discharge time, V is the voltage window of MSC, and Δt is the discharging time.

6.3. AEROSOL JET PRINTING OF MX@TEXTILE MICROSUPERCAPACITORS & OPTIMISATION

Building upon the successful study of AJP $\text{Ti}_3\text{C}_2\text{T}_x$ MX@Fabric electrodes, which demonstrated impressive electrochemical properties and resilience to washing, the investigation was extended to MX@Fabric MSCs with AJP, which facilitates the fabrication of versatile and reliable symmetric IDD prototypes. Symmetrical current collector-free $\text{Ti}_3\text{C}_2\text{T}_x$ MXene IDD designs were optimised with specifications that yielded an active area of 18.375 mm^2 , incorporating four finger electrodes (each 3.85 mm length and 0.5 mm width) with 0.5 mm interfinger gaps, shown in **Figure 46** and **Figure S20**, Supplementary Information.

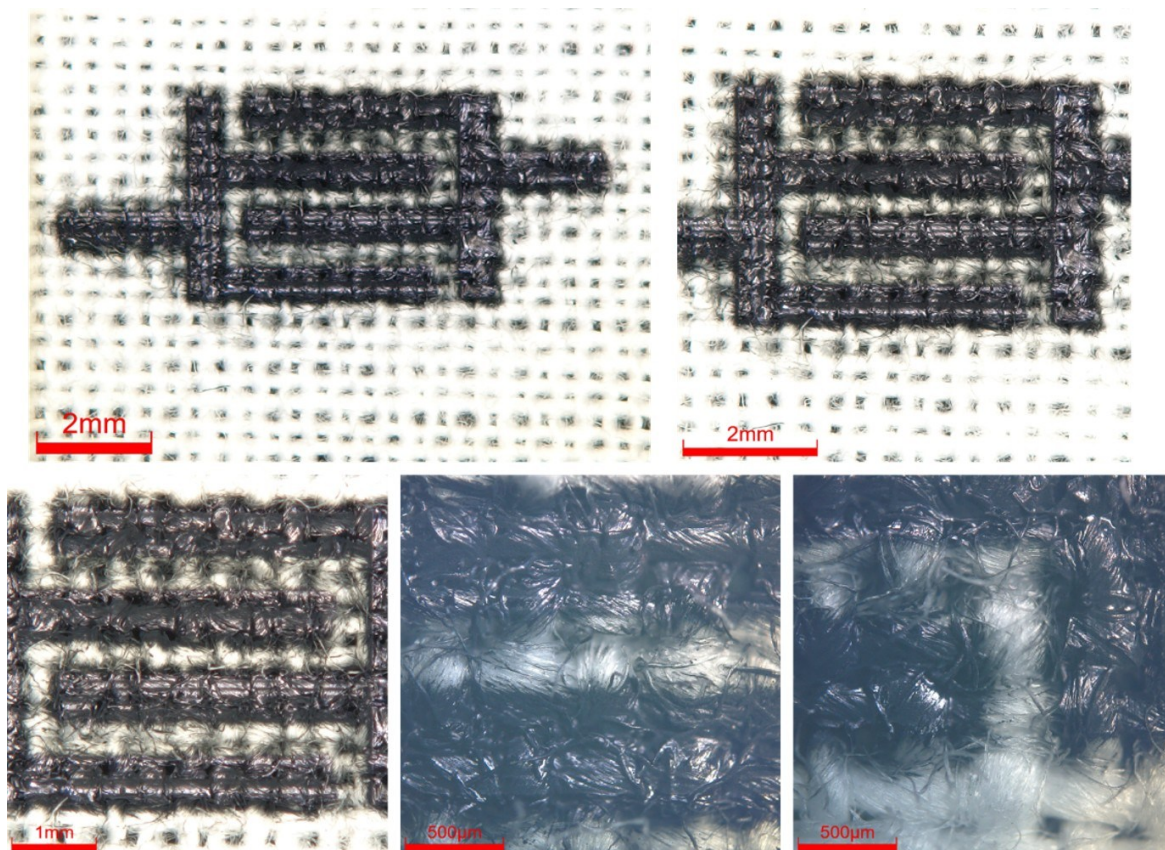


Figure 46: Characteristic images obtained with a digital microscope (Olympus DSX1000) of MX@C IDD pattern providing an overview of the entire IDD structure and detailed zoom-ins showcasing the intricate arrangement of finger electrodes and interfinger gaps.

The samples are labelled as MX@Fabric-#L IDD MSC, where "MX" represents $\text{Ti}_3\text{C}_2\text{T}_x$ MXene ink, "@C" indicates cotton, "@PC" denotes polycotton, "@PR" stands for polyester, "#L" refers to the number of printed layers, "IDD" specifies the interdigitated electrode design, and "MSC" stands for MSC.

It is important to note that this chapter presents the results of the optimised design, achieved through a meticulous trial-and-error process using AJP. The optimisation was focused on ensuring that multiple layers could be deposited without finger electrodes merging, thereby preventing short circuits - unintended conductive bridges between neighbouring finger electrodes that would bypass the device's active region and potentially cause irreversible damage or performance degradation. To confirm the reliability of the electrode pattern, two-point probe measurements were routinely conducted between adjacent electrodes. These tests revealed only negligible leakage current (on the order of microamperes) across the operative voltage window, thereby verifying that the printed electrodes remained effectively isolated and resistant to short-circuit formation.

6.4. ELECTROCHEMICAL EVALUATION OF MX@TEXTILE MICROSUPERCAPACITORS

The MX@C IDD MSCs with 15, 20, and 30 AJP layers were evaluated electrochemically using a two-electrode setup, with a PVA/H₂SO₄ gel electrolyte drop-cast onto the active area. CV studies of supercapacitors fabricated with this electrolyte typically produce rectangular curves without visible redox peaks, indicating capacitance stored through ion accumulation at the electrode/electrolyte interfaces, characteristic of EDLC. The GCD curves generally demonstrate high coulombic efficiency,^[638] and the PVA/H₂SO₄ gel electrolyte operates effectively within a voltage window of 0 to 1 V.^[195] Concerning Ti₃C₂T_x MXenes, studies showed that polymers that have polar functional groups in their chains (as PVA does) could prevent Ti₃C₂T_x MXene layers from restacking by intercalating in between them, in turn improving their mechanical properties.^[323]

For two-electrode supercapacitor devices, the cell voltage should be cycled from 0 V to a maximum positive voltage rather than across a range from negative to positive. Cycling from negative to positive offers no additional performance benefits and can cause issues like reversing cell polarisation, which does not improve charge storage. Therefore, starting from 0 V to a positive voltage is the standard practice for reliable and accurate electrochemical evaluation.^[569]

In this case, the MX@C IDD MSCs were cycled from 0 V to 0.5 V which is optimal to avoid the oxidation of Ti₃C₂T_x MXene.^[370,617] Operating within this range is critical because Ti₃C₂T_x MXene is susceptible to oxidation at higher voltages, which can compromise the material's structural integrity and degrade its electrochemical performance. Oxidation not only reduces the electrical conductivity of the MXene but also diminishes its capacity to store and release energy efficiently, ultimately shortening the device's lifespan.

The MX@C MSCs with 15, 20, and 30 AJP layers were subjected to CV and GCD tests to evaluate their electrochemical characteristics. The results for the best-performing device, MX@C-30L MSC, are presented here, while data for the MX@C-15L and MX@C-20L devices are provided in **Figure S21**, Supplementary Information.

The symmetrical current collector-free MX@C-30L IDD MSC yielded rectangular CVs, as shown in **Figure 47(a)**, indicative of good electronic and ionic conductivity, which is

also approved by the symmetrical GCD curves with low IR drops across various current densities (**Figure 47(b)**).

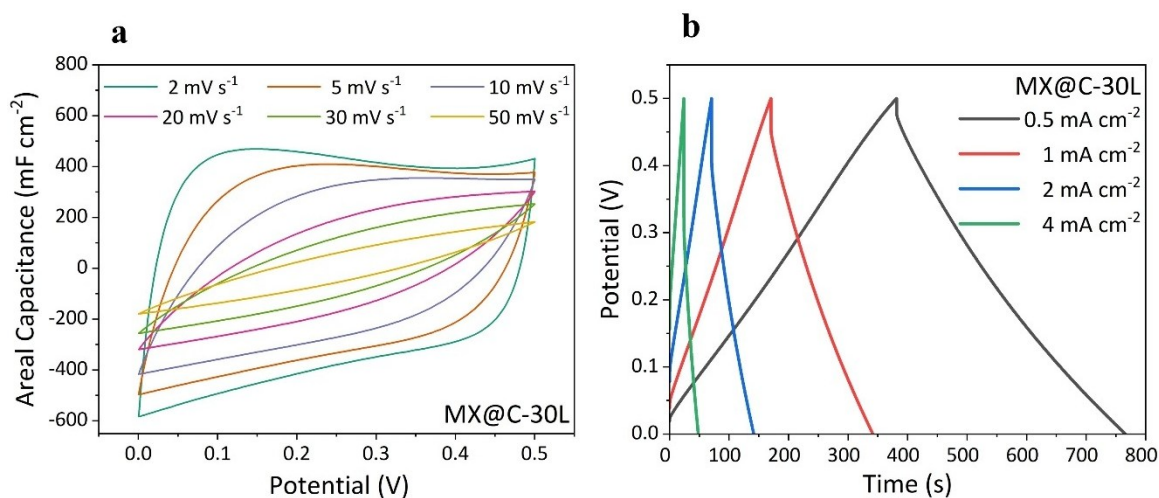


Figure 47: AJP $\text{Ti}_3\text{C}_2\text{T}_x$ MXene MSCs on cotton fabric (MX@C) with an IDD electrode configuration. **(a)** MX@C-30L MSC's CVs at 2, 5, 10, 20, 30, and 50 mV s^{-1} scan rates. **(b)** MX@C-30L MSC's GCD curves at 0.5, 1, 2, 4 mA cm^{-2} current densities.

These observations confirm the efficient charge storage and release mechanisms, suggesting that the AJP process produces high-quality deposits with good conductivity and electrochemical stability.

The areal capacitance of MSC is vital for practical application and was calculated by normalising with respect to the active area of the device, according to **Equation 27**. Excitingly, MX@C-30L MSC exhibited an exceptional areal capacitance of 381 mF cm^{-2} at 2 mV s^{-1} , surpassing the most state-of-the-art reports (**Figure 48(a)** and **Table S1**, Supplementary Information).

Furthermore, MX@C-30L demonstrated an impressive areal energy density of $10.89 \text{ } \mu\text{Wh cm}^{-2}$ and power density of 0.10 mW cm^{-2} , as shown in the Ragone plot (**Figure 48(b)** and **Table S2**, Supplementary Information), indicating efficient energy storage suitability for applications requiring sustained energy output. This superior performance can be linked to the enhanced electrical conductivity and ion transport provided by the uniform MXene deposition with AJP, which minimizes resistive losses and facilitates rapid charge/discharge cycles.

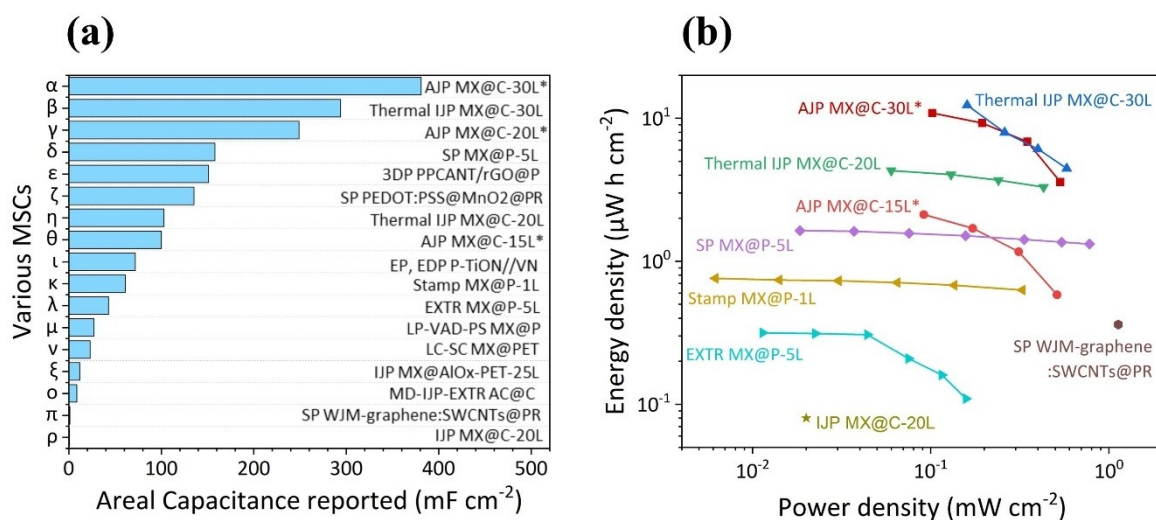


Figure 48: Comparative study in the field of printed MSCs. **(a)** Areal capacitance comparison in the field of printed MSCs^[106,258,288,298,451,637,639–644], where samples highlighted with * are fabricated in this study: MX@C-30L, MX@C-20L, and MX@C-15L (analyzed at 2 mV s⁻¹), with details provided in Table S1, Supporting Information. **(b)** Ragone plot, showcasing comparison among reported printed MSCs^[106,258,288,451,639,644], where samples highlighted with * are fabricated in this study: MX@C-30L and MX@C-15L, with details provided in Table S2, Supporting Information.

6.4.1. BENDING TEST

Integrating Ti₃C₂T_x MXene onto fabric substrates further enhances the practicality of these MSCs for wearable applications. The flexibility and porous nature of fabrics can influence electrochemical performance by providing a supportive yet pliable matrix that accommodates mechanical deformation without compromising the structural integrity of the active material. The fabric substrates act as a robust scaffold, maintaining the uniform dispersion and adhesion of the MXene flakes, which is crucial for sustaining consistent electrochemical properties under mechanical stress. Additionally, the fabric's inherent breathability aids in efficient electrolyte diffusion, potentially enhancing ion transport to and from the electrode surfaces. This synergy between the MXene and fabric substrate ensures that the MSCs retain high performance, even when subjected to mechanical forces such as bending. To assess the device's resilience to bending, the MX@C MSC was subjected to electrochemical testing at varying angles (from 0 to 180 degrees) at 10 mV s⁻¹, and the results are depicted in **Figure 49**.

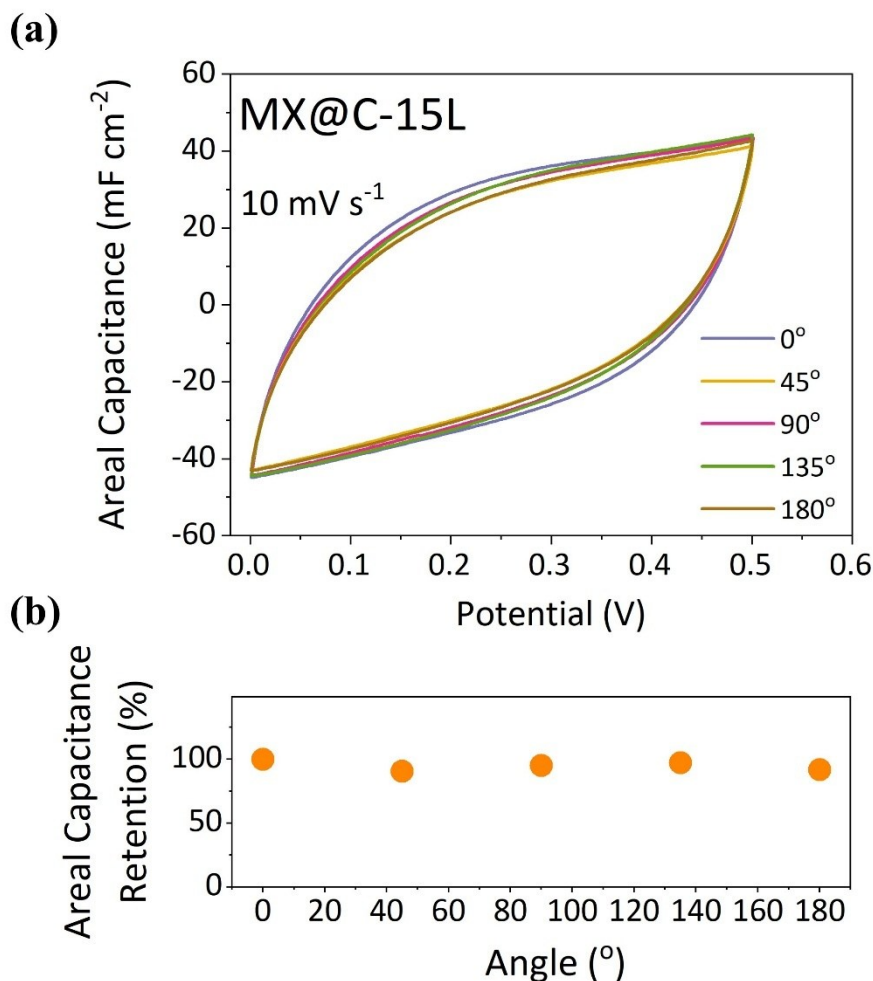


Figure 49: (a) The electrochemical performance of MX@C MSC at 10 mV s⁻¹ under bending conditions at 0, 45, 90, 135, and 180 degrees. (b) Retention of areal capacitance as a function of bending angle.

Remarkably, CVs remained consistent across all tested angles (**Figure 49(a)**), indicating the device's stability and robustness under mechanical deformation. The areal capacitance retention (**Figure 49(b)**) remains nearly unchanged with angle variation, affirming minimal impact on performance even when bent to extreme angles. These results demonstrate that the MX@C MSCs maintain excellent electrochemical performance and mechanical integrity, making them suitable for flexible and wearable electronic applications.

6.4.2. TANDEM DEVICES – LED

The versatility of AJP allows printing devices in series and parallel configurations to meet specific energy and power needs for various practical applications.

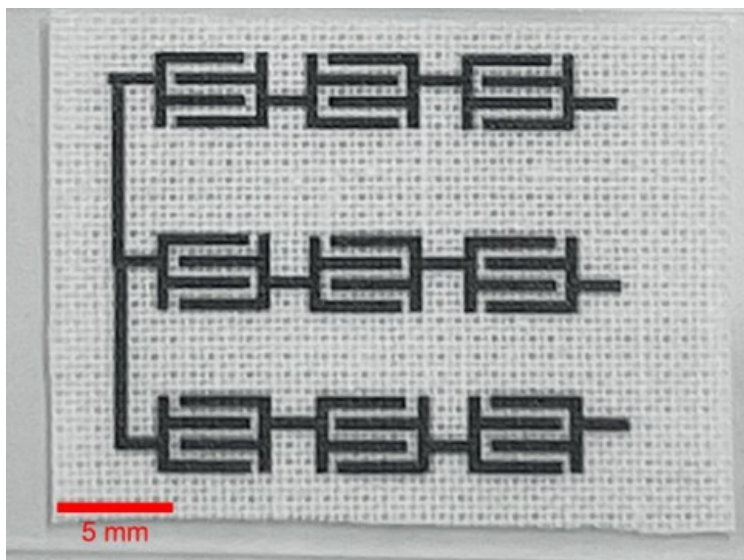


Figure 50: Example of a more complex MSC configuration, highlighting the versatility of AJP.

The flexibility of AJP becomes pivotal in enabling the parallel and in-series printing of MSC arrays, **Figure 50**, catering precisely to the energy demands of diverse applications. This is evidenced by the single MSC, two MSCs connected in series (2S), and two MSCs connected in parallel (2P) devices shown in **Figure 51**.

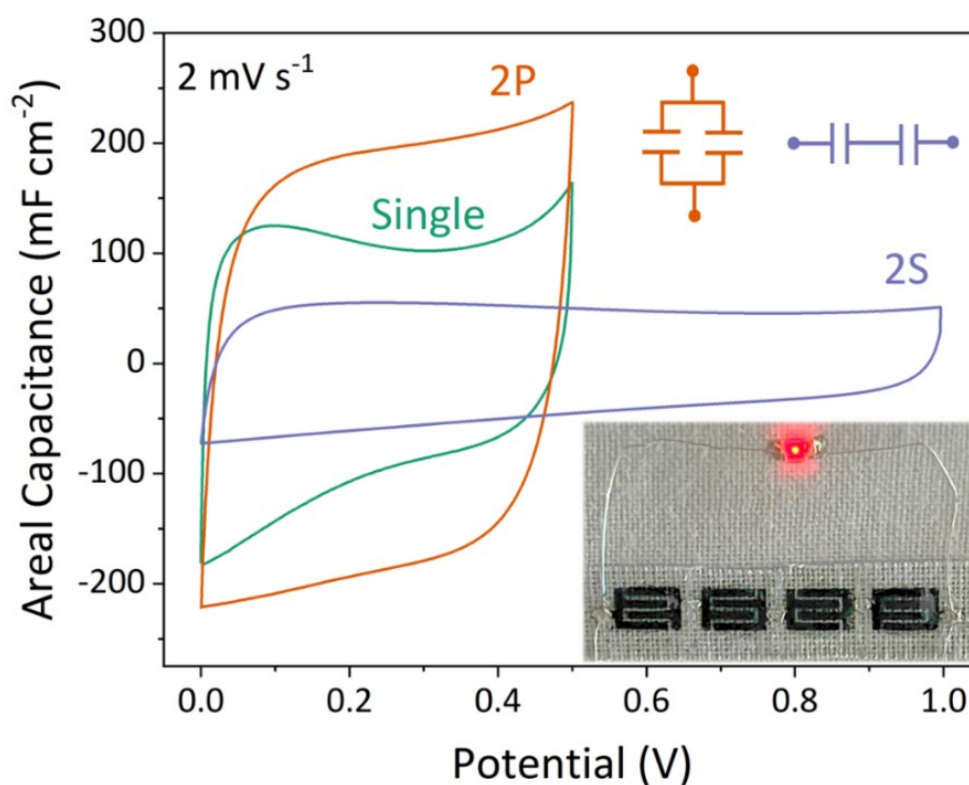


Figure 51: A comparison of one, two-in-series (2S), and two in-parallel (2P) MSCs, along with a four-in-series tandem device powering an LED bulb, is shown in the inset.

Connecting MSCs in series (2S) results in a cumulative increase in the overall voltage output while maintaining the same capacitance, which is beneficial for applications requiring higher operating voltages. This configuration enhances the energy density, as energy is proportional to the square of the voltage. Conversely, connecting MSCs in parallel (2P) increases the overall capacitance by summing the individual capacitances while maintaining the same voltage, thus enhancing the power density and allowing for longer operational periods at higher currents. The ability to customize these configurations highlights the inherent versatility of AJP in accommodating various electrochemical demands.

The four-in-series tandem device's successful operation in powering an LED bulb (**inset of Figure 51**) exemplifies the practical utility of these configurations, underscoring the potential of AJP MSCs to deliver reliable and efficient energy storage solutions.

6.5. CONCLUSIONS

This chapter has explored the development and electrochemical evaluation of AJP $\text{Ti}_3\text{C}_2\text{T}_x$ MXene textile MSCs, highlighting their potential for seamless integration into wearable electronics. The research focused on optimizing AJP techniques to fabricate symmetric interdigitated designs directly onto various fabric substrates, ensuring robust performance and flexibility. Through systematic trials and adjustments, an optimized design was achieved that prevents short-circuiting and allows for the precise layering necessary for high-performance energy storage devices.

The electrochemical performance of the MXene MSCs was rigorously assessed, demonstrating exceptional charge storage capabilities. The optimised MX@C-30L MSC exhibited an impressive areal capacitance of 381 mF cm^{-2} at 2 mV s^{-1} , outperforming many state-of-the-art printed MSCs. Furthermore, the device achieved an areal energy density of $10.89 \text{ } \mu\text{Wh cm}^{-2}$ and a power density of 0.10 mW cm^{-2} , confirming its ability to deliver both sustained energy storage and rapid charge-discharge capability. The rectangular CV profiles and nearly symmetrical GCD curves with minimal IR drop further validated the high electronic and ionic conductivity of AJP-printed MXene electrodes.

To further assess the device's performance under real-world conditions, the electrochemical response of the MSCs was tested at various bending angles (0° , 45° , 90° , 135° , and 180°) using CV measurements at 10 mV s^{-1} . The results demonstrated that capacitance retention remained nearly unchanged, confirming that the MSCs maintain

stable electrochemical performance regardless of bending angle. This finding is crucial for wearable electronics, as it ensures consistent energy storage and power delivery even when the textile is flexed or deformed during use.

Additionally, the chapter demonstrated the versatility of AJP in creating tandem device configurations to meet specific energy and power requirements, from increasing voltage output through series connections to enhancing capacitance via parallel connections. The successful powering of an LED by a four-in-series tandem MSC device showcased the practical potential of these configurations for real-world applications.

In summary, the findings presented in this chapter pave the way for the development of next-generation wearable electronics, where energy storage can be seamlessly integrated into textiles without compromising comfort or durability. By optimizing fabrication processes and demonstrating the practical applications of MXene-based MSCs, this research sets a foundation for further advancements in flexible and efficient energy storage solutions for wearable technology. Collectively, these findings position AJP-printed $\text{Ti}_3\text{C}_2\text{T}_x$ MSCs as a promising solution for advanced energy storage applications in next-generation e-textiles.

6.6. ACKNOWLEDGEMENTS

I want to thank *Dr Dafnan Spurling* for synthesising the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene inks used in the printing of the MX@Fabric-#L IDD MSCs and *Dr Ke Li* for his thorough training in the electrochemical and data analysis of the printed MSCs.

7 CONCLUSIONS & OUTLOOK

This thesis has presented a comprehensive study on the development of e-textiles through the innovative integration of MXene-based MSCs using AJP technology. The findings demonstrate significant advancements in wearable energy storage, particularly in overcoming challenges related to material formulation, deposition techniques, and device performance optimisation. This work has established AJP as a powerful tool for precise, scalable, and flexible fabrication of energy storage devices onto textile substrates, bringing e-textiles closer to real-world applications.

7.1. SUMMARY OF KEY CONTRIBUTIONS

A major achievement of this work is demonstrating the feasibility and effectiveness of AJP for fabricating high-performance MSCs directly onto various textile substrates, eliminating the need for external current collectors while maintaining strong electrochemical performance. Utilising a less hazardous 'MILD' route for synthesising $\text{Ti}_3\text{C}_2\text{T}_x$ MXene, the inks were formulated without additives, ensuring stability and exceptional electroactive properties ideal for AJP.

Through systematic optimisation of AJP parameters, including sheath gas flow, atomiser gas flow, nozzle selection, and process speed, it was possible to achieve defect-free, high-resolution deposits while preventing common issues such as overspray, short-circuit formation, and non-uniform ink absorption. Additionally, the study introduced a mass loading-to-layer correlation model ($R^2 = 0.98896$), demonstrating that AJP enables precise control over deposition thickness, a critical factor for optimising the electrochemical properties of printed devices.

This study established a comprehensive framework for troubleshooting and optimising AJP on textiles, addressing key fabrication challenges to enhance deposition precision and reproducibility. Nozzle clogging was effectively mitigated through ink dispersion

optimisation, pre-printing sonication, and controlled ink flow management, ensuring stable and uninterrupted deposition. Overspray and feature resolution were refined by precisely adjusting sheath-to-atomizer gas flow ratios, modulating process speed, and optimising nozzle standoff height, which prevented unintended material spreading and improved pattern fidelity. Deposition instability and ink transport contamination were minimised through real-time process monitoring and mist tubing cleaning strategies, reducing the risk of ink buildup and uncontrolled droplet ejection. Additionally, mass quantification inaccuracies were resolved through the implementation of a deposition rate monitoring strategy using peelable polymer membranes, enabling precise, consistent, and reproducible material deposition while eliminating variability caused by textile porosity and moisture absorption. Collectively, these optimisations establish a robust methodology for achieving high-resolution, uniform, and conductive MXene coatings, significantly enhancing the reliability of AJP for e-textile fabrication.

By overcoming these technical limitations, AJP enabled the precise deposition of MXene inks, enhancing both electrical conductivity and electrochemical performance. The fabricated MXene@Fabric electrodes displayed remarkable performance, with areal capacitances reaching up to 4.4 F cm^{-2} with 100 AJP layers. These results underscore the potential of MXenes as a powerful component for energy storage in wearable electronics, setting new benchmarks for future advancements. Electrochemical analyses, including CV, GCD, and EIS, confirmed strong performance across different fabric types and layer counts, with notable capacitance retention even at lower mass loadings. The consistent increase in capacitance with additional layers highlights the scalability of this approach, making it applicable to a broad range of textile substrates. Additionally, the study demonstrated minimal ESR and outstanding cycling stability, with nearly 100% capacitance retention after 10,000 cycles, confirming the durability and long-term viability of MXene-based energy storage for e-textiles. Beyond electrochemical performance, this study also addressed the washability of these electrodes in real-world conditions, a critical aspect of wearable technology. The results showed resilience to washing, reinforcing the potential for these e-textiles to withstand everyday use.

The research expands the scope of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene electrodes, particularly in the context of MSCs, which offer advantages over traditional micro-batteries, such as faster charge/discharge rates, higher power densities, and longer lifespans. By leveraging AJP, this study successfully fabricated current collector-free MX@Fabric MSCs with an interdigitated electrode design directly on cotton, achieving impressive areal capacitance,

and energy and power density metrics. Importantly, these MSCs maintained their electrochemical behaviour under mechanical deformation, proving their suitability for wearable applications. Additionally, tandem device configurations were explored, demonstrating the ability to scale voltage and capacitance for different energy storage needs. A four-in-series MSC configuration successfully powered an LED, validating its practical potential in real-world applications.

7.2. FUTURE RESEARCH DIRECTIONS

While this research has made significant strides in advancing MXene-based e-textiles through AJP for wearable energy storage, several areas remain for future exploration to further advance the field. Future investigations should address key aspects related to scalability, ink-substrate interactions, durability, electrolyte development, device optimisation, and multifunctionality to enhance the feasibility of MXene-based e-textiles for real-world applications.

7.2.1. MXENE INK WETTING & ADHESION ON FABRICS

A key consideration in furthering the development of MXene-based e-textiles is achieving precise control over ink wetting and adhesion on textile substrates. Unlike rigid materials, fabrics exhibit variable porosity, fibre roughness, and absorption characteristics, all of which influence how the ink spreads, penetrates, and adheres to the surface. While MXene inks generally adhere well to fabrics due to their surface chemistry and interaction with fibre networks, optimising wetting behaviour remains crucial to ensure consistent film morphology, mechanical stability, and long-term durability.

Future research should focus on systematically investigating the interfacial interactions between MXene inks and textile fibres, considering factors such as surface energy, ink viscosity, and fabric hydrophilicity. Modifying textile surfaces through plasma treatment, chemical functionalisation, or hydrophilic/hydrophobic coatings could enhance ink-substrate interactions, enabling controlled wetting dynamics and improved adhesion. Additionally, adjusting MXene flake size distribution, dispersion stability, and ink formulation parameters may provide greater control over ink penetration depth and lateral spreading, ensuring reliable deposition across different fabric types.

Beyond wetting behaviour, a deeper understanding of the bonding mechanisms between MXene coatings and textile fibres is essential for enhancing mechanical robustness. Investigating chemical bonding, van der Waals forces and hydrogen interactions will offer insights into strengthening adhesion without compromising flexibility or electrochemical performance. The incorporation of cross-linking agents, polymer binders, or multi-layer deposition strategies could further reinforce interfacial stability, preventing delamination under mechanical stress.

To validate these improvements, future studies should incorporate comprehensive mechanical testing, including shear, tensile, and abrasion resistance assessments, to evaluate the resilience of MXene-coated fabrics under stretching, bending, and repeated washing cycles.

7.2.2. ENHANCING ELECTROCHEMICAL PERFORMANCE THROUGH ADVANCED ELECTROLYTES

While this research has demonstrated the feasibility of MXene-based MSCs for textile-integrated energy storage, further advancements in electrolyte design could significantly enhance electrochemical performance by fully leveraging the redox activity of $\text{Ti}_3\text{C}_2\text{T}_x$. In this study, MXene electrodes were evaluated using H_2SO_4 and MSCs with PVA/ H_2SO_4 , as these electrolytes effectively facilitate proton intercalation, enabling the pseudocapacitive charge storage behaviour of $\text{Ti}_3\text{C}_2\text{T}_x$. The acidic environment promotes redox reactions at the MXene surface, contributing to high capacitance, as observed in electrochemical performance measurements. However, the potential safety risks associated with acidic electrolytes, particularly their corrosive nature and potential for leakage, pose challenges for their practical implementation in wearable applications. Developing safer, high-performance electrolyte systems that maintain or even enhance the pseudocapacitive behaviour of MXenes is, therefore, a critical future research direction.

Potential alternatives include ionic liquid electrolytes, hybrid organic-inorganic electrolytes, and redox-active electrolytes, which could introduce additional faradaic charge storage mechanisms and further enhance pseudocapacitive behaviour in $\text{Ti}_3\text{C}_2\text{T}_x$ MXene-based MSCs. Understanding how different electrolyte compositions interact with MXene surface terminations, interlayer spacing, and charge transport dynamics will be critical for optimising ion intercalation kinetics, improving charge storage efficiency, and ensuring long-term cycling stability.

Additionally, future efforts should focus on formulating solid-state and gel-based electrolytes with optimised ionic conductivity, viscosity, gelation properties, and mechanical flexibility to enable safe, durable, and high-performance energy storage solutions. These advancements are particularly important for wearable MSCs, where electrolyte leakage or degradation could compromise both device functionality and user safety.

To further enhance the stability and reliability of MXene-based MSCs, research should explore advanced encapsulation strategies that provide robust environmental protection while maintaining device flexibility and electrochemical performance. Potential encapsulation approaches include thin, stretchable polymer coatings, multilayer encapsulation techniques using hydrophobic barriers, and nanocomposite films designed to prevent moisture and oxygen diffusion. These methods would be particularly beneficial for protecting MXene electrodes from oxidation, improving washability, and extending device lifespan in real-world conditions.

By developing electrolyte systems that strike a balance between electrochemical efficiency, mechanical stability, and user safety, alongside effective encapsulation techniques, future research can help bridge the gap between lab-scale MXene MSCs and their real-world implementation in next-generation wearable and flexible electronics.

7.2.3. REFINING AJP PARAMETERS ACCORDING TO THEORETICAL MODELS

The optimization of AJP deposition for MXene-based textile devices has primarily relied on empirical adjustments to parameters such as sheath gas flow, atomizer gas flow, process speed, and nozzle size to achieve uniform, conductive coatings. While this approach has been effective in fine-tuning deposition conditions, it lacks a comprehensive theoretical foundation that could further enhance precision, reproducibility, and scalability.

Future research should integrate aerosol dynamics, fluid mechanics, and ink-substrate interaction models to develop a more systematic and predictive approach for AJP optimization. By employing computational modelling, it would be possible to simulate droplet formation, predict deposition uniformity, and analyze ink behaviour on textile surfaces, leading to improved control over printing parameters. A deeper understanding of MXene flake alignment during deposition, ink evaporation kinetics, and interfacial

interactions with fabric fibres could enable the development of higher-resolution, defect-free, and scalable AJP-printed MXene devices.

7.2.4. EXPANDING RESEARCH ON POLYCOTTON-BASED PRINTED DEVICES

This study explored cotton, polycotton, and polyester as textile substrates for MXene electrodes, revealing that polycotton-based electrodes exhibited better electrochemical performance compared to both cotton and polyester. However, when fabricating MXene-based MSCs, cotton was selected as the representative textile, primarily due to its well-defined composition. The precise fibre ratio in the polycotton blend was unknown, raising concerns about potential composition-dependent variability in device performance. As a result, a single-fiber textile was chosen to ensure consistency when evaluating MXene MSCs. Given the promising performance of polycotton-based electrodes, further research is needed to determine whether polycotton-based MSCs can enhance energy storage performance while maintaining strong mechanical durability.

Future studies should focus on a systematic investigation of MXene-polycotton interactions, assessing how fibre composition, blend ratios, and surface morphology affect ink adhesion, charge transport, and mechanical stability. Additionally, a direct comparative analysis of MSCs fabricated on cotton, polycotton, and polyester under identical conditions would provide valuable insights into the influence of fabric type on electrochemical behaviour.

7.2.5. INVESTIGATING LONG-TERM DEGRADATION OF TEXTILE-BASED MXENE ELECTRODES & MSCs

Ensuring the long-term stability of MXene-based MSCs is essential for their practical use in wearable electronics. While MXenes offer excellent conductivity and energy storage capabilities, they are susceptible to oxidation, structural degradation, and performance loss over time. Future research should focus on understanding these aging mechanisms under real-world conditions, including extended electrochemical cycling, environmental exposure, and mechanical stress from bending, stretching, and washing.

7.2.6. SCALING UP AJP FOR INDUSTRIAL FABRICATION

AJP has proven to be a highly effective method for printing MXene-based MSCs onto textiles, but its application at an industrial scale remains a challenge. Future research should explore strategies to increase throughput, improve deposition consistency across large textile surfaces, and reduce material waste to enable mass production.

7.2.7. MULTIFUNCTIONALITY EXPLORATION

The integration of multiple functionalities into a single e-textile platform is also a promising area for future research. Beyond energy storage, incorporating sensing, communication, heating, or energy harvesting capabilities could transform e-textiles into multifunctional devices, expanding their application in sectors such as healthcare, sports, and fashion. This level of integration could revolutionise wearable technology, creating complex systems that interact dynamically with users and their environments. For instance, incorporating triboelectric nanogenerators or piezoelectric materials could enable self-powered sensing textiles, while integrating MXene-based thermal management coatings could enhance adaptive heating textiles for applications in extreme environments.

7.2.8. ALTERNATIVE MATERIALS & COMPOSITE SYSTEMS

The integration of alternative materials and composite systems presents a promising avenue for enhancing the functionality, stability, and electrochemical performance of MXene-based e-textiles. By combining MXenes with complementary nanomaterials, such as graphene, CNTs or conductive polymers, future research can optimise conductivity, mechanical flexibility, and energy storage efficiency. These hybrid systems could synergistically enhance charge transport, improve structural integrity, and extend cycling stability, making them highly attractive for next-generation wearable energy storage solutions. Beyond improving intrinsic properties, these composite approaches could expand the application scope of MXene-based MSCs, enabling customised material formulations tailored for specific wearable applications. Future research should focus on understanding the interactions between MXenes and secondary materials, optimising processing conditions for scalable deposition, and ensuring compatibility with textile substrates. By leveraging the strengths of hybrid material systems, the performance, durability, and practicality of MXene-based e-textiles could be significantly advanced, bringing them closer to real-world commercialisation.

Chapter 7: Conclusions & Outlook

In conclusion, this thesis has laid the groundwork for the development of MXene-based MSCs on textiles using AJP, demonstrating the feasibility of scalable, flexible, and high-performance energy storage for wearable electronics. However, several key challenges and future research directions remain to be explored. Optimising wetting and adhesion behavior, developing advanced electrolyte systems, refining AJP printing parameters, investigating polycotton-based printed devices, and scaling up the fabrication process will be critical in furthering the development of e-textiles. Beyond optimising energy storage capabilities, expanding multifunctionality and composite integration into e-textile platforms could unlock new application possibilities in healthcare, sports, fashion, and beyond. By addressing these research gaps, future studies can drive the development of highly efficient, durable, and multifunctional e-textiles, transforming them into seamless, real-world solutions that bridge technology and everyday life.

REFERENCES

- [1] N. MacGregor, *A History of the World in 100 Objects*, Penguin UK, **2011**.
- [2] J. R. Davis, *Copper and Copper Alloys*, ASM International, **2001**.
- [3] G. F. Bass, *Nautical Archeology* **1991**.
- [4] R. Maddin, J. D. Muhly, T. S. Wheeler, *Scientific American* **1977**, 237, 122.
- [5] V. F. Buchwald, *Iron and Steel in Ancient Times*, Kgl. Danske Videnskabernes Selskab, **2005**.
- [6] L. T. W. III, *The Industrial Revolution*, Bloomsbury Publishing USA, **2008**.
- [7] A. E. Musson, E. Robinson, *Science and Technology in the Industrial Revolution*, Taylor & Francis, **1989**.
- [8] W. K. V. GALE, *Transactions of the Newcomen Society* **1973**.
- [9] R. Thorne, *Structural Iron and Steel, 1850–1900*, Routledge, **2017**.
- [10] J. Loadman, *Tears of the Tree: The Story of Rubber - A Modern Marvel*, OUP Oxford, **2005**.
- [11] J. F. Ryan, *J. Chem. Educ.* **1929**, 6, 1854.
- [12] M. Batty, In *Evaluation in Planning: Facing the Challenge of Complexity* (Eds.: Lichfield, N.; Barbanente, A.; Borri, D.; Khakee, A.; Prat, A.), Springer Netherlands, Dordrecht, **1998**, pp. 251–272.
- [13] E. Braun, S. MacDonald, *Revolution in Miniature: The History and Impact of Semiconductor Electronics*, Cambridge University Press, **1982**.
- [14] G. Pearson, W. Brattain, *Proc. IRE* **1955**, 43, 1794.
- [15] M. Riordan, L. Hoddeson, C. Herring, *Rev. Mod. Phys.* **1999**, 71, S336.
- [16] H. Iwai, D. Misra, *Electrochem. Soc. Interface* **2022**, 31, 65.
- [17] G. O'Regan, In *Introduction to the History of Computing: A Computing History Primer* (Ed.: O'Regan, G.), Springer International Publishing, Cham, **2016**, pp. 93–100.
- [18] D. Pavlov, *Lead-Acid Batteries: Science and Technology*, Elsevier, **2011**.
- [19] T. Wulandari, D. Fawcett, S. B. Majumder, G. E. J. Poinern, *Battery Energy* **2023**, 2, 20230030.

References

- [20] X.-X. Zeng, Y.-T. Xu, Y.-X. Yin, X.-W. Wu, J. Yue, Y.-G. Guo, *Materials Today Nano* **2019**, 8, 100057.
- [21] G. L. Hornyak, J. J. Moore, H. F. Tibbals, J. Dutta, *Fundamentals of Nanotechnology*, CRC Press, Boca Raton, **2018**.
- [22] R. P. Feynman, **2011**.
- [23] J. H. Warner, F. Schaffel, M. Rummeli, A. Bachmatiuk, *Graphene: Fundamentals and Emergent Applications*, Newnes, **2012**.
- [24] Y. Che, H. Chen, H. Gui, J. Liu, B. Liu, C. Zhou, *Semicond. Sci. Technol.* **2014**, 29, 073001.
- [25] M. J. O'Connell, *Carbon Nanotubes: Properties and Applications*, CRC Press, **2018**.
- [26] A. VahidMohammadi, J. Rosen, Y. Gogotsi, *Science* **2021**, 372, eabf1581.
- [27] G. Hodes, *Advanced Materials* **2007**, 19, 639.
- [28] A. B. Asha, R. Narain, In *Polymer Science and Nanotechnology* (Ed.: Narain, R.), Elsevier, **2020**, pp. 343–359.
- [29] R. Jin, *Nanotechnology Reviews* **2012**, 1, 31.
- [30] F. P. García de Arquer, D. V. Talapin, V. I. Klimov, Y. Arakawa, M. Bayer, E. H. Sargent, *Science* **2021**, 373, eaaz8541.
- [31] Q. Wu, W. Miao, Y. Zhang, H. Gao, D. Hui, *Nanotechnology Reviews* **2020**, 9, 259.
- [32] J. Pelleg, In *Mechanical Properties of Ceramics* (Ed.: Pelleg, J.), Springer International Publishing, Cham, **2014**, pp. 705–759.
- [33] S. A. Catledge, M. D. Fries, Y. K. Vohra, W. R. Lacefield, J. E. Lemons, S. Woodard, R. Venugopalanc, *Journal of Nanoscience and Nanotechnology* **2002**, 2, 293.
- [34] E. Vunain, S. B. Mishra, A. K. Mishra, B. B. Mamba, In *Sol-gel Based Nanoceramic Materials: Preparation, Properties and Applications* (Ed.: Mishra, A. K.), Springer International Publishing, Cham, **2017**, pp. 1–20.
- [35] D. Roy, A. Kr. Srivastava, K. Mukhopadhyay, E. P. Namburi, In *Novel Defence Functional and Engineering Materials (NDFEM) Volume 1: Functional Materials for Defence Applications* (Eds.: Namburi, E. P.; Wanhill, R. J. H.; Setua, D. K.), Springer Nature, Singapore, **2024**, pp. 73–91.

References

- [36] L. H. Madkour, In *Nanoelectronic Materials: Fundamentals and Applications* (Ed.: Madkour, L. H.), Springer International Publishing, Cham, **2019**, pp. 269–307.
- [37] S. Kargozar, S. J. Hoseini, P. B. Milan, S. Hooshmand, H.-W. Kim, M. Mozafari, *Biotechnology Journal* **2020**, *15*, 2000117.
- [38] R. Nagarajan, In *Nanoparticles: Synthesis, Stabilization, Passivation, and Functionalization*, American Chemical Society, **2008**, pp. 2–14.
- [39] A. Machín, K. Fontánez, J. C. Arango, D. Ortiz, J. De León, S. Pinilla, V. Nicolosi, F. I. Petrescu, C. Morant, F. Márquez, *Materials* **2021**, *14*, 2609.
- [40] M. S. Dresselhaus, Y.-M. Lin, O. Rabin, M. R. Black, J. Kong, G. Dresselhaus, In *Springer Handbook of Nanotechnology* (Ed.: Bhushan, B.), Springer, Berlin, Heidelberg, **2010**, pp. 119–167.
- [41] C. Jia, Z. Lin, Y. Huang, X. Duan, *Chem. Rev.* **2019**, *119*, 9074.
- [42] U. Yogeswaran, S.-M. Chen, *Sensors* **2008**, *8*, 290.
- [43] G. Rahman, Z. Najaf, A. Mehmood, S. Bilal, A. ul H. A. Shah, S. A. Mian, G. Ali, *C* **2019**, *5*, 3.
- [44] H. Dai, *Surface Science* **2002**, *500*, 218.
- [45] M. S. Ghamsari, S. Dhara, *Nanorods and Nanocomposites*, BoD – Books on Demand, **2020**.
- [46] N. M. Ali, N. H. Rafat, *Renewable and Sustainable Energy Reviews* **2017**, *68*, 212.
- [47] X. Huang, S. Neretina, M. A. El-Sayed, *Advanced Materials* **2009**, *21*, 4880.
- [48] Kenry, C. T. Lim, *Progress in Polymer Science* **2017**, *70*, 1.
- [49] Y. Chen, X. Dong, M. Shafiq, G. Myles, N. Radacsi, X. Mo, *Adv. Fiber Mater.* **2022**, *4*, 959.
- [50] N. Baig, *Composites Part A: Applied Science and Manufacturing* **2023**, *165*, 107362.
- [51] X. Peng, L. Peng, C. Wu, Y. Xie, *Chem. Soc. Rev.* **2014**, *43*, 3303.
- [52] J. Zeng, X. Ji, Y. Ma, Z. Zhang, S. Wang, Z. Ren, C. Zhi, J. Yu, *Advanced Materials* **2018**, *30*, 1705380.
- [53] M. Carey, M. W. Barsoum, *Materials Today Advances* **2021**, *9*, 100120.

References

- [54] Y. Zheng, F.-Z. Sun, X. Han, J. Xu, X.-H. Bu, *Advanced Optical Materials* **2020**, 8, 2000110.
- [55] Y. Wang, L. Wang, X. Zhang, X. Liang, Y. Feng, W. Feng, *Nano Today* **2021**, 37, 101059.
- [56] Z. Li, D. Li, H. Wang, P. Chen, L. Pi, X. Zhou, T. Zhai, *Small Methods* **2021**, 5, 2100567.
- [57] E. Pomerantseva, F. Bonaccorso, X. Feng, Y. Cui, Y. Gogotsi, *Science* **2019**, 366, eaan8285.
- [58] Y. Zheng, X. Hong, J. Wang, L. Feng, T. Fan, R. Guo, H. Zhang, *Advanced Healthcare Materials* **2021**, 10, 2001743.
- [59] V. S. Bhati, M. Kumar, R. Banerjee, *J. Mater. Chem. C* **2021**, 9, 8776.
- [60] J. Zhang, Z. Li, K. Zhan, R. Sun, Z. Sheng, M. Wang, S. Wang, X. Hou, *ELECTROPHORESIS* **2019**, 40, 2029.
- [61] Y. Zhu, L. Peng, Z. Fang, C. Yan, X. Zhang, G. Yu, *Advanced Materials* **2018**, 30, 1706347.
- [62] V. P. Kumar, D. K. Panda, *ECS J. Solid State Sci. Technol.* **2022**, 11, 033012.
- [63] D. Gupta, V. Chauhan, R. Kumar, *Inorganic Chemistry Communications* **2020**, 121, 108200.
- [64] B. McLean, A. J. Page, *Boron Nitride Nanomaterials: Properties, Fabrication, and Applications*, Jenny Stanford Publishing, New York, **2022**.
- [65] H. Fang, S.-L. Bai, C. P. Wong, *Composites Communications* **2016**, 2, 19.
- [66] T. I. Awan, A. Bashir, A. Tehseen, *Chemistry of Nanomaterials: Fundamentals and Applications*, Elsevier, **2020**.
- [67] C. Verma, E. Berdimurodov, D. K. Verma, K. Berdimuradov, A. Alfantazi, C. M. Hussain, *Inorganic Chemistry Communications* **2023**, 156, 111163.
- [68] J. Martín, M. Martín-González, J. Francisco Fernández, O. Caballero-Calero, *Nat Commun* **2014**, 5, 5130.
- [69] T. Adam, S. C. B. Gopinath, In *Hybrid-Nanomaterials: Fabrication, Characterization and Applications* (Eds.: Gopinath, S. C. B.; Ramli, M. M.), Springer Nature, Singapore, **2024**, pp. 73–87.
- [70] S. NajafiKhoshnood, T. Kim, J. A. Tavares-Negrete, X. Pei, P. Das, S. W. Lee, J. Rajendran, R. Esfandyarpour, *Advanced Materials Technologies* **2023**, 8, 2201655.

References

- [71] L. Yao, Q. Gu, X. Yu, *ACS Nano* **2021**, *15*, 3228.
- [72] Z. Xu, W. Deng, X. Wang, *Electrochem. Energ. Rev.* **2021**, *4*, 269.
- [73] A. Aghababai Beni, H. Jabbari, *Results in Engineering* **2022**, *15*, 100467.
- [74] H. Furukawa, K. E. Cordova, M. O’Keeffe, O. M. Yaghi, *Science* **2013**, *341*, 1230444.
- [75] H. D. Lawson, S. P. Walton, C. Chan, *ACS Appl. Mater. Interfaces* **2021**, *13*, 7004.
- [76] E. Barrios, D. Fox, Y. Y. Li Sip, R. Catarata, J. E. Calderon, N. Azim, S. Afrin, Z. Zhang, L. Zhai, *Polymers* **2019**, *11*, 726.
- [77] J. S. Heo, J. Eom, Y.-H. Kim, S. K. Park, *Small* **2018**, *14*, 1703034.
- [78] S. M. A. Iqbal, I. Mahgoub, E. Du, M. A. Leavitt, W. Asghar, *npj Flex Electron* **2021**, *5*, 1.
- [79] A. Talitckii, E. Kovalenko, A. Anikina, O. Zimniakova, M. Semenov, E. Bril, A. Shcherbak, D. V. Dylov, A. Somov, *IEEE Sensors Journal* **2021**, *21*, 3738.
- [80] G. Aroganam, N. Manivannan, D. Harrison, *Sensors* **2019**, *19*, 1983.
- [81] F. Memarian, S. Rahmani, M. Yousefzadeh, M. Latifi, In *Materials in Sports Equipment (Second Edition)* (Ed.: Subic, A.), Woodhead Publishing, **2019**, pp. 123–160.
- [82] J. J. Ferreira, C. I. Fernandes, H. G. Rammal, P. M. Veiga, *Computers in Human Behavior* **2021**, *118*, 106710.
- [83] M. Mardonova, Y. Choi, *Energies* **2018**, *11*, 547.
- [84] E. Svertoka, S. Saafi, A. Rusu-Casandra, R. Burget, I. Marghescu, J. Hosek, A. Ometov, *Sensors* **2021**, *21*, 3844.
- [85] T. Hughes-Riley, T. Dias, C. Cork, *Fibers* **2018**, *6*, 34.
- [86] J. S. Meena, S. B. Choi, S.-B. Jung, J.-W. Kim, *Materials Today Bio* **2023**, *19*, 100565.
- [87] M. R. Islam, S. Afroj, K. S. Novoselov, N. Karim, *Advanced Science* **2022**, *9*, 2203856.
- [88] R. and M. ltd, *Global Smart Textiles Market by Type (Active Smart Textiles, Passive Smart Textiles, Ultra Smart Textiles), Function (Energy Harvesting, Luminescence & Aesthetics, Sensing), End User - Forecast 2024-2030*.

References

- [89] T. Linz, C. Kallmayer, R. Aschenbrenner, H. Reichl, In *International Workshop on Wearable and Implantable Body Sensor Networks (BSN'06)*, **2006**, p. 4 pp. – 26.
- [90] S. Uzun, S. Seyedin, A. L. Stoltzfus, A. S. Levitt, M. Alhabeb, M. Anayee, C. J. Strobel, J. M. Razal, G. Dion, Y. Gogotsi, *Advanced Functional Materials* **2019**, 29, 1905015.
- [91] I. Wicaksono, C. I. Tucker, T. Sun, C. A. Guerrero, C. Liu, W. M. Woo, E. J. Pence, C. Dagdeviren, *npj Flex Electron* **2020**, 4, 1.
- [92] X. Dong, *Smart and Functional Soft Materials*, BoD – Books on Demand, **2019**.
- [93] L. Bi, W. Perry, R. (John) Wang, R. Lord, T. Hryhorchuk, A. Inman, O. Gogotsi, V. Balitskiy, V. Zahorodna, I. Baginskiy, S. Vorotilo, Y. Gogotsi, *Advanced Functional Materials* **2024**, 34, 2312434.
- [94] W. Son, K.-B. Kim, S. Lee, G. Hyeon, K.-G. Hwang, W. Park, *Journal of Nanoscience and Nanotechnology* **2019**, 19, 6690.
- [95] H. Probst, K. Katzer, A. Nocke, R. Hickmann, M. Zimmermann, C. Cherif, *Polymers* **2021**, 13, 590.
- [96] X. Zheng, P. Wang, X. Zhang, Q. Hu, Z. Wang, W. Nie, L. Zou, C. Li, X. Han, *Composites Part A: Applied Science and Manufacturing* **2022**, 152, 106700.
- [97] Z. Shao, Y. Zhang, N. Zhang, J. Xia, *Materials and Manufacturing Processes* **2016**, 31, 12.
- [98] E. C. Igbokwe, M. O. Daramola, S. E. Iyuke, *Results in Physics* **2019**, 15, 102705.
- [99] I. R. Radulescu, L. Surdu, R. Scarlat, C. Constantin, B. Mitu, C. Morari, M. Costea, *Textiles* **2021**, 1, 4.
- [100] T. Kuroda, H. Takahashi, A. Masuda, In *Wearable Sensors (Second Edition)* (Ed.: Sazonov, E.), Academic Press, Oxford, **2021**, pp. 249–275.
- [101] S. Krinner, In *Smart Clothes and Wearable Technology (Second Edition)* (Eds.: McCann, J.; Bryson, D.), Woodhead Publishing, **2023**, pp. 125–151.
- [102] B. Moradi, R. Fernández-García, I. Gil, *Materials* **2018**, 11, 955.
- [103] C. Gonçalves, A. Ferreira da Silva, J. Gomes, R. Simoes, *Inventions* **2018**, 3, 14.
- [104] S. Afroj, S. Tan, A. M. Abdelkader, K. S. Novoselov, N. Karim, *Advanced Functional Materials* **2020**, 30, 2000293.

References

- [105] Y. Li, S. Yong, N. Hillier, S. Arumugam, S. Beeby, *IEEE Access* **2020**, 8, 206958.
- [106] S. Uzun, M. Schelling, K. Hantanasirisakul, T. S. Mathis, R. Askeland, G. Dion, Y. Gogotsi, *Small* **2021**, 17, 2006376.
- [107] M. R. Islam, S. Afroj, J. Yin, K. S. Novoselov, J. Chen, N. Karim, *Advanced Science* **2024**, 11, 2304140.
- [108] N. Khair, R. Islam, H. Shahariar, *J Mater Sci* **2019**, 54, 10079.
- [109] K. Cherenack, L. van Pieterse, *Journal of Applied Physics* **2012**, 112, 091301.
- [110] K. Jost, G. Dion, Y. Gogotsi, *J. Mater. Chem. A* **2014**, 2, 10776.
- [111] Hexoskin, *Hexoskin Smart Shirts - Cardiac, Respiratory, Sleep & Activity Metrics*.
- [112] Athos Coaching System, .
- [113] Sensoria Home Page, .
- [114] N. U. of Singapore, *Spider-Inspired Soft Fibres Unleash New Potential for Wearable Technology*, **2023**.
- [115] K. Shah, *How Is Wearable Technology Changing the eSports Industry?*, **2023**.
- [116] Jacquard by Google - Technology.
- [117] H. Atkins, *Ralph Lauren's Futuristic Fashion: The PoloTech Smart Shirt*.
- [118] Infoscitex | A DCS Company, .
- [119] Broadsword® Spine® at Dubai Air Show 2017.
- [120] E Textiles – The Next Generation of Military Clothing - Aviation and Defense Market Reports, **2022**.
- [121] G. Chen, X. Xiao, X. Zhao, T. Tat, M. Bick, J. Chen, *Chem. Rev.* **2022**, 122, 3259.
- [122] N. Karim, S. Afroj, A. Malandraki, S. Butterworth, C. Beach, M. Rigout, K. S. Novoselov, A. J. Casson, S. G. Yeates, *Journal of Materials Chemistry C* **2017**, 5, 11640.
- [123] S. S, K. E, *Non-Invasive Blood Glucose Monitoring with Armband-Embedded Antenna Sensor and RADWT Algorithm*, **2024**.
- [124] J. Yin, J. Li, V. S. Reddy, D. Ji, S. Ramakrishna, L. Xu, *Biosensors* **2023**, 13, 127.

References

- [125] Y. Cheng, R. Wang, J. Sun, L. Gao, *Advanced Materials* **2015**, 27, 7365.
- [126] I. Z. Hossain, A. Khan, G. Hossain, *Energies* **2022**, 15, 5541.
- [127] Y. Zou, V. Raveendran, J. Chen, *Nano Energy* **2020**, 77, 105303.
- [128] J. Lama, A. Yau, G. Chen, A. Sivakumar, X. Zhao, J. Chen, *J. Mater. Chem. A* **2021**, 9, 19149.
- [129] N. Zhang, J. Chen, Y. Huang, W. Guo, J. Yang, J. Du, X. Fan, C. Tao, *Advanced Materials* **2016**, 28, 263.
- [130] P. Walter, B. Podsiadły, M. Zych, M. Kamiński, A. Skalski, T. Raczyński, D. Janczak, M. Jakubowska, *Sensors* **2022**, 22, 800.
- [131] W. Liu, N. Liu, Y. Gao, S. Wang, Q. Cheng, F. Xu, *Textile Research Journal* **2019**, 89, 3048.
- [132] X. Chen, Y. Ma, *Advanced Materials Technologies* **2018**, 3, 1800041.
- [133] U. Gulzar, S. Goriparti, E. Miele, T. Li, G. Maidecchi, A. Toma, F. D. Angelis, C. Capiglia, R. P. Zaccaria, *J. Mater. Chem. A* **2016**, 4, 16771.
- [134] M. R. Islam, S. Afroj, C. Beach, M. H. Islam, C. Parraman, A. Abdelkader, A. J. Casson, K. S. Novoselov, N. Karim, *iScience* **2022**, 25.
- [135] J. Chan, R. Torah, *Engineering Proceedings* **2022**, 15, 1.
- [136] K. Motiepor, A. M. Yaghouti, S. Bakhtiyari, A. Jahanshahi, R. Bagherzadeh, In *2023 31st International Conference on Electrical Engineering (ICEE)*, **2023**, pp. 662–666.
- [137] J. S. Heo, M. F. Hossain, I. Kim, *Sensors* **2020**, 20, 3927.
- [138] W. Weng, P. Chen, S. He, X. Sun, H. Peng, *Angewandte Chemie International Edition* **2016**, 55, 6140.
- [139] W. Liu, M.-S. Song, B. Kong, Y. Cui, *Advanced Materials* **2017**, 29, 1603436.
- [140] D. Yu, Q. Qian, L. Wei, W. Jiang, K. Goh, J. Wei, J. Zhang, Y. Chen, *Chem. Soc. Rev.* **2015**, 44, 647.
- [141] B. E. Conway, *Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications*, Springer Science & Business Media, **2013**.
- [142] J. Wang, F. Li, F. Zhu, O. G. Schmidt, *Small Methods* **2019**, 3, 1800367.
- [143] M. Beidaghi, Y. Gogotsi, *Energy Environ. Sci.* **2014**, 7, 867.
- [144] S. Rotzler, M. Schneider-Ramelow, *Textiles* **2021**, 1, 37.

References

- [145] S. U. Zaman, X. Tao, C. Cochrane, V. Koncar, *IOP Conf. Ser.: Mater. Sci. Eng.* **2018**, 459, 012071.
- [146] X. Tao, V. Koncar, T.-H. Huang, C.-L. Shen, Y.-C. Ko, G.-T. Jou, *Sensors* **2017**, 17, 673.
- [147] A. Samir, F. H. Ashour, A. A. A. Hakim, M. Bassyouni, *npj Mater Degrad* **2022**, 6, 1.
- [148] X. He, C. Fan, T. Xu, X. Zhang, *Nano Lett.* **2021**, 21, 8880.
- [149] J. Li, S. Li, J. Huang, A. Q. Khan, B. An, X. Zhou, Z. Liu, M. Zhu, *Advanced Science* **2022**, 9, 2103965.
- [150] H. Pan, G. Chen, Y. Chen, A. Di Carlo, M. A. Mayer, S. Shen, C. Chen, W. Li, S. Subramaniam, H. Huang, H. Tai, Y. Jiang, G. Xie, Y. Su, J. Chen, *Biosensors and Bioelectronics* **2023**, 222, 114999.
- [151] S. Rotzler, M. von Krshiwoblozki, M. Schneider-Ramelow, *Textile Research Journal* **2021**, 91, 2401.
- [152] ATA, *The long road to smart fabric standards*, **2023**.
- [153] Staff, *2020 AATCC Technical Manual Includes New E-Textile Standards*, **2020**.
- [154] ATA, *Smart fabrics testing and standards under development*, **2024**.
- [155] J. Liu, J. Wang, C. Xu, H. Jiang, C. Li, L. Zhang, J. Lin, Z. X. Shen, *Advanced Science* **2018**, 5, 1700322.
- [156] V. Malik, S. Srivastava, M. K. Bhatnagar, M. Vishnoi, *Materials Today: Proceedings* **2021**, 47, 2270.
- [157] A. Coralli, B. J. M. Sarruf, P. E. V. de Miranda, Luigi Osmieri, S. Specchia, N. Q. Minh, In *Science and Engineering of Hydrogen-Based Energy Technologies* (Ed.: Miranda, P. E. V. de), Academic Press, **2019**, pp. 39–122.
- [158] U. of C. Department of Chemical Engineering and Biotechnology, *Fuel Cells*, **2013**.
- [159] B. Cook, .
- [160] Y. Wang, F. Chu, J. Zeng, Q. Wang, T. Naren, Y. Li, Y. Cheng, Y. Lei, F. Wu, *ACS Nano* **2021**, 15, 210.
- [161] C. Choi, D. S. Ashby, D. M. Butts, R. H. DeBlock, Q. Wei, J. Lau, B. Dunn, *Nature Reviews Materials* **2020**, 5, 5.
- [162] J. Sun, B. Luo, H. Li, *Advanced Energy and Sustainability Research* **2022**, 3, 2100191.

References

- [163] T. Kim, W. Song, D.-Y. Son, L. K. Ono, Y. Qi, *J. Mater. Chem. A* **2019**, 7, 2942.
- [164] X. Yuan, H. Liu, J. Zhang, *Lithium-Ion Batteries: Advanced Materials and Technologies*, CRC Press, **2011**.
- [165] M. R. Palacín, A. de Guibert, *Science* **2016**, 351, 1253292.
- [166] J. Kasnatscheew, R. Wagner, M. Winter, I. Cekic-Laskovic, *Top Curr Chem (Z)* **2018**, 376, 16.
- [167] N. H. F. Ismail, S. F. Toha, N. A. M. Azubir, N. H. M. Ishak, M. K. Hassan, B. S. K. Ibrahim, *IOP Conf. Ser.: Mater. Sci. Eng.* **2013**, 53, 012014.
- [168] A. Yu, V. Chabot, J. Zhang, *Electrochemical Supercapacitors for Energy Storage and Delivery: Fundamentals and Applications*, CRC Press, Boca Raton, **2017**.
- [169] W. Storr, *Capacitor Tutorial and Capacitor Basics Summary*, **2013**.
- [170] K. K. Kar, Ed., *Handbook of Nanocomposite Supercapacitor Materials I: Characteristics*, Vol. 300, Springer International Publishing, Cham, **2020**.
- [171] P. Simon, Y. Gogotsi, *Nanoscience and Technology* **2009**, 320.
- [172] M. A. A. Mohd Abdah, N. H. N. Azman, S. Kulandaivalu, Y. Sulaiman, *Materials & Design* **2020**, 186, 108199.
- [173] A. G. Pandolfo, A. F. Hollenkamp, *Journal of Power Sources* **2006**, 157, 11.
- [174] A. González, E. Goikolea, J. A. Barrena, R. Mysyk, *Renewable and Sustainable Energy Reviews* **2016**, 58, 1189.
- [175] G. Wang, L. Zhang, J. Zhang, *Chemical Society Reviews* **2012**, 41, 797.
- [176] Q. Gou, S. Zhao, J. Wang, M. Li, J. Xue, *Nano-Micro Lett.* **2020**, 12, 98.
- [177] L. M. Da Silva, R. Cesar, C. M. R. Moreira, J. H. M. Santos, L. G. De Souza, B. M. Pires, R. Vicentini, W. Nunes, H. Zanin, *Energy Storage Materials* **2020**, 27, 555.
- [178] L. Kouchachvili, W. Yaïci, E. Entchev, *Journal of Power Sources* **2018**, 374, 237.
- [179] C. Zhong, Y. Deng, W. Hu, J. Qiao, L. Zhang, J. Zhang, *Chemical Society Reviews* **2015**, 44, 7484.
- [180] D. Tie, S. Huang, J. Wang, J. Ma, J. Zhang, Y. Zhao, *Energy Storage Materials* **2019**, 21, 22.
- [181] M. Li, J. Lu, Z. Chen, K. Amine, *Advanced Materials* **2018**, 30, 1800561.
- [182] S. Huang, X. Zhu, S. Sarkar, Y. Zhao, *APL Materials* **2019**, 7, 100901.

References

- [183] Ueber einige Gesetze der Vertheilung elektrischer Ströme in körperlichen Leitern, mit Anwendung auf die thierisch-elektrischen Versuche (Schluss.) - Helmholtz - 1853 - Annalen der Physik - Wiley Online Library, .
- [184] H. I. Becker, *Low voltage electrolytic capacitor*, **1957**.
- [185] D. L. Boos, *Electrolytic capacitor having carbon paste electrodes*, **1970**.
- [186] A. Burke, *Journal of Power Sources* **2000**, 91, 37.
- [187] J. R. Miller, In *Supercapacitors*, John Wiley & Sons, Ltd, **2013**, pp. 509–526.
- [188] Department of Electrical and Electronics Engineering, SRM University, Kattankulathur, India 603203., Z. S. Iro, *Int. J. Electrochem. Sci.* **2016**, 10628.
- [189] L. J. Deiner, T. L. Reitz, *Advanced Engineering Materials* **2017**, 19, 1600878.
- [190] Y. Wang, Y. Song, Y. Xia, *Chem. Soc. Rev.* **2016**, 45, 5925.
- [191] N. Jung, S. Kwon, D. Lee, D.-M. Yoon, Y. M. Park, A. Benayad, J.-Y. Choi, J. S. Park, *Adv Mater* **2013**, 25, 6854.
- [192] C. Wolff, S. Jeong, E. Paillard, A. Balducci, S. Passerini, *Journal of Power Sources* **2015**, 293, 65.
- [193] H. Fei, C. Yang, H. Bao, G. Wang, *Journal of Power Sources* **2014**, 266, 488.
- [194] Q. Chen, X. Li, X. Zang, Y. Cao, Y. He, P. Li, K. Wang, J. Wei, D. Wu, H. Zhu, *RSC Adv.* **2014**, 4, 36253.
- [195] R. Jia, G. Shen, F. Qu, D. Chen, *Energy Storage Materials* **2020**, 27, 169.
- [196] K. Tönurist, T. Thomberg, A. Jänes, I. Kink, E. Lust, *Electrochemistry Communications* **2012**, 22, 77.
- [197] P. E. Lokhande, U. S. Chavan, A. Pandey, *Electrochem. Energ. Rev.* **2020**, 3, 155.
- [198] L. L. Zhang, X. S. Zhao, *Chem. Soc. Rev.* **2009**, 38, 2520.
- [199] A. Afif, S. M. Rahman, A. Tasfiah Azad, J. Zaini, M. A. Islan, A. K. Azad, *Journal of Energy Storage* **2019**, 25, 100852.
- [200] P. Forouzandeh, V. Kumaravel, S. C. Pillai, *Catalysts* **2020**, 10, 969.
- [201] Y. Zhou, P. Jin, Y. Zhou, Y. Zhu, *Sci Rep* **2018**, 8, 9005.
- [202] Z. Yang, J. Tian, Z. Yin, C. Cui, W. Qian, F. Wei, *Carbon* **2019**, 141, 467.
- [203] A. Borenstein, O. Hanna, R. Attias, S. Luski, T. Brousse, D. Aurbach, *J. Mater. Chem. A* **2017**, 5, 12653.

References

- [204] Y. Wang, L. Zhang, H. Hou, W. Xu, G. Duan, S. He, K. Liu, S. Jiang, *J Mater Sci* **2021**, 56, 173.
- [205] S. I. Wong, J. Sunarso, B. T. Wong, H. Lin, A. Yu, B. Jia, *Journal of Power Sources* **2018**, 396, 182.
- [206] L. Chang, D. J. Stacchiola, Y. H. Hu, *ACS Appl. Mater. Interfaces* **2017**, 9, 24655.
- [207] S. W. Bokhari, A. H. Siddique, P. C. Sherrell, X. Yue, K. M. Karumbaiah, S. Wei, A. V. Ellis, W. Gao, *Energy Reports* **2020**, 6, 2768.
- [208] J. L. edu\$Department of M. and A. Engineering, the G. W. University, W. Dc, U. C. of M. and A. Engineering, the G. W. University, W. Dc, U. S. of M. and A. Engineering, the G. W. University, W. Dc, U. K. edu\$Department of M. and A. Engineering, the G. W. University, W. Dc, USA, *Graphene* **2012**, 01, 1.
- [209] S. Zhu, J. Ni, Y. Li, *Nano Res.* **2020**, 13, 1825.
- [210] L. Zhang, X. Yang, F. Zhang, G. Long, T. Zhang, K. Leng, Y. Zhang, Y. Huang, Y. Ma, M. Zhang, Y. Chen, *J. Am. Chem. Soc.* **2013**, 135, 5921.
- [211] J. Huang, B. G. Sumpter, V. Meunier, *Chemistry – A European Journal* **2008**, 14, 6614.
- [212] V. Augustyn, P. Simon, B. Dunn, *Energy Environ. Sci.* **2014**, 7, 1597.
- [213] E. Herrero, L. J. Buller, H. D. Abruña, *Chem Rev* **2001**, 101, 1897.
- [214] S. Trasatti, *Electrochimica Acta* **1991**, 36, 225.
- [215] Probing the Charge Storage Mechanism of a Pseudocapacitive MnO₂ Electrode Using in Operando Raman Spectroscopy | Chemistry of Materials.
- [216] M. Hu, H. Zhang, T. Hu, B. Fan, X. Wang, Z. Li, *Chem. Soc. Rev.* **2020**, 49, 6666.
- [217] P. Sharma, V. Kumar, *Journal of Elec Materi* **2020**, 49, 3520.
- [218] S. Jayakumar, P. C. Santhosh, M. M. Mohideen, A. V. Radhamani, *Journal of Alloys and Compounds* **2024**, 976, 173170.
- [219] K. Brousse, S. Pinaud, S. Nguyen, P.-F. Fazzini, R. Makarem, C. Josse, Y. Thimont, B. Chaudret, P.-L. Taberna, M. Respaud, P. Simon, *Advanced Energy Materials* **2020**, 10, 1903136.
- [220] Q. Meng, K. Cai, Y. Chen, L. Chen, *Nano Energy* **2017**, 36, 268.
- [221] R. B. Choudhary, S. Ansari, M. Majumder, *Renewable and Sustainable Energy Reviews* **2021**, 145, 110854.

References

- [222] G. A. Snook, P. Kao, A. S. Best, *Journal of Power Sources* **2011**, 196, 1.
- [223] M. Naguib, V. N. Mochalin, M. W. Barsoum, Y. Gogotsi, *Advanced Materials* **2014**, 26, 992.
- [224] Y. Ando, M. Okubo, A. Yamada, M. Otani, *Advanced Functional Materials* **2020**, 30, 2000820.
- [225] S. Panda, K. Deshmukh, S. K. Khadheer Pasha, J. Theerthagiri, S. Manickam, M. Y. Choi, *Coordination Chemistry Reviews* **2022**, 462, 214518.
- [226] M. Ghidui, M. R. Lukatskaya, M.-Q. Zhao, Y. Gogotsi, M. W. Barsoum, *Nature* **2014**, 516, 78.
- [227] R. B. Rakhi, B. Ahmed, M. N. Hedhili, D. H. Anjum, H. N. Alshareef, *Chem. Mater.* **2015**, 27, 5314.
- [228] J. Halim, S. Kota, M. R. Lukatskaya, M. Naguib, M.-Q. Zhao, E. J. Moon, J. Pitock, J. Nanda, S. J. May, Y. Gogotsi, M. W. Barsoum, *Advanced Functional Materials* **2016**, 26, 3118.
- [229] Q. Tao, M. Dahlgqvist, J. Lu, S. Kota, R. Meshkian, J. Halim, J. Palisaitis, L. Hultman, M. W. Barsoum, P. O. Å. Persson, J. Rosen, *Nat Commun* **2017**, 8, 14949.
- [230] B. Anasori, Y. Xie, M. Beidaghi, J. Lu, B. C. Hosler, L. Hultman, P. R. C. Kent, Y. Gogotsi, M. W. Barsoum, *ACS Nano* **2015**, 9, 9507.
- [231] Q. Shan, X. Mu, M. Alhabeb, C. E. Shuck, D. Pang, X. Zhao, X.-F. Chu, Y. Wei, F. Du, G. Chen, Y. Gogotsi, Y. Gao, Y. Dall'Agnese, *Electrochemistry Communications* **2018**, 96, 103.
- [232] X. Wang, S. Lin, H. Tong, Y. Huang, P. Tong, B. Zhao, J. Dai, C. Liang, H. Wang, X. Zhu, Y. Sun, S. Dou, *Electrochimica Acta* **2019**, 307, 414.
- [233] S. Zhao, C. Chen, X. Zhao, X. Chu, F. Du, G. Chen, Y. Gogotsi, Y. Gao, Y. Dall'Agnese, *Advanced Functional Materials* **2020**, 30, 2000815.
- [234] M. R. Lukatskaya, O. Mashtalir, C. E. Ren, Y. Dall'Agnese, P. Rozier, P. L. Taberna, M. Naguib, P. Simon, M. W. Barsoum, Y. Gogotsi, *Science* **2013**, 341, 1502.
- [235] M. R. Lukatskaya, S. Kota, Z. Lin, M.-Q. Zhao, N. Shpigel, M. D. Levi, J. Halim, P.-L. Taberna, M. W. Barsoum, P. Simon, Y. Gogotsi, *Nat Energy* **2017**, 2, 1.
- [236] Y. Gogotsi, R. M. Penner, *ACS Nano* **2018**, 12, 2081.
- [237] H. Tomiyasu, H. Shikata, K. Takao, N. Asanuma, S. Taruta, Y.-Y. Park, *Sci Rep* **2017**, 7, 45048.

References

- [238] Titanium Disulfide Coated Carbon Nanotube Hybrid Electrodes Enable High Energy Density Symmetric Pseudocapacitors - Zang - 2018 - *Advanced Materials* - Wiley Online Library.
- [239] J. R. Rani, R. Thangavel, S.-I. Oh, Y. S. Lee, J.-H. Jang, *Nanomaterials* **2019**, *9*, 148.
- [240] A. Muzaffar, M. B. Ahamed, K. Deshmukh, J. Thirumalai, *Renewable and Sustainable Energy Reviews* **2019**, *101*, 123.
- [241] K. K. Kar, Ed., *Handbook of Nanocomposite Supercapacitor Materials II: Performance*, 1st ed., Vol. 302, Springer, **2020**.
- [242] J. H. Jang, S. Han, T. Hyeon, S. M. Oh, *Journal of Power Sources* **2003**, *123*, 79.
- [243] M. Zhou, J. Gomez, B. Li, Y.-B. Jiang, S. Deng, *Applied Materials Today* **2017**, *7*, 47.
- [244] K. Li, X. Wang, S. Li, P. Urbankowski, J. Li, Y. Xu, Y. Gogotsi, *Small* **2020**, *16*, 1906851.
- [245] F. Wang, X. Zhan, Z. Cheng, Z. Wang, Q. Wang, K. Xu, M. Safdar, J. He, *Small* **2015**, *11*, 749.
- [246] S. Zheng, X. Shi, P. Das, Z.-S. Wu, X. Bao, *Advanced Materials* **2019**, *31*, 1900583.
- [247] L. Yuan, X. Xiao, T. Ding, J. Zhong, X. Zhang, Y. Shen, B. Hu, Y. Huang, J. Zhou, Z. L. Wang, *Angew Chem Int Ed Engl* **2012**, *51*, 4934.
- [248] Y. T. Jao, P. K. Yang, C. M. Chiu, Y. J. Lin, S. W. Chen, D. Choi, Z. H. Lin, *Nano Energy* **2018**, *50*, 513.
- [249] H. Liu, G. Zhang, X. Zheng, F. Chen, H. Duan, *Int. J. Extrem. Manuf.* **2020**, *2*, 042001.
- [250] W. Yang, J. Yang, J. J. Byun, F. P. Moissinac, J. Xu, S. J. Haigh, M. Domingos, M. A. Bissett, R. A. W. Dryfe, S. Barg, *Advanced Materials* **2019**, *31*, 1902725.
- [251] A. M. Patil, A. A. Jadhav, N. R. Chodankar, A. T. Avatare, J. Hong, S. D. Dhas, U. M. Patil, S. C. Jun, *Coordination Chemistry Reviews* **2024**, *517*, 216020.
- [252] E. Kim, B.-J. Lee, K. Maleski, Y. Chae, Y. Lee, Y. Gogotsi, C. W. Ahn, *Nano Energy* **2021**, *81*, 105616.
- [253] Q. Jiang, Y. Lei, H. Liang, K. Xi, C. Xia, H. N. Alshareef, *Energy Storage Materials* **2020**, *27*, 78.
- [254] H. Li, J. Liang, *Advanced Materials* **2020**, *32*, 1805864.

References

- [255] H. Hu, Z. Pei, C. Ye, *Energy Storage Materials* **2015**, *1*, 82.
- [256] N. Liu, Y. Gao, *Small* **2017**, *13*, 1701989.
- [257] F. Bu, W. Zhou, Y. Xu, Y. Du, C. Guan, W. Huang, *npj Flex Electron* **2020**, *4*, 1.
- [258] C. (John) Zhang, L. McKeon, M. P. Kremer, S.-H. Park, O. Ronan, A. Seral-Ascaso, S. Barwich, C. Ó. Coileáin, N. McEvoy, H. C. Nerl, B. Anasori, J. N. Coleman, Y. Gogotsi, V. Nicolosi, *Nat Commun* **2019**, *10*, 1795.
- [259] T. M. Dinh, K. Armstrong, D. Guay, D. Pech, *J. Mater. Chem. A* **2014**, *2*, 7170.
- [260] N. Kurra, Q. Jiang, P. Nayak, H. N. Alshareef, *Nano Today* **2019**, *24*, 81.
- [261] J. Liang, A. K. Mondal, D. Wang, F. Iacopi, *Adv Materials Technologies* **2019**, *4*, 1800200.
- [262] J. Lin, C. Zhang, Z. Yan, Y. Zhu, Z. Peng, R. H. Hauge, D. Natelson, J. M. Tour, *Nano Lett.* **2013**, *13*, 72.
- [263] D. Pech, M. Brunet, P.-L. Taberna, P. Simon, N. Fabre, F. Mesnilgrete, V. Conédéra, H. Durou, *Journal of Power Sources* **2010**, *195*, 1266.
- [264] J. Chmiola, C. Largeot, P.-L. Taberna, P. Simon, Y. Gogotsi, *Science* **2010**, *328*, 480.
- [265] D. P. Dubal, N. R. Chodankar, D.-H. Kim, P. Gomez-Romero, *Chem. Soc. Rev.* **2018**, *47*, 2065.
- [266] W. Si, C. Yan, Y. Chen, S. Oswald, L. Han, O. G. Schmidt, *Energy & Environmental Science* **2013**, *6*, 3218.
- [267] Q. Jiang, N. Kurra, M. Alhabeib, Y. Gogotsi, H. N. Alshareef, *Advanced Energy Materials* **2018**, *8*, 1703043.
- [268] K. Brousse, P. L. Taberna, P. Simon, *J. Electrochem. Soc.* **2022**, *169*, 070534.
- [269] K.-W. Kim, T. Y. Yun, S.-H. You, X. Tang, J. Lee, Y. Seo, Y.-T. Kim, S. H. Kim, H. C. Moon, J. K. Kim, *NPG Asia Mater* **2020**, *12*, 1.
- [270] Amar. M. Patil, S. Moon, A. A. Jadhav, J. Hong, K. Kang, S. C. Jun, *Advanced Functional Materials* **2023**, *33*, 2305264.
- [271] J. Yang, Z. Pan, Q. Yu, Q. Zhang, X. Ding, X. Shi, Y. Qiu, K. Zhang, J. Wang, Y. Zhang, *ACS Appl. Mater. Interfaces* **2019**, *11*, 5938.
- [272] N. Kurra, M. K. Hota, H. N. Alshareef, *Nano Energy* **2015**, *13*, 500.
- [273] B. Zhu, D. Wen, Z. Liang, R. Zou, *Coordination Chemistry Reviews* **2021**, *446*, 214119.

References

- [274] R. Lv, J. A. Robinson, R. E. Schaak, D. Sun, Y. Sun, T. E. Mallouk, M. Terrones, *Acc. Chem. Res.* **2015**, *48*, 56.
- [275] Z. Sun, T. Liao, Y. Dou, S. M. Hwang, M.-S. Park, L. Jiang, J. H. Kim, S. X. Dou, *Nat Commun* **2014**, *5*, 3813.
- [276] J. Zhu, P. Xiao, H. Li, S. A. C. Carabineiro, *ACS Appl. Mater. Interfaces* **2014**, *6*, 16449.
- [277] L. Liu, J. Park, D. A. Siegel, K. F. McCarty, K. W. Clark, W. Deng, L. Basile, J. C. Idrobo, A.-P. Li, G. Gu, *Science* **2014**, *343*, 163.
- [278] S. Venkateshalu, A. N. Grace, *Electrochimica Acta* **2020**, *341*, 136035.
- [279] W. Li, S. Yang, A. Shamim, *npj Flex Electron* **2019**, *3*, 1.
- [280] J.-K. Chih, A. Jamaluddin, F. Chen, J.-K. Chang, C.-Y. Su, *J. Mater. Chem. A* **2019**, *7*, 12779.
- [281] X. Li, R. Chen, Y. Zhao, Q. Liu, J. Liu, J. Yu, J. Li, P. Liu, J. Li, J. Wang, *Chemical Engineering Journal* **2019**, *375*, 121988.
- [282] P. Das, X. Shi, Q. Fu, Z.-S. Wu, *Advanced Functional Materials* **2020**, *30*, 1908758.
- [283] Z. Niu, L. Zhang, L. Liu, B. Zhu, H. Dong, X. Chen, *Advanced Materials* **2013**, *25*, 4035.
- [284] N. Wang, J. Liu, Y. Zhao, M. Hu, R. Qin, G. Shan, *ChemNanoMat* **2019**, *5*, 658.
- [285] J. Gao, C. Shao, S. Shao, F. Wan, C. Gao, Y. Zhao, L. Jiang, L. Qu, *Small* **2018**, *14*, 1801809.
- [286] H. Xiao, Z.-S. Wu, L. Chen, F. Zhou, S. Zheng, W. Ren, H.-M. Cheng, X. Bao, *ACS Nano* **2017**, *11*, 7284.
- [287] X. Huang, P. Wu, *Advanced Functional Materials* **2020**, *30*, 1910048.
- [288] C. (John) Zhang, M. P. Kremer, A. Seral-Ascaso, S.-H. Park, N. McEvoy, B. Anasori, Y. Gogotsi, V. Nicolosi, *Advanced Functional Materials* **2018**, *28*, 1705506.
- [289] P. Salles, E. Quain, N. Kurra, A. Sarycheva, Y. Gogotsi, *Small* **2018**, *14*, 1802864.
- [290] J. P. Mensing, T. Lomas, A. Tuantranont, *Sustainable Materials and Technologies* **2020**, *25*, e00190.
- [291] Z. Cui, *Printed Electronics: Materials, Technologies and Applications*, John Wiley & Sons, **2016**.

References

- [292] E. B. Secor, *Flex. Print. Electron.* **2018**, 3, 035002.
- [293] J. M. Hoey, A. Lutfurakhmanov, D. L. Schulz, I. S. Akhatov, *Journal of Nanotechnology* **2012**, 2012, 1.
- [294] J. Zhang, G. Zhang, T. Zhou, S. Sun, *Advanced Functional Materials* **2020**, 30, 1910000.
- [295] J. Yun, Y. Lim, H. Lee, G. Lee, H. Park, S. Y. Hong, S. W. Jin, Y. H. Lee, S.-S. Lee, J. S. Ha, *Advanced Functional Materials* **2017**, 27, 1700135.
- [296] Z. Liu, H. I. Wang, A. Narita, Q. Chen, Z. Mics, D. Turchinovich, M. Kläui, M. Bonn, K. Müllen, *J. Am. Chem. Soc.* **2017**, 139, 9443.
- [297] P. Zhang, F. Zhu, F. Wang, J. Wang, R. Dong, X. Zhuang, O. G. Schmidt, X. Feng, *Advanced Materials* **2017**, 29, 1604491.
- [298] Q. Jiang, C. Wu, Z. Wang, A. C. Wang, J.-H. He, Z. L. Wang, H. N. Alshareef, *Nano Energy* **2018**, 45, 266.
- [299] J. Maeng, C. Meng, P. P. Irazoqui, *Biomed Microdevices* **2015**, 17, 7.
- [300] D. Zhao, W. Chang, C. Lu, C. Yang, K. Jiang, X. Chang, H. Lin, F. Zhang, S. Han, Z. Hou, X. Zhuang, *Small* **2019**, 15, 1901494.
- [301] M. Naguib, M. Kurtoglu, V. Presser, J. Lu, J. Niu, M. Heon, L. Hultman, Y. Gogotsi, M. W. Barsoum, *Advanced Materials* **2011**, 23, 4248.
- [302] A. S. Zeraati, S. A. Mirkhani, P. Sun, M. Naguib, P. V. Braun, U. Sundararaj, *Nanoscale* **2021**, 13, 3572.
- [303] L. Yu, L. Lu, X. Zhou, L. Xu, *Advanced Materials Interfaces* **2023**, 10, 2201818.
- [304] A. Amiri, Y. Chen, C. Bee Teng, M. Naraghi, *Energy Storage Materials* **2020**, 25, 731.
- [305] S. Kumar, N. Kumari, Y. Seo, *Journal of Energy Chemistry* **2024**, 90, 253.
- [306] J. K. El-Demellawi, A. E. Mansour, A. M. El-Zohry, M. N. Hedhili, J. Yin, A.-H. M. Emwas, P. Maity, X. Xu, O. M. Bakr, O. F. Mohammed, H. N. Alshareef, *ACS Materials Lett.* **2022**, 4, 2480.
- [307] L. Zhao, L. Wang, Y. Zheng, S. Zhao, W. Wei, D. Zhang, X. Fu, K. Jiang, G. Shen, W. Han, *Nano Energy* **2021**, 84, 105921.
- [308] J. Wozniak, M. Petrus, T. Cygan, A. Lachowski, M. Kostecki, A. Jastrzębska, A. Wojciechowska, T. Wojciechowski, A. Olszyna, *Materials* **2021**, 14, 6011.
- [309] U. Yorulmaz, A. Özden, N. K. Perkgöz, F. Ay, C. Sevik, *Nanotechnology* **2016**, 27, 335702.

References

- [310] X. Xu, Y. Zhang, H. Sun, J. Zhou, F. Yang, H. Li, H. Chen, Y. Chen, Z. Liu, Z. Qiu, D. Wang, L. Ma, J. Wang, Q. Zeng, Z. Peng, *Advanced Electronic Materials* **2021**, 7, 2000967.
- [311] Q. Zhu, J. Li, P. Simon, B. Xu, *Energy Storage Materials* **2021**, 35, 630.
- [312] Á. Morales-García, F. Calle-Vallejo, F. Illas, *ACS Catal.* **2020**, 10, 13487.
- [313] A. Hamzehlouy, M. Soroush, *Materials Today Catalysis* **2024**, 5, 100054.
- [314] Y. Wang, T. Guo, Z. Tian, K. Bibi, Y.-Z. Zhang, H. N. Alshareef, *Advanced Materials* **2022**, 34, 2108560.
- [315] Z. Li, Z. Li, J. Chang, L. Chen, *Materials Today Chemistry* **2024**, 37, 101989.
- [316] A. S. Jatoti, N. M. Mubarak, Z. Hashmi, N. H. Solangi, R. R. Karri, Y. H. Tan, S. A. Mazari, J. R. Koduru, A. Alfantazi, *Chemosphere* **2023**, 313, 137497.
- [317] R. Verma, A. Sharma, V. Dutta, A. Chauhan, D. Pathak, S. Ghotekar, *emergent mater.* **2024**, 7, 35.
- [318] MXetronics: Electronic and photonic applications of MXenes, *Nano Energy* **2019**, 60, 179.
- [319] R. E. Ustad, S. S. Kundale, K. A. Rokade, S. L. Patil, V. D. Chavan, K. D. Kadam, H. S. Patil, S. P. Patil, R. K. Kamat, D. Kim, T. D. Dongale, *Nanoscale* **2023**, 15, 9891.
- [320] L. Chen, X. Dai, W. Feng, Y. Chen, *Acc. Mater. Res.* **2022**, 3, 785.
- [321] A. Szuplewska, D. Kulpińska, A. Dybko, M. Chudy, A. M. Jastrzębska, A. Olszyna, Z. Brzózka, *Trends in Biotechnology* **2020**, 38, 264.
- [322] M. Naguib, O. Mashtalir, J. Carle, V. Presser, J. Lu, L. Hultman, Y. Gogotsi, M. W. Barsoum, *ACS Nano* **2012**, 6, 1322.
- [323] B. Anasori, M. R. Lukatskaya, Y. Gogotsi, *Nat Rev Mater* **2017**, 2, 1.
- [324] S. Pinilla, J. Coelho, K. Li, J. Liu, V. Nicolosi, *Nat Rev Mater* **2022**, 7, 717.
- [325] K. Li, M. Liang, H. Wang, X. Wang, Y. Huang, J. Coelho, S. Pinilla, Y. Zhang, F. Qi, V. Nicolosi, Y. Xu, *Advanced Functional Materials* **2020**, 30, 2000842.
- [326] C. Zhang, M. Naguib, *Transition Metal Carbides and Nitrides (MXenes) Handbook: Synthesis, Processing, Properties and Applications*, John Wiley & Sons, **2024**.
- [327] Y. Gogotsi, B. Anasori, *ACS Nano* **2019**, 13, 8491.

References

- [328] B. Anasori, Y. Gogotsi, Eds., *2D Metal Carbides and Nitrides (MXenes): Structure, Properties and Applications*, Springer International Publishing, Cham, **2019**.
- [329] M. Shekhirev, C. E. Shuck, A. Sarycheva, Y. Gogotsi, *Progress in Materials Science* **2021**, *120*, 100757.
- [330] M. W. Barsoum, *Progress in Solid State Chemistry* **2000**, *28*, 201.
- [331] M. W. Barsoum, M. Radovic, *Annual Review of Materials Research* **2011**, *41*, 195.
- [332] M. Dahlqvist, M. W. Barsoum, J. Rosen, *Materials Today* **2024**, *72*, 1.
- [333] Z. Sun, D. Music, R. Ahuja, S. Li, J. M. Schneider, *Phys. Rev. B* **2005**, *71*, 059903.
- [334] M. W. Barsoum, T. El-Raghy, *Journal of the American Ceramic Society* **1996**, *79*, 1953.
- [335] T. Lapauw, B. Tunca, T. Cabioc'h, J. Vleugels, K. Lambrinou, *Journal of the European Ceramic Society* **2017**, *37*, 4539.
- [336] M. Akhlaghi, S. A. Tayebifard, E. Salahi, M. Shahedi Asl, G. Schmidt, *Ceramics International* **2018**, *44*, 9671.
- [337] N. Kubitza, R. Xie, I. Tarasov, C. Shen, H. Zhang, U. Wiedwald, C. S. Birkel, *Chem. Mater.* **2023**, *35*, 4427.
- [338] W. Luo, Y. Liu, C. Wang, D. Zhao, X. Yuan, L. Wang, J. Zhu, S. Guo, X. Kong, *J. Mater. Chem. C* **2021**, *9*, 7697.
- [339] A. V. Pshyk, E. Coy, M. Kempiński, B. Scheibe, S. Jurga, *Materials Research Letters* **2019**, *7*, 244.
- [340] H. Fakih, S. Jacques, M.-P. Berthet, F. Bosselet, O. Dezellus, J.-C. Viala, *Surface and Coatings Technology* **2006**, *201*, 3748.
- [341] B. R. Maier, B. L. Garcia-Diaz, B. Hauch, L. C. Olson, R. L. Sindelar, K. Sridharan, *Journal of Nuclear Materials* **2015**, *466*, 712.
- [342] J. P. Siebert, K. Patarakun, C. S. Birkel, *Inorg. Chem.* **2022**, *61*, 1603.
- [343] M. Alhabeb, K. Maleski, B. Anasori, P. Lelyukh, L. Clark, S. Sin, Y. Gogotsi, *Chem. Mater.* **2017**, *29*, 7633.
- [344] M. A. Hope, A. C. Forse, K. J. Griffith, M. R. Lukatskaya, M. Ghidui, Y. Gogotsi, C. P. Grey, *Physical Chemistry Chemical Physics* **2016**, *18*, 5099.

References

- [345] A. Lipatov, M. Alhabeab, M. R. Lukatskaya, A. Boson, Y. Gogotsi, A. Sinitskii, *Advanced Electronic Materials* **2016**, 2, 1600255.
- [346] C. E. Shuck, M. Han, K. Maleski, K. Hantanasirisakul, S. J. Kim, J. Choi, W. E. B. Reil, Y. Gogotsi, *ACS Appl. Nano Mater.* **2019**, 2, 3368.
- [347] A. Feng, Y. Yu, F. Jiang, Y. Wang, M. Le, Y. Yu, L. Song, *Ceramics International* **2017**, 43.
- [348] F. Liu, A. Zhou, J. Chen, J. Jia, W. Zhou, L. Wang, Q. Hu, *Applied Surface Science* **2017**, 416, 781.
- [349] X. Wang, C. Garnero, G. Rochard, D. Magne, S. Morisset, S. Hurand, P. Chartier, J. Rousseau, T. Cabioch, C. Coutanceau, V. Mauchamp, S. Célrier, *J. Mater. Chem. A* **2017**, 5, 22012.
- [350] Y. Huang, W. Li, B. Mei, Y. Yang, Z. Liu, *NANO* **2020**, 15, 2050058.
- [351] J. Xuan, Z. Wang, Y. Chen, D. Liang, L. Cheng, X. Yang, Z. Liu, R. Ma, T. Sasaki, F. Geng, *Angewandte Chemie* **2016**, 128, 14789.
- [352] W. Sun, S. A. Shah, Y. Chen, Z. Tan, H. Gao, T. Habib, M. Radovic, M. J. Green, *J. Mater. Chem. A* **2017**, 5, 21663.
- [353] S.-Y. Pang, Y.-T. Wong, S. Yuan, Y. Liu, M.-K. Tsang, Z. Yang, H. Huang, W.-T. Wong, J. Hao, *J. Am. Chem. Soc.* **2019**, 141, 9610.
- [354] P. Urbankowski, B. Anasori, T. Makaryan, D. Er, S. Kota, P. L. Walsh, M. Zhao, V. B. Shenoy, M. W. Barsoum, Y. Gogotsi, *Nanoscale* **2016**, 8, 11385.
- [355] Y. Li, H. Shao, Z. Lin, J. Lu, L. Liu, B. Duployer, P. O. Å. Persson, P. Eklund, L. Hultman, M. Li, K. Chen, X.-H. Zha, S. Du, P. Rozier, Z. Chai, E. Raymundo-Piñero, P.-L. Taberna, P. Simon, Q. Huang, *Nat. Mater.* **2020**, 19, 894.
- [356] P. Urbankowski, B. Anasori, K. Hantanasirisakul, L. Yang, L. Zhang, B. Haines, S. J. May, S. J. L. Billinge, Y. Gogotsi, *Nanoscale* **2017**, 9, 17722.
- [357] J. Zhou, X. Zha, F. Y. Chen, Q. Ye, P. Eklund, S. Du, Q. Huang, *Angewandte Chemie International Edition* **2016**, 55, 5008.
- [358] R. Meshkian, L.-Å. Näslund, J. Halim, J. Lu, M. W. Barsoum, J. Rosen, *Scripta Materialia* **2015**, 108, 147.
- [359] J. Pang, R. G. Mendes, A. Bachmatiuk, L. Zhao, H. Q. Ta, T. Gemming, H. Liu, Z. Liu, M. H. Rummeli, *Chem. Soc. Rev.* **2019**, 48, 72.
- [360] J. Halim, K. M. Cook, M. Naguib, P. Eklund, Y. Gogotsi, J. Rosen, M. W. Barsoum, *Applied Surface Science* **2016**, 362, 406.

References

- [361] K. J. Harris, M. Bugnet, M. Naguib, M. W. Barsoum, G. R. Goward, *J. Phys. Chem. C* **2015**, *119*, 13713.
- [362] X. Sang, Y. Xie, M.-W. Lin, M. Alhabeb, K. L. Van Aken, Y. Gogotsi, P. R. C. Kent, K. Xiao, R. R. Unocic, *ACS Nano* **2016**, *10*, 9193.
- [363] S. Lai, J. Jeon, S. K. Jang, J. Xu, Y. J. Choi, J.-H. Park, E. Hwang, S. Lee, *Nanoscale* **2015**, *7*, 19390.
- [364] M. Hu, Z. Li, H. Zhang, T. Hu, C. Zhang, Z. Wu, X. Wang, *Chem. Commun.* **2015**, *51*, 13531.
- [365] O. Mashtalir, M. Naguib, V. N. Mochalin, Y. Dall'Agnese, M. Heon, M. W. Barsoum, Y. Gogotsi, *Nat Commun* **2013**, *4*, 1716.
- [366] O. Mashtalir, M. R. Lukatskaya, M.-Q. Zhao, M. W. Barsoum, Y. Gogotsi, *Adv Mater* **2015**, *27*, 3501.
- [367] M. Naguib, R. R. Unocic, B. L. Armstrong, J. Nanda, *Dalton Transactions* **2015**, *44*, 9353.
- [368] J. Wu, Y. Wang, Y. Zhang, H. Meng, Y. Xu, Y. Han, Z. Wang, Y. Dong, X. Zhang, *Journal of Energy Chemistry* **2020**, *47*, 203.
- [369] M. Mariano, O. Mashtalir, F. Q. Antonio, W.-H. Ryu, B. Deng, F. Xia, Y. Gogotsi, A. D. Taylor, *Nanoscale* **2016**, *8*, 16371.
- [370] Y.-Y. Peng, B. Akuzum, N. Kurra, M.-Q. Zhao, M. Alhabeb, B. Anasori, E. C. Kumbur, H. N. Alshareef, M.-D. Ger, Y. Gogotsi, *Energy Environ. Sci.* **2016**, *9*, 2847.
- [371] E. Quain, T. S. Mathis, N. Kurra, K. Maleski, K. L. Van Aken, M. Alhabeb, H. N. Alshareef, Y. Gogotsi, *Advanced Materials Technologies* **2019**, *4*, 1800256.
- [372] P. Collini, S. Kota, A. D. Dillon, M. W. Barsoum, A. T. Fafarman, *J. Electrochem. Soc.* **2017**, *164*, D573.
- [373] C. A. Voigt, M. Ghidui, V. Natu, M. W. Barsoum, *J. Phys. Chem. C* **2018**, *122*, 23172.
- [374] C. Xu, L. Wang, Z. Liu, L. Chen, J. Guo, N. Kang, X.-L. Ma, H.-M. Cheng, W. Ren, *Nature Mater* **2015**, *14*, 1135.
- [375] D. Wang, C. Zhou, A. S. Filatov, W. Cho, F. Lagunas, M. Wang, S. Vaikuntanathan, C. Liu, R. F. Klie, D. V. Talapin, *Science* **2023**, *379*, 1242.
- [376] K. R. G. Lim, M. Shekhiriev, B. C. Wyatt, B. Anasori, Y. Gogotsi, Z. W. Seh, *Nat. Synth* **2022**, *1*, 601.

References

- [377] J. S. Meena, S. B. Choi, S.-B. Jung, J.-W. Kim, *Applied Materials Today* **2022**, 29, 101612.
- [378] K. Jost, D. P. Durkin, L. M. Haverhals, E. K. Brown, M. Langenstein, H. C. De Long, P. C. Trulove, Y. Gogotsi, G. Dion, *Advanced Energy Materials* **2015**, 5, 1401286.
- [379] A. Levitt, S. Seyedin, J. Zhang, X. Wang, J. M. Razal, G. Dion, Y. Gogotsi, *Small* **2020**, 16, 2002158.
- [380] B. Ozipek, H. Karakas, In *Advances in Filament Yarn Spinning of Textiles and Polymers* (Ed.: Zhang, D.), Woodhead Publishing, **2014**, pp. 174–186.
- [381] K. A. S. Usman, S. Qin, L. C. Henderson, J. Zhang, D. Y. Hegh, J. M. Razal, *Mater. Horiz.* **2021**, 8, 2886.
- [382] A. Levitt, J. Zhang, G. Dion, Y. Gogotsi, J. M. Razal, *Advanced Functional Materials* **2020**, 30, 2000739.
- [383] Multifunctional Carbon Nanotube Yarns by Downsizing an Ancient Technology | Science.
- [384] M. D. Lima, S. Fang, X. Lepró, C. Lewis, R. Ovalle-Robles, J. Carretero-González, E. Castillo-Martínez, M. E. Kozlov, J. Oh, N. Rawat, C. S. Haines, M. H. Haque, V. Aare, S. Stoughton, A. A. Zakhidov, R. H. Baughman, *Science* **2011**, 331, 51.
- [385] W. Eom, H. Shin, R. B. Ambade, S. H. Lee, K. H. Lee, D. J. Kang, T. H. Han, *Nat Commun* **2020**, 11, 2825.
- [386] A. S. Levitt, M. Alhabeb, C. B. Hatter, A. Sarycheva, G. Dion, Y. Gogotsi, *Journal of Materials Chemistry A* **2019**, 7, 269.
- [387] Recent Advances in 2D MXene Integrated Smart-Textile Interfaces for Multifunctional Applications | Chemistry of Materials, .
- [388] Y.-Z. Zhang, Y. Wang, Q. Jiang, J. K. El-Demellawi, H. Kim, H. N. Alshareef, *Advanced Materials* **2020**, 32, 1908486.
- [389] S. Uzun, M. Han, C. J. Strobel, K. Hantanasirisakul, A. Goad, G. Dion, Y. Gogotsi, *Carbon* **2021**, 174, 382.
- [390] X. Zheng, W. Nie, Q. Hu, X. Wang, Z. Wang, L. Zou, X. Hong, H. Yang, J. Shen, C. Li, *Materials & Design* **2021**, 200, 109442.
- [391] Flexible MXene-Decorated Fabric with Interwoven Conductive Networks for Integrated Joule Heating, Electromagnetic Interference Shielding, and Strain Sensing Performances | ACS Applied Materials & Interfaces.

References

- [392] W. Chen, M. Luo, K. Yang, C. Liu, D. Zhang, X. Zhou, *Chemical Engineering Journal* **2021**, 423, 130242.
- [393] Flexible single-electrode triboelectric nanogenerators with MXene/PDMS composite film for biomechanical motion sensors - ScienceDirect.
- [394] L. Liu, L. Wang, X. Liu, W. Yuan, M. Yuan, Q. Xia, Q. Hu, A. Zhou, *Nanomaterials* **2021**, 11, 889.
- [395] X. Zheng, Q. Hu, Z. Wang, W. Nie, P. Wang, C. Li, *Journal of Colloid and Interface Science* **2021**, 602, 680.
- [396] X. Jia, B. Shen, L. Zhang, W. Zheng, *Composites Part B: Engineering* **2020**, 198, 108250.
- [397] S. P. Sreenilayam, I. Ul Ahad, V. Nicolosi, D. Brabazon, *Materials Today* **2021**, 43, 99.
- [398] X. Zang, J. Wang, Y. Qin, T. Wang, C. He, Q. Shao, H. Zhu, N. Cao, *Nano-Micro Lett.* **2020**, 12, 77.
- [399] Y. Wang, X. Wang, X. Li, X. Li, Y. Liu, Y. Bai, H. Xiao, G. Yuan, *Advanced Functional Materials* **2021**, 31, 2008185.
- [400] A. Levitt, D. Hegh, P. Phillips, S. Uzun, M. Anayee, J. M. Razal, Y. Gogotsi, G. Dion, *Materials Today* **2020**, 34, 17.
- [401] M. S. Rasel, P. Maharjan, J. Y. Park, *Nano Energy* **2019**, 63, 103816.
- [402] M. Salauddin, S. M. S. Rana, M. T. Rahman, Md. Sharifuzzaman, P. Maharjan, T. Bhatta, H. Cho, S. H. Lee, C. Park, K. Shrestha, S. Sharma, J. Y. Park, *Advanced Functional Materials* **2022**, 32, 2107143.
- [403] M. Dehghan, F. Farahbod, *J Clin Diagn Res* **2014**, 8, LC01.
- [404] C. Deng, S. Zhao, E. Su, Y. Li, F. Wu, *Advanced Materials Technologies* **2021**, 6, 2100574.
- [405] M. Chao, Y. Wang, D. Ma, X. Wu, W. Zhang, L. Zhang, P. Wan, *Nano Energy* **2020**, 78, 105187.
- [406] C.-Y. Tang, X. Zhao, J. Jia, S. Wang, X.-J. Zha, B. Yin, K. Ke, R.-Y. Bao, Z.-Y. Liu, Y. Wang, K. Zhang, M.-B. Yang, W. Yang, *Nano Energy* **2021**, 90, 106603.
- [407] A highly flexible and sensitive piezoresistive sensor based on MXene with greatly changed interlayer distances | Nature Communications.
- [408] B. Cheng, P. Wu, *ACS Nano* **2021**, 15, 8676.

References

- [409] Y. Pei, X. Zhang, Z. Hui, J. Zhou, X. Huang, G. Sun, W. Huang, *ACS Nano* **2021**, *15*, 3996.
- [410] S. J. Kim, H.-J. Koh, C. E. Ren, O. Kwon, K. Maleski, S.-Y. Cho, B. Anasori, C.-K. Kim, Y.-K. Choi, J. Kim, Y. Gogotsi, H.-T. Jung, *ACS Nano* **2018**, *12*, 986.
- [411] Ti3C2 MXene-Based Sensors with High Selectivity for NH3 Detection at Room Temperature | *ACS Sensors*, .
- [412] S. H. Lee, W. Eom, H. Shin, R. B. Ambade, J. H. Bang, H. W. Kim, T. H. Han, *ACS Appl. Mater. Interfaces* **2020**, *12*, 10434.
- [413] S. B. Kondawar, P. R. Modak, In *Materials for Potential EMI Shielding Applications* (Eds.: Joseph, K.; Wilson, R.; George, G.), Elsevier, **2020**, pp. 9–25.
- [414] Electromagnetic interference shielding with 2D transition metal carbides (MXenes) | *Science*, .
- [415] Q.-W. Wang, H.-B. Zhang, J. Liu, S. Zhao, X. Xie, L. Liu, R. Yang, N. Koratkar, Z.-Z. Yu, *Advanced Functional Materials* **2019**, *29*, 1806819.
- [416] N. Driscoll, A. G. Richardson, K. Maleski, B. Anasori, O. Adewole, P. Lelyukh, L. Escobedo, D. K. Cullen, T. H. Lucas, Y. Gogotsi, F. Vitale, *ACS Nano* **2018**, *12*, 10419.
- [417] X. Zhao, L.-Y. Wang, C.-Y. Tang, X.-J. Zha, Y. Liu, B.-H. Su, K. Ke, R.-Y. Bao, M.-B. Yang, W. Yang, *ACS Nano* **2020**, *14*, 8793.
- [418] T. H. Park, S. Yu, M. Koo, H. Kim, E. H. Kim, J.-E. Park, B. Ok, B. Kim, S. H. Noh, C. Park, E. Kim, C. M. Koo, C. Park, *ACS Nano* **2019**, *13*, 6835.
- [419] S. Abdolhosseinzadeh, X. Jiang, H. Zhang, J. Qiu, C. (John) Zhang, *Materials Today* **2021**, *48*, 214.
- [420] J. Dai, O. Ogbeide, N. Macadam, Q. Sun, W. Yu, Y. Li, B.-L. Su, T. Hasan, X. Huang, W. Huang, *Chem. Soc. Rev.* **2020**, *49*, 1756.
- [421] M. R. Somalu, A. Muchtar, W. R. W. Daud, N. P. Brandon, *Renewable and Sustainable Energy Reviews* **2017**, *75*, 426.
- [422] G. Hu, J. Kang, L. W. T. Ng, X. Zhu, R. C. T. Howe, C. G. Jones, M. C. Hersam, T. Hasan, *Chem. Soc. Rev.* **2018**, *47*, 3265.
- [423] B. Derby, *Annual Review of Materials Research* **2010**, *40*, 395.
- [424] S. Chung, K. Cho, T. Lee, *Advanced Science* **2019**, *6*, 1801445.
- [425] X. Wang, M. Zhang, L. Zhang, J. Xu, X. Xiao, X. Zhang, *Materials Today Communications* **2022**, *31*, 103263.

References

- [426] S.-T. Huo, L.-Q. Shao, T. Dong, J.-S. Liang, Z.-T. Bi, M. He, Z. Li, Z. Gao, J.-Y. Song, *Journal of the Society for Information Display* **2020**, 28, 36.
- [427] X. Li, H. Li, X. Fan, X. Shi, J. Liang, *Advanced Energy Materials* **2020**, 10, 1903794.
- [428] M. Serpelloni, E. Cantù, M. Borghetti, E. Sardini, *Sensors* **2020**, 20, 841.
- [429] T. Seifert, E. Sowade, F. Roscher, M. Wiemer, T. Gessner, R. R. Baumann, *Ind. Eng. Chem. Res.* **2015**, 54, 769.
- [430] S. Agarwala, W. Y. Yeong, G. L. Goh, *Nanyang Technological University. Proceedings of the 3rd International Conference on Progress in Additive Manufacturing (Pro-AM 2018)* **2018**, 88.
- [431] A. A. Gupta, A. Bolduc, S. G. Cloutier, R. Izquierdo, In *2016 IEEE International Symposium on Circuits and Systems (ISCAS)*, **2016**, pp. 866–869.
- [432] M. Stoppa, A. Chiolerio, *Sensors (Basel)* **2014**, 14, 11957.
- [433] K.-H. Choi, D. B. Ahn, S.-Y. Lee, *ACS Energy Lett.* **2018**, 3, 220.
- [434] E. W. Flick, *Printing Ink and Overprint Varnish Formulations*, 2nd ed., Noyes PublicationsfWilliam Andrew Publishing, **1999**.
- [435] A. Goldschmidt, H.-J. Streitberger, *BASF Handbook Basics of Coating Technology*, 3rd Revised Edition., Vincentz Network, Hannover, Germany, **2018**.
- [436] J. Sun, B. Cui, F. Chu, C. Yun, M. He, L. Li, Y. Song, *Nanomaterials* **2018**, 8, 528.
- [437] C. Lethien, J. L. Bideau, T. Brousse, *Energy & Environmental Science* **2019**, 12, 96.
- [438] L. Li, E. B. Secor, K.-S. Chen, J. Zhu, X. Liu, T. Z. Gao, J.-W. T. Seo, Y. Zhao, M. C. Hersam, *Advanced Energy Materials* **2016**, 6, 1600909.
- [439] S. Abdolhosseinzadeh, J. Heier, C. (John) Zhang, *J. Phys. Energy* **2020**, 2, 031004.
- [440] C. J. Zhang, S. Pinilla, N. McEvoy, C. P. Cullen, B. Anasori, E. Long, S.-H. Park, A. Seral-Ascaso, A. Shmeliov, D. Krishnan, C. Morant, X. Liu, G. S. Duesberg, Y. Gogotsi, V. Nicolosi, *Chem. Mater.* **2017**, 29, 4848.
- [441] W. Cao, J. Nie, Y. Cao, C. Gao, M. Wang, W. Wang, X. Lu, X. Ma, P. Zhong, *Chemical Engineering Journal* **2024**, 496, 154097.
- [442] M. Naguib, O. Mashtalir, M. R. Lukatskaya, B. Dyatkin, C. Zhang, V. Presser, Y. Gogotsi, M. W. Barsoum, *Chemical Communications* **2014**, 50, 7420.

References

- [443] H. Pazniak, I. A. Plugin, M. J. Loes, T. M. Inerbaev, I. N. Burmistrov, M. Gorshenkov, J. Polcak, A. S. Varezchnikov, M. Sommer, D. V. Kuznetsov, M. Bruns, F. S. Fedorov, N. S. Vorobeve, A. Sinitskii, V. V. Sysoev, *ACS Appl. Nano Mater.* **2020**, 3, 3195.
- [444] X. Zhao, A. Vashisth, E. Prehn, W. Sun, S. A. Shah, T. Habib, Y. Chen, Z. Tan, J. L. Lutkenhaus, M. Radovic, M. J. Green, *Matter* **2019**, 1, 513.
- [445] V. Natu, J. L. Hart, M. Sokol, H. Chiang, M. L. Taheri, M. W. Barsoum, *Angewandte Chemie* **2019**, 131, 12785.
- [446] C.-W. Wu, B. Unnikrishnan, I.-W. P. Chen, S. G. Harroun, H.-T. Chang, C.-C. Huang, *Energy Storage Materials* **2020**, 25, 563.
- [447] H. Li, X. Li, J. Liang, Y. Chen, *Advanced Energy Materials* **2019**, 9, 1803987.
- [448] S. Xu, Y. Dall'Agnese, G. Wei, C. Zhang, Y. Gogotsi, W. Han, *Nano Energy* **2018**, 50, 479.
- [449] N. He, A.-F. Seyam, W. Gao, *Adv. Fiber Mater.* **2024**.
- [450] C. Jin, Z. Bai, *ACS Sens.* **2022**, 7, 929.
- [451] E. Gibertini, F. Lissandrello, L. Bertoli, P. Viviani, L. Magagnin, *Coatings* **2023**, 13, 230.
- [452] US7270844.pdf, .
- [453] T. S. Srivatsan, T. S. Sudarshan, *Additive Manufacturing: Innovations, Advances, and Applications*, CRC Press, **2015**.
- [454] S. Binder, M. Glatthaar, E. Rädlein, *Aerosol Science and Technology* **2014**, 48, 924.
- [455] N. J. Wilkinson, M. A. A. Smith, R. W. Kay, R. A. Harris, *Int J Adv Manuf Technol* **2019**, 105, 4599.
- [456] J. A. Paulsen, M. Renn, K. Christenson, R. Plourde, In *2012 Future of Instrumentation International Workshop (FIIW) Proceedings*, **2012**, pp. 1–4.
- [457] A. Elmogi, W. Soenen, H. Ramon, X. Yin, J. Missinne, S. Spiga, M.-C. Amann, A. Srinivasan, P. De Heyn, J. Van Campenhout, J. Bauwelinck, G. Van Steenberge, *Journal of Lightwave Technology* **2018**, 36, 3528.
- [458] R. (Ross) Salary, J. P. Lombardi, D. L. Weerawarne, P. Rao, M. D. Poliks, *Journal of Micro and Nano-Manufacturing* **2021**, 9.
- [459] A. Glushkova, P. Andričević, R. Smajda, B. Náfrádi, M. Kollár, V. Djokić, A. Arakcheeva, L. Forró, R. Pugin, E. Horváth, *ACS Nano* **2021**, 15, 4077.

References

- [460] 3D Printing of Millimetre Wave and Low-Terahertz Frequency Selective Surfaces Using Aerosol Jet Technology | IEEE Journals & Magazine | IEEE Xplore.
- [461] S. Agarwala, G. L. Goh, T.-S. Dinh Le, J. An, Z. K. Peh, W. Y. Yeong, Y.-J. Kim, *ACS Sens.* **2019**, *4*, 218.
- [462] T. Rahman, L. Renaud, D. Heo, M. Renn, R. Panat, *J. Micromech. Microeng.* **2015**, *25*, 107002.
- [463] Atmospheric Pressure and Ambient Temperature Plasma Jet Sintering of Aerosol Jet Printed Silver Nanoparticles | ACS Applied Materials & Interfaces.
- [464] S. P. Sreenilayam, É. McCarthy, L. McKeon, O. Ronan, R. McCann, K. Fleischer, B. Freeland, V. Nicolosi, D. Brabazon, *Chemical Engineering Journal* **2022**, *449*, 137817.
- [465] K. Parate, S. V. Rangnekar, D. Jing, D. L. Mendivelso-Perez, S. Ding, E. B. Secor, E. A. Smith, J. M. Hostetter, M. C. Hersam, J. C. Claussen, *ACS Appl. Mater. Interfaces* **2020**, *12*, 8592.
- [466] L. Gamba, Z. T. Johnson, J. Atterberg, S. Diaz-Arauzo, J. R. Downing, J. C. Claussen, M. C. Hersam, E. B. Secor, *ACS Appl. Mater. Interfaces* **2023**, *15*, 3325.
- [467] G. L. Goh, S. Agarwala, W. Y. Yeong, *ACS Appl. Mater. Interfaces* **2019**, *11*, 43719.
- [468] S. Lu, J. Zheng, J. A. Cardenas, N. X. Williams, Y.-C. Lin, A. D. Franklin, *ACS Appl. Mater. Interfaces* **2020**, *12*, 43083.
- [469] N. M. Pereira, N. P. Rezende, T. H. R. Cunha, A. P. M. Barboza, G. G. Silva, D. Lippross, B. R. A. Neves, H. Chacham, A. S. Ferlauto, R. G. Lacerda, *ACS Omega* **2022**, *7*, 9388.
- [470] Y. Li, X. Feng, M. Sivan, J. F. Leong, B. Tang, X. Wang, J. N. Tey, J. Wei, K. W. Ang, A. V. Y. Thean, *IEEE Sensors Journal* **2020**, *20*, 4653.
- [471] S. Bag, J. R. Deneault, M. F. Durstock, *Advanced Energy Materials* **2017**, *7*, 1701151.
- [472] Y. Wu, A. Lin, J. Zhang, D. Zhao, X. Bai, C. Lu, S. Wang, L. Fan, L. Cao, S. Liu, F. Gu, *Advanced Engineering Materials* **2022**, *24*, 2101556.
- [473] M. Borghetti, M. Serpelloni, E. Sardini, D. Spurling, V. Nicolosi, *Sensors and Actuators A: Physical* **2021**, *332*, 113185.
- [474] V. Vlnieska, E. Gilshtein, D. Kunka, J. Heier, Y. E. Romanyuk, *Polymers* **2022**, *14*, 3411.

References

- [475] L. J. Deiner, T. Jenkins, T. Howell, M. Rottmayer, *Advanced Engineering Materials* **2019**, *21*, 1900952.
- [476] C. E. Folgar, C. Suchicital, S. Priya, *Materials Letters* **2011**, *65*, 1302.
- [477] W. Xie, X. Zhang, C. Leighton, C. D. Frisbie, *2D Insulator–Metal Transition in Aerosol-Jet-Printed Electrolyte-Gated Indium Oxide Thin Film Transistors*. | *Advanced Electronic Materials* | EBSCOhost, Vol. 3, **2017**, p. 1.
- [478] N. X. Williams, N. Watson, D. Y. Joh, A. Chilkoti, A. D. Franklin, *Biofabrication* **2020**, *12*, 025004.
- [479] O. Degryse, V. Bloemen, E. Ferraris, *Procedia CIRP* **2022**, *110*, 180.
- [480] W. Spain, Z. Darpinian, C. Crump, J. Papapolymerou, P. Chahal, J. D. Albrecht, In *2021 IEEE International Conference on Microwaves, Antennas, Communications and Electronic Systems (COMCAS)*, **2021**, pp. 107–110.
- [481] Considerations of aerosol-jet printing for the fabrication of printed hybrid electronic circuits - ScienceDirect.
- [482] S. Lu, J. A. Cardenas, R. Worsley, N. X. Williams, J. B. Andrews, C. Casiraghi, A. D. Franklin, *ACS Nano* **2019**, *13*, 11263.
- [483] C. Cao, J. B. Andrews, A. D. Franklin, *Advanced Electronic Materials* **2017**, *3*, 1700057.
- [484] L. J. Deiner, T. Jenkins, A. Powell, T. Howell, M. Rottmayer, *Advanced Engineering Materials* **2019**, *21*, 1801281.
- [485] Y. Wu, A. Lin, J. Zhang, D. Zhao, L. Fan, C. Lu, S. Wang, L. Cao, F. Gu, *Front. Chem.* **2022**, *10*.
- [486] J. Feng, B. Germann, A. Ramm, F. Herrault, J. Hamre, *Journal of Surface Mount Technology* **2023**, *36*, 20.
- [487] A. E. Uya, S. Lamsal, S. Itapu, F. X. Li, P. Cortes, G. Trovato, L. Dong, V. Borra, In *2023 IEEE 23rd International Conference on Nanotechnology (NANO)*, **2023**, pp. 157–161.
- [488] Preparation of Active Layers in Polymer Solar Cells by Aerosol Jet Printing | ACS Applied Materials & Interfaces.
- [489] P. Kopola, B. Zimmermann, A. Filipovic, H.-F. Schleiermacher, J. Greulich, S. Rousu, J. Hast, R. Myllylä, U. Würfel, *Solar Energy Materials and Solar Cells* **2012**, *107*, 252.
- [490] A. A. Gupta, S. Arunachalam, S. G. Cloutier, R. Izquierdo, *ACS Photonics* **2018**, *5*, 3923.

References

- [491] C. Cooper, B. Hughes, In *2020 Pan Pacific Microelectronics Symposium (Pan Pacific)*, **2020**, pp. 1–11.
- [492] C. Fisher, L. N. Skolrood, K. Li, P. C. Joshi, T. Aytug, *Advanced Materials Technologies* **2023**, 8, 2300030.
- [493] S. Bi, B. Gao, X. Han, Z. He, J. Metts, C. Jiang, K. Asare-Yeboah, *Sci. China Technol. Sci.* **2024**, 67, 2363.
- [494] 3D Printed Electronics - Aerosol Jet Technology, .
- [495] M. Smith, Y. S. Choi, C. Boughey, S. Kar-Narayan, *Flex. Print. Electron.* **2017**, 2, 015004.
- [496] OPTOMECA AEROSOL JET® DEPOSITION SYSTEM MANUAL, Optomec, Inc., **2011**.
- [497] K. K. Christenson, J. A. Paulsen, M. J. Renn, K. McDonald, J. Bourassa, .
- [498] Y. Gu, D. Gutierrez, S. Das, D. R. Hines, *J. Micromech. Microeng.* **2017**, 27, 097001.
- [499] R. (Ross) Salary, J. P. Lombardi, M. Samie Tootooni, R. Donovan, P. K. Rao, P. Borgeesen, M. D. Poliks, *Journal of Manufacturing Science and Engineering* **2016**, 139.
- [500] A. Mahajan, C. D. Frisbie, L. F. Francis, *ACS Appl. Mater. Interfaces* **2013**, 5, 4856.
- [501] A. Mette, P. L. Richter, M. Hörteis, S. W. Glunz, *Progress in Photovoltaics: Research and Applications* **2007**, 15, 621.
- [502] T. D. Donnelly, J. Hogan, A. Mugler, M. Schubmehl, N. Schommer, A. J. Bernoff, S. Dasnurkar, T. Ditmire, *Review of Scientific Instruments* **2005**, 76, 113301.
- [503] J. D. N. Cheeke, J. D. N. Cheeke, *Fundamentals and Applications of Ultrasonic Waves*, CRC Press, Boca Raton, **2002**.
- [504] D. B. Moyano, D. A. Paraiso, R. A. González-Lezcano, *Healthcare* **2022**, 10, 423.
- [505] D. Williams, *Anaesthesia & Intensive Care Medicine* **2012**, 13, 264.
- [506] Y. Yao, Y. Pan, S. Liu, *Ultrasonics Sonochemistry* **2020**, 62, 104722.
- [507] H. D. Cenicerros, T. Y. Hou, *Physics of Fluids* **1999**, 11, 1042.

References

- [508] XVII. On a peculiar class of acoustical figures; and on certain forms assumed by groups of particles upon vibrating elastic surfaces, *Philosophical Transactions of the Royal Society of London* **1831**.
- [509] C. L. Goodridge, H. G. E. Hentschel, D. P. Lathrop, *Phys. Rev. Lett.* **1999**, 82, 3062.
- [510] Dynamics of ultrasonic atomization of droplets - ScienceDirect.
- [511] B. W. Mwakikunga, *Critical Reviews in Solid State and Materials Sciences* **2014**, 39, 46.
- [512] R. J. Lang, *The Journal of the Acoustical Society of America* **1962**, 34, 6.
- [513] J. W. S. B. Rayleigh, *The Theory Of Sound Vol.2*, **1896**.
- [514] W. Eisenmenger, *Acta Acustica united with Acustica* **1959**, 9, 327.
- [515] B. W. Mwakikunga, *Critical Reviews in Solid State and Materials Sciences* **2014**.
- [516] S. and A. I. HORIBA, *Understanding & Interpreting Particle Size Distribution Calculations*.
- [517] T. D. Donnelly, J. Hogan, A. Mugler, N. Schommer, M. Schubmehl, A. J. Bernoff, B. Forrest, *Physics of Fluids* **2004**, 16, 2843.
- [518] G. Chen, Y. Gu, H. Tsang, D. R. Hines, S. Das, *Advanced Engineering Materials* **2018**, 20, 1701084.
- [519] C. L. Goodridge, W. T. Shi, H. G. E. Hentschel, D. P. Lathrop, *Phys. Rev. E* **1997**, 56, 472.
- [520] J. W. Thomas, *Journal of the Air Pollution Control Association* **1958**, 8, 32.
- [521] P. G. Gormley, M. Kennedy, *Proceedings of the Royal Irish Academy. Section A: Mathematical and Physical Sciences* **1948**, 52, 163.
- [522] B. Kahn, *Organic and Printed Electronics* **2007**, 1, 14.
- [523] W. C. Hinds, Y. Zhu, *Aerosol Technology: Properties, Behavior, and Measurement of Airborne Particles*, John Wiley & Sons, **2022**.
- [524] P. Liu, P. J. Ziemann, D. B. Kittelson, P. H. McMurry, *Aerosol Science and Technology* **1995**, 22, 293.
- [525] P. Liu, P. J. Ziemann, D. B. Kittelson, P. H. McMurry, *Aerosol Science and Technology* **1995**, 22, 314.
- [526] J. F. D. L. Mora, P. Riesco-Chueca, *Journal of Fluid Mechanics* **1988**, 195, 1.

References

- [527] J. Q. Feng, *Theor. Comput. Fluid Dyn.* **2015**, 29, 277.
- [528] R. P. Chhabra, In *Rheology of Complex Fluids* (Eds.: Krishnan, J. M.; Deshpande, A. P.; Kumar, P. B. S.), Springer, New York, NY, **2010**, pp. 3–34.
- [529] S. M. Al-Zahrani, *Journal of Petroleum Science and Engineering* **1997**, 17, 211.
- [530] S. Gürgen, M. C. Kuşhan, W. Li, *Progress in Polymer Science* **2017**, 75, 48.
- [531] R. G. Larson, Y. Wei, *Journal of Rheology* **2019**, 63, 477.
- [532] I. Introduction, In *Engineering Properties of Foods*, CRC Press, **2005**.
- [533] H. Huang, W. Yang, *ACS Nano* **2024**, 18, 4651.
- [534] B. Akuzum, K. Maleski, B. Anasori, P. Lelyukh, N. J. Alvarez, E. C. Kumbar, Y. Gogotsi, *ACS Nano* **2018**, 12, 2685.
- [535] A. L. Yarin, *Annual Review of Fluid Mechanics* **2006**, 38, 159.
- [536] E. B. Secor, *Flex. Print. Electron.* **2018**, 3, 035007.
- [537] A. Denneulin, J. Bras, A. Blayo, C. Neuman, *Applied Surface Science* **2011**, 257, 3645.
- [538] C. W. Kan, *Journal of Adhesion Science and Technology* **2007**, 21, 911.
- [539] R. Liu, J. Li, M. Li, Q. Zhang, G. Shi, Y. Li, C. Hou, H. Wang, *ACS Appl. Mater. Interfaces* **2020**, 12, 46446.
- [540] Z. Lyu, L. Yao, W. Chen, F. C. Kalutantirige, Q. Chen, *Chem. Rev.* **2023**, 123, 4051.
- [541] L. Shaber, *The History of the Electron Microscope*, **2018**.
- [542] B. J. Inkson, In *Materials Characterization Using Nondestructive Evaluation (NDE) Methods*, Elsevier, **2016**, pp. 17–43.
- [543] A. Nanakoudis, *SEM: Types of Electrons and the Information They Provide*, **2019**.
- [544] D. B. Williams, C. B. Carter, *Transmission Electron Microscopy*, Springer US, Boston, MA, **2009**.
- [545] J. C. H. Spence, J. M. Zuo, *Electron Microdiffraction*, Springer US, Boston, MA, **1992**.
- [546] D. C. Bell, A. J. Garratt-Reed, *Energy Dispersive X-ray Analysis in the Electron Microscope*, Garland Science, London, **2003**.

References

- [547] L. Reimer, *Scanning Electron Microscopy: Physics of Image Formation and Microanalysis*, Vol. 45, Springer, Berlin, Heidelberg, **1998**.
- [548] L. Reimer, H. Kohl, *Transmission Electron Microscopy: Physics of Image Formation*, Springer Science & Business Media, **2008**.
- [549] A. Nanakoudis, *EDX Analysis with SEM: How Does it Work?*, **2019**.
- [550] J. Epp, In *Materials Characterization Using Nondestructive Evaluation (NDE) Methods* (Eds.: Hübschen, G.; Altpeter, I.; Tschuncky, R.; Herrmann, H.-G.), Woodhead Publishing, **2016**, pp. 81–124.
- [551] L. H. Schwartz, J. B. Cohen, *Diffraction from Materials*, Springer, Berlin, Heidelberg, **1987**.
- [552] W. L. Bragg, *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character* **1913**, 89.
- [553] Powder Diffraction: Theory and Practice, .
- [554] S. Gates-Rector, T. Blanton, *Powder Diffraction* **2019**, 34, 352.
- [555] K. D. M. Harris, M. Tremayne, *Chem. Mater.* **1996**, 8, 2554.
- [556] V. S. Bagockij, *Fundamentals of electrochemistry*, 2. ed., Wiley-Interscience, Hoboken, NJ, **2006**.
- [557] U. Lab, *Fundamentals of Electrochemical Experiments - Part 2: Construction and Testing of Three-Electrode and Two-Electrode Systems*, **2024**.
- [558] A. B. V. Metrohm, *Basic overview of the working principle of a potentiostat/galvanostat (PGSTAT) – Electrochemical cell setup*.
- [559] Electrochemistry on the Bench and in the Field.
- [560] Gamry Instruments, *Technical Note: Two-, Three-, and Four-Electrode Experiments*, **2011**.
- [561] D. Pletcher, R. Greff, R. Peat, L. M. Peter, J. Robinson, *Instrumental Methods in Electrochemistry*, Elsevier, **2001**.
- [562] K. H. An, K. K. Jeon, J. K. Heo, S. C. Lim, D. J. Bae, Y. H. Lee, *J. Electrochem. Soc.* **2002**, 149, A1058.
- [563] Q. Wang, Z. H. Wen, J. H. Li, *Advanced Functional Materials* **2006**, 16, 2141.
- [564] Gamry Instruments, *Testing Super-Capacitors*.
- [565] M. D. Stoller, R. S. Ruoff, *Energy & Environmental Science* **2010**, 3, 1294.

References

- [566] P. T. Kissinger, W. R. Heineman, *J. Chem. Educ.* **1983**, 60, 702.
- [567] Cyclic Voltammetry - CV Electrochemical Technique Gamry Instruments.
- [568] S. Zhang, N. Pan, *Advanced Energy Materials* **2015**, 5, 1401401.
- [569] T. S. Mathis, N. Kurra, X. Wang, D. Pinto, P. Simon, Y. Gogotsi, *Advanced Energy Materials* **2019**, 9, 1902007.
- [570] Gamry Instruments, *Basics of Electrochemical Impedance Spectroscopy*.
- [571] J. R. Macdonald, E. Barsoukov, *Impedance Spectroscopy: Theory, Experiment, and Applications*, John Wiley & Sons, **2018**.
- [572] P. L. Taberna, P. Simon, J. F. Fauvarque, *J. Electrochem. Soc.* **2003**, 150, A292.
- [573] R. Vicentini, L. M. Da Silva, E. P. Cecilio Junior, T. A. Alves, W. G. Nunes, H. Zanin, *Molecules* **2019**, 24, 1452.
- [574] W. Zeng, L. Shu, Q. Li, S. Chen, F. Wang, X.-M. Tao, *Advanced Materials* **2014**, 26, 5310.
- [575] E. Sazonov, M. R. Neuman, Eds., *Wearable Sensors: Fundamentals, Implementation and Applications*, 1st ed., Elsevier, **2014**.
- [576] J. Wilson, *Handbook of textile design: Principles, processes and practice*, CRC Press, **2000**.
- [577] H. Khanzada, M. Q. Khan, S. Kayani, In *Cotton Science and Processing Technology: Gene, Ginning, Garment and Green Recycling* (Eds.: Wang, H.; Memon, H.), Springer, Singapore, **2020**, pp. 377–391.
- [578] M. Xiao, J. Chéry, I. Keresztes, D. B. Zax, M. W. Frey, *Carbohydrate Polymers* **2017**, 174, 377.
- [579] Y. L. Hsieh, In *Cotton*, Elsevier, **2007**, pp. 3–34.
- [580] J. Liang, Y. Zhou, G. Jiang, R. Wang, X. Wang, R. Hu, X. Xi, *The Journal of The Textile Institute* **2013**, 104, 305.
- [581] Polyester | What Is It, Characteristic, Properties, Types, and Uses, .
- [582] S. Kronberg, B. Baghaei, *Advances in Polymer Technology* **2024**, 2024, 5239028.
- [583] Gelato, *A guide to polyester, cotton, and blended fabrics*.
- [584] MXenes: From Discovery to Applications of Two-Dimensional Metal Carbides and Nitrides.

References

- [585] Y. Chae, S. Joon Kim, S.-Y. Cho, J. Choi, K. Maleski, B.-J. Lee, H.-T. Jung, Y. Gogotsi, Y. Lee, C. Won Ahn, *Nanoscale* **2019**, *11*, 8387.
- [586] S. Huang, V. N. Mochalin, *Inorg. Chem.* **2019**, *58*, 1958.
- [587] L. Mao, S. Hu, Y. Gao, L. Wang, W. Zhao, L. Fu, H. Cheng, L. Xia, S. Xie, W. Ye, Z. Shi, G. Yang, *Advanced Healthcare Materials* **2020**, *9*, 2000872.
- [588] L. K. Adams, D. Y. Lyon, P. J. J. Alvarez, *Water Research* **2006**, *40*, 3527.
- [589] M. Simonin, A. Richaume, J. P. Guyonnet, A. Dubost, J. M. F. Martins, T. Pommier, *Sci Rep* **2016**, *6*, 33643.
- [590] J. Zhang, N. Kong, D. Hegh, K. A. S. Usman, G. Guan, S. Qin, I. Jurewicz, W. Yang, J. M. Razal, *ACS Appl. Mater. Interfaces* **2020**, *12*, 34032.
- [591] C. (John) Zhang, Y. Ma, X. Zhang, S. Abdolhosseinzadeh, H. Sheng, W. Lan, A. Pakdel, J. Heier, F. Nüesch, *Energy Environ. Mater.* **2020**, *3*, 29.
- [592] V. M. H. Ng, H. Huang, K. Zhou, P. See Lee, W. Que, J. Zhichuan Xu, L. Bing Kong, *Journal of Materials Chemistry A* **2017**, *5*, 3039.
- [593] Z. Ling, C. E. Ren, M.-Q. Zhao, J. Yang, J. M. Giammarco, J. Qiu, M. W. Barsoum, Y. Gogotsi, *Proceedings of the National Academy of Sciences* **2014**, *111*, 16676.
- [594] University of Regina, *Guidelines for the Safe Use of Hydrofluoric Acid*.
- [595] Teflon PTFE Chemical Compatibility Reference Chart.
- [596] C. E. Shuck, K. Ventura-Martinez, A. Goad, S. Uzun, M. Shekhirev, Y. Gogotsi, *ACS Chem. Health Saf.* **2021**, *28*, 326.
- [597] J. E. von Treifeldt, K. L. Firestein, J. F. S. Fernando, C. Zhang, D. P. Siriwardena, C.-E. M. Lewis, D. V. Golberg, *Materials & Design* **2021**, *199*, 109403.
- [598] J. Ward, S. Middleburgh, M. Topping, A. Garner, D. Stewart, M. W. Barsoum, M. Preuss, P. Frankel, *Journal of Nuclear Materials* **2018**, *502*, 220.
- [599] F. Chang, C. Li, J. Yang, H. Tang, M. Xue, *Materials Letters* **2013**, *109*, 295.
- [600] C. E. Shuck, A. Sarycheva, M. Anayee, A. Levitt, Y. Zhu, S. Uzun, V. Balitskiy, V. Zahorodna, O. Gogotsi, Y. Gogotsi, *Advanced Engineering Materials* **2020**, *22*, 1901241.
- [601] D. Xiong, X. Li, Z. Bai, S. Lu, *Small* **2018**, *14*, 1703419.
- [602] Y. Wu, D. Zhao, J. Zhang, A. Lin, Y. Wang, L. Cao, S. Wang, S. Xiong, F. Gu, *ACS Omega* **2021**, *6*, 33067.

References

- [603] S. Nam, A. D. French, B. D. Condon, M. Concha, *Carbohydrate Polymers* **2016**, 135, 1.
- [604] Y. Liu, D. Thibodeaux, G. Gamble, P. Bauer, D. VanDerveer, *Appl Spectrosc* **2012**, 66, 983.
- [605] M. M. Kamel, M. M. El Zawahry, H. Helmy, M. A. Eid, *Journal of the Textile Institute* **2011**, 102, 220.
- [606] H. Wu, B. Wang, T. Li, Y. Wu, R. Yang, H. Gao, Y. Nie, *Journal of Molecular Liquids* **2023**, 388, 122757.
- [607] M. Ghidui, M. W. Barsoum, *Journal of the American Ceramic Society* **2017**, 100, 5395.
- [608] S. Suwas, R. K. Ray, *Crystallographic Texture of Materials*, Springer London, London, **2014**.
- [609] D. Ayodhya, *Diamond and Related Materials* **2023**, 132, 109634.
- [610] K. Li, J. Zhao, A. Zhussupbekova, C. E. Shuck, L. Hughes, Y. Dong, S. Barwich, S. Vaesen, I. V. Shvets, M. Möbius, W. Schmitt, Y. Gogotsi, V. Nicolosi, *Nat Commun* **2022**, 13, 6884.
- [611] K. L. Firestein, J. E. von Treifeldt, D. G. Kvashnin, J. F. S. Fernando, C. Zhang, A. G. Kvashnin, E. V. Podryabinkin, A. V. Shapeev, D. P. Siriwardena, P. B. Sorokin, D. Golberg, *Nano Lett.* **2020**, 20, 5900.
- [612] V. N. Borysiuk, V. N. Mochalin, Y. Gogotsi, *Nanotechnology* **2015**, 26, 265705.
- [613] A. M. Patil, N. R. Chodankar, E. Jung, S. Roy, D. P. Dubal, G. Guan, Y.-K. Han, S. C. Jun, *J. Mater. Chem. A* **2021**, 9, 26135.
- [614] P. Forouzandeh, S. C. Pillai, *Current Opinion in Chemical Engineering* **2021**, 33, 100710.
- [615] J. D. Benck, B. A. Pinaud, Y. Gorlin, T. F. Jaramillo, *PLOS ONE* **2014**, 9, e107942.
- [616] S.-Y. Lin, X. Zhang, *Journal of Power Sources* **2015**, 294, 354.
- [617] N. Kurra, B. Ahmed, Y. Gogotsi, H. N. Alshareef, *Advanced Energy Materials* **2016**, 6, 1601372.
- [618] M. R. Lukatskaya, S.-M. Bak, X. Yu, X.-Q. Yang, M. W. Barsoum, Y. Gogotsi, *Advanced Energy Materials* **2015**, 5, 1500589.
- [619] K. Wang, Q. Meng, Y. Zhang, Z. Wei, M. Miao, *Advanced Materials* **2013**, 25, 1494.

References

- [620] K. Jost, C. R. Perez, J. K. McDonough, V. Presser, M. Heon, G. Dion, Y. Gogotsi, *Energy Environ. Sci.* **2011**, *4*, 5060.
- [621] D. A. Hardy, Z. Rahemtulla, A. Satharasinghe, A. Shahidi, C. Oliveira, I. Anastasopoulos, M. N. Nashed, M. Kgatuke, A. Komolafe, R. Torah, J. Tudor, T. Hughes-Riley, S. Beeby, T. Dias, *Materials* **2020**, *13*, 1228.
- [622] S. uz Zaman, X. Tao, C. Cochrane, V. Koncar, *Sensors* **2020**, *20*, 1272.
- [623] V. Gaubert, H. Gidik, N. Bodart, V. Koncar, *Sensors* **2020**, *20*, 1739.
- [624] C. Zeagler, S. Gilliland, S. Audy, T. Starner, In *Proceedings of the 2013 International Symposium on Wearable Computers*, Association for Computing Machinery, New York, NY, USA, **2013**, pp. 143–144.
- [625] H. Kim, S. Lee, *Fibers Polym* **2018**, *19*, 2351.
- [626] V. Malm, F. Seoane, V. Nierstrasz, *Materials* **2019**, *12*, 3537.
- [627] A. Ankhili, X. Tao, C. Cochrane, D. Coulon, V. Koncar, *Materials* **2018**, *11*, 256.
- [628] M. A. Yokus, R. Foote, J. S. Jur, *IEEE Sensors J.* **2016**, *16*, 7967.
- [629] A. Ankhili, S. uz Zaman, X. Tao, C. Cochrane, V. Koncar, D. Coulon, *Textile & Leather Review* **2019**, *2*, 126.
- [630] Insulation Of Flexible Light Emitting Display For Smart Clothing.
- [631] X. Tao, T.-H. Huang, C.-L. Shen, Y.-C. Ko, G.-T. Jou, V. Koncar, *Advanced Materials Technologies* **2018**, *3*, 1700309.
- [632] P. Veske, P. Bauwens, F. Bossuyt, T. Sterken, J. Vanfleteren, *Applied Sciences* **2020**, *10*, 9057.
- [633] A. Komolafe, Reliability and interconnections for printed circuits on fabrics. PhD, University of Southampton, **2016**.
- [634] ISO, *ISO 105-C06:2010*.
- [635] Y. Zhu, S. Wang, J. Ma, P. Das, S. Zheng, Z.-S. Wu, *Energy Storage Materials* **2022**, *51*, 500.
- [636] X. Pu, M. Liu, L. Li, S. Han, X. Li, C. Jiang, C. Du, J. Luo, W. Hu, Z. L. Wang, *Advanced Energy Materials* **2016**, *6*, 1601254.
- [637] H. Guo, Z. Jiang, D. Ren, S. Li, J. Wang, X. Cai, D. Zhang, Q. Guo, J. Xiao, J. Yang, *ChemElectroChem* **2021**, *8*, 1574.
- [638] G. Ma, M. Dong, K. Sun, E. Feng, H. Peng, Z. Lei, *Journal of Materials Chemistry A* **2015**, *3*, 4035.

References

- [639] S. Abdolhosseinzadeh, R. Schneider, A. Verma, J. Heier, F. Nüesch, C. (John) Zhang, *Advanced Materials* **2020**, 32, 2000716.
- [640] Y. Zhang, T. Ji, S. Hou, L. Zhang, Y. Shi, J. Zhao, X. Xu, *Journal of Power Sources* **2018**, 403, 109.
- [641] D. Li, S. Yang, X. Chen, W.-Y. Lai, W. Huang, *Advanced Functional Materials* **2021**, 31, 2107484.
- [642] W. Yang, Y. Zhu, Z. Jia, L. He, L. Xu, J. Meng, M. Tahir, Z. Zhou, X. Wang, L. Mai, *Advanced Energy Materials* **2020**, 10, 2001873.
- [643] H. Hu, T. Hua, *J. Mater. Chem. A* **2017**, 5, 19639.
- [644] S. Bellani, E. Petroni, A. E. Del Rio Castillo, N. Curreli, B. Martín-García, R. Oropesa-Nuñez, M. Prato, F. Bonaccorso, *Advanced Functional Materials* **2019**, 29, 1807659.

SUPPLEMENTARY INFORMATION

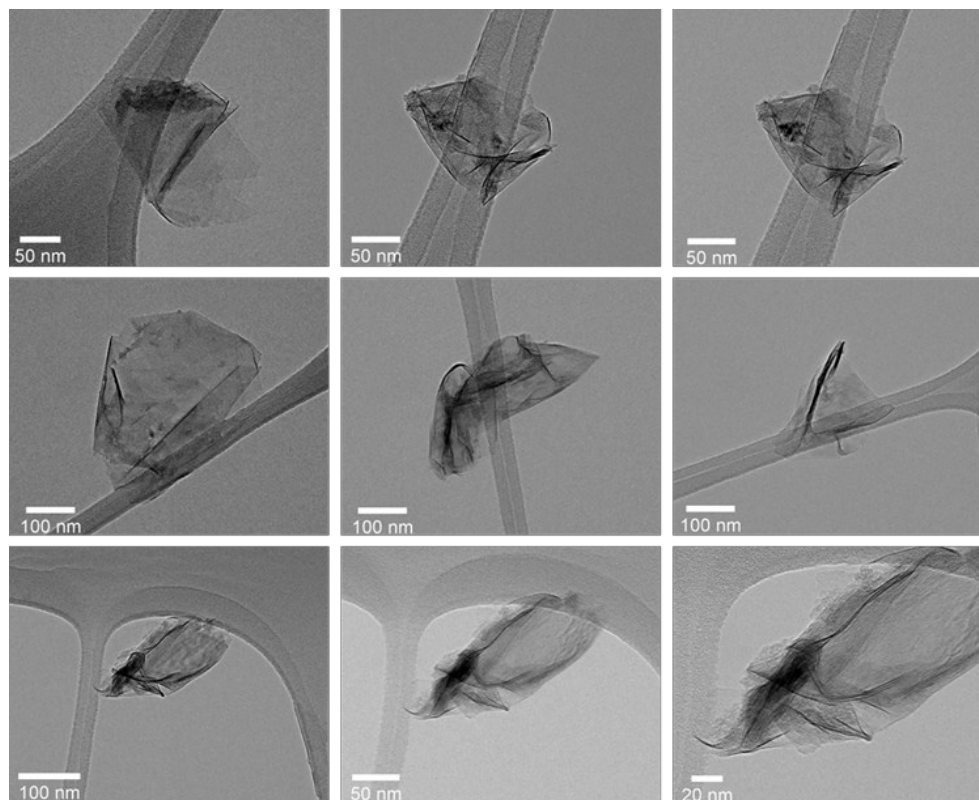


Figure S1: Representative TEM images capturing the crumpled morphology of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene flakes due to the AJP's ultrasonic atomization (UA).

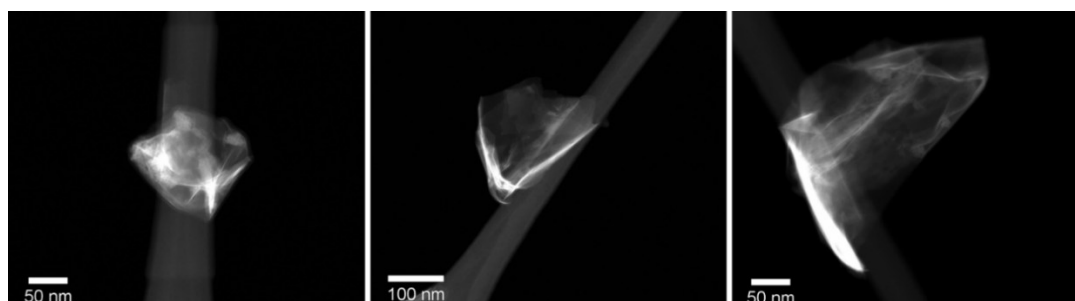


Figure S2: HAADF scanning transmission electron microscopy (STEM) images revealing the microstructure of AJP $\text{Ti}_3\text{C}_2\text{T}_x$ MXene inks. The crumpled morphology of $\text{Ti}_3\text{C}_2\text{T}_x$ flakes is evident, attributed to the UA during printing.

Status Primary **Quality Mark:** Star **Environment:** Ambient **Temp:** 298.0 K (Assigned by ICDD editor)
Chemical Formula: (C₆H₁₀O₅)_n **Empirical Formula:** C₆H₁₀O₅ **Weight %:** C44.45 H6.22 O49.34
Atomic %: C28.57 H47.62 O23.81 **Compound Name:** Cellulose I β **Entry Date:** 09/01/2006
Modification Date: 09/01/2007 **Modifications:** Quality

Radiation: CuK α 1 (1.5406 Å) **d-Spacing:** Diffractometer **Cutoff:** 29.40 Å **Intensity:** Diffractometer - Integrated
I/I_c: 8.27

Crystal System: Monoclinic **SPGR:** P21 (4)
Author's Unit Cell [a: 7.784(8) Å b: 8.201(8) Å c: 10.38(1) Å γ : 96.5° Volume: 658.36 Å³ Z: 4.00
MolVol: 164.59 **c/a:** 1.334 **a/b:** 0.949 **c/b:** 1.266 **Calculated Density:** 1.636 g/cm³
Structural Density: 1.635 g/cm³ **SS/FOM:** F(30) = 43.2(0.0095, 73)

Space Group: P21 (4) **Molecular Weight:** 162.14 g/mol
Crystal Data [a: 8.201 Å b: 10.380 Å c: 7.784 Å α : 90.00° β : 96.50° γ : 90.00° XtlCell Vol: 658.36 Å³
XtlCell Z: 4.00 c/a: 0.949 a/b: 0.790 c/b: 0.750]
Reduced Cell [a: 7.784 Å b: 8.201 Å c: 10.380 Å α : 90.00° β : 90.00° γ : 96.50° RedCell Vol: 658.36 Å³]

Crystal (Symmetry Allowed): Non-centrosymmetric - Enantiomorphic, Optical Activity, Pyro / Piezo (p), Piezo (2nd Harm.)

Subfiles: Carbohydrate, Organic, Pharmaceutical (Excipient), Polymer **Pearson Symbol:** mP 84.00
Pearson Symbol w/o H: mP44

Cross-Ref PDF #'s: 00-050-2241 (Deleted), 00-060-1502 (Primary)

References:

Type	DOI	Reference
Primary Reference		Kaduk, J., BP Chemical, Naperville, IL, USA. Private Communication 2005.
Unit Cell		Nishiyama, Y., Langan, P., Chanzy, H. J. Am. Chem. Soc. 2002, 124, 9074.

Database Comments: Additional Patterns: To replace 00-050-2241. See PDF 00-060-1502. Sample Preparation: The sample was a sheet of Whatman No.42 filter paper. Structures: Crystal structure optimized by a density functional plane wave pseudopotential quantum mechanical calculation, with fixed experimental lattice parameters.

d-Spacings (58) - (C₆H₁₀O₅)_n - 00-056-1718 (Stick, Fixed Slit Intensity) - Cu K α 1.54056 Å

2 θ (°)	d (Å)	I	h	k	l	*	2 θ (°)	d (Å)	I	h	k	l	*
13.80586	6.408980	34	0	1	1		38.57761	2.331850	7	1	1	4	
14.27040	6.201380	15	1	0	1		39.23963	2.294020	35	-2	2	3	1
14.85510	5.958580	245	-1	1	0		39.89819	2.257660	11	-2	2	3	
16.66785	5.314400	237	1	1	0		40.12201	2.245580	5	-3	2	1	
18.74291	4.730450	21	1	1	1		41.89164	2.154720	29	2	0	4	
20.27026	4.377330	35	0	1	2		42.14357	2.142420	17	-2	3	2	
20.59304	4.309440	59	1	0	2		42.26946	2.136330	13	0	3	3	
22.98197	3.866600	1000	2	0	0		42.86987	2.107790	20m	2	2	3	
23.43951	3.792150	7	0	2	1		42.86987	2.107790	20m	-1	3	3	
24.54796	3.623370	10	2	0	1		43.70189	2.069570	5	2	3	1	
25.01041	3.557410	12	-1	2	1		44.99549	2.013030	36m	0	1	5	
27.98747	3.185400	23m	0	1	3		44.99549	2.013030	36m	1	3	3	
27.98747	3.185400	23m	2	1	1		45.54843	1.989870	5	-1	4	1	
29.16854	3.059050	27	-1	2	2		46.24939	1.961330	8	3	1	3	
29.84261	2.991470	14m	-1	1	3		46.51366	1.950800	10	-3	3	1	
29.84261	2.991470	14m	-2	1	2		46.95803	1.933370	33m	1	1	5	
30.81110	2.899610	28	1	1	3		46.95803	1.933370	33m	4	0	0	
31.14880	2.868940	32m	1	2	2		48.01173	1.893370	6	-2	4	0	
31.14880	2.868940	32m	-2	2	1		48.14364	1.888490	11	-1	4	2	
31.77714	2.813630	35	2	1	2		49.02614	1.856540	10	2	2	4	
33.96588	2.637160	43	0	2	3		50.59230	1.802680	11	2	3	3	
34.09617	2.627380	36	0	3	1		50.93813	1.791250	8	1	3	4	
34.53489	2.595000	35	0	0	4		51.77018	1.764400	13	2	1	5	
34.80036	2.575810	42	-1	3	1		52.08990	1.754320	5	3	1	4	
35.10276	2.554310	19	-1	2	3		52.88672	1.729750	9	4	1	2	
35.86516	2.501740	8	3	0	1		57.11918	1.611220	10	-3	4	2	
36.78057	2.441550	15	1	2	3		58.05322	1.587500	6	-4	3	2	
37.32497	2.407180	33	1	3	1		58.48436	1.576820	8	3	3	3	
37.75408	2.380800	9	3	1	0		60.15416	1.536980	6	2	1	6	

Figure S3: XRD PDF card depicting the characteristic diffraction pattern for pristine cotton fabric, revealing the presence of the cellulose I β crystalline structure.

Status Primary **Quality Mark:** Blank **Environment:** Ambient **Temp:** 298.0 K (Assigned by ICDD editor)
Chemical Formula: (C₁₀H₈O₄)_n **Empirical Formula:** C₁₀H₈O₄ **Weight %:** C62.50 H4.20 O33.30
Atomic %: C45.45 H36.36 O18.18 **Compound Name:** Polyethylene terephthalate **CAS Number:** 25038-59-9
Entry Date: 09/01/2010

Radiation: CuKα (1.5418 Å) **Filter:** Graph Mono **d-Spacing:** Diffractometer **Cutoff:** 17.70 Å
Intensity: Diffractometer - Peak

Crystal System: Triclinic (Anorthic) **SPGR:** P-1 (2)
Author's Unit Cell [a: 4.561(5) Å b: 5.970(5) Å c: 10.84(1) Å α: 98.3(2)° β: 118.5(1)° γ: 112.45(9)°
Volume: 219.50 Å³ **Z:** 1.00 **MolVol:** 219.50 **c/a:** 2.377 **a/b:** 0.764 **c/b:** 1.816]
Calculated Density: 1.452 g/cm³ **SS/FOM:** F(12) = 1.1(0.1155, 93)

Space Group: P-1 (2) **Molecular Weight:** 192.17 g/mol
Crystal Data [a: 5.971 Å b: 9.040 Å c: 4.561 Å α: 100.65° β: 112.46° γ: 75.93° XtlCell Vol: 219.50 Å³
XtlCell Z: 1.00 **c/a:** 0.764 **a/b:** 0.661 **c/b:** 0.505]
Reduced Cell [a: 4.561 Å b: 5.971 Å c: 9.040 Å α: 75.93° β: 79.36° γ: 67.54° RedCell Vol: 219.50 Å³]

Crystal (Symmetry Allowed): Centrosymmetric

Subfiles: Forensic, Organic, Polymer **Pearson Symbol:** aP 22.00 **Pearson Symbol w/o H:** aP14

Cross-Ref PDF #'s: 00-050-2275 (Primary), 00-058-1447 (Primary), 02-072-2445 (Experimental <-> CSD PDF-4 Organics),
 02-072-2446 (Experimental <-> CSD PDF-4 Organics)

References:

Type	DOI	Reference
Primary Reference		Blanton, T., Murthy, S., Eastman Kodak Co., Rochester, NY, USA. Private Communication 2009.
Contributed		Blanton, T., Rochester, New York, USA. Private Communication 2009.

Database Comments: Additional Patterns: See PDF 00-050-2275, 00-058-1447 and 02-072-2446. General Comments: The initial lattice parameters were taken from PDF 02-072-2446 and refined using the program unit cell. Warning: Lines with abs(delta 2Theta)>0.2 DEG.

d-Spacings (15) - (C10 H8 O4) n - 00-060-0989 (Stick, Fixed Slit Intensity) - Cu Ka1 1.54056 Å													
2θ (°)	d (Å)	I	h	k	l	*	2θ (°)	d (Å)	I	h	k	l	*
16.14650	5.484800	77	0	-1	1		32.53220	2.750030	17m	0	-2	1	
17.41543	5.087920	79	0	1	0		32.53220	2.750030	17m	1	1	-3	
21.61182	4.108540	65m	-1	0	1		42.37319	2.131340	17	1	0	-5	
21.61182	4.108540	65m	-1	0	2		44.24131	2.045580	8	2	0	-4	
22.72087	3.910440	85	1	-1	0		46.63897	1.945850	11	1	2	-2	
25.98804	3.425760	100m	1	0	0		49.56617	1.837570	8	0	3	-2	
25.98804	3.425760	100m	-1	0	3		52.93256	1.728360	6	2	-3	0	
27.70651	3.217060	39	1	-1	1								

Figure S4: XRD PDF card illustrating the distinctive diffraction pattern for pristine polyester fabric, indicative of the crystalline structure of PET.

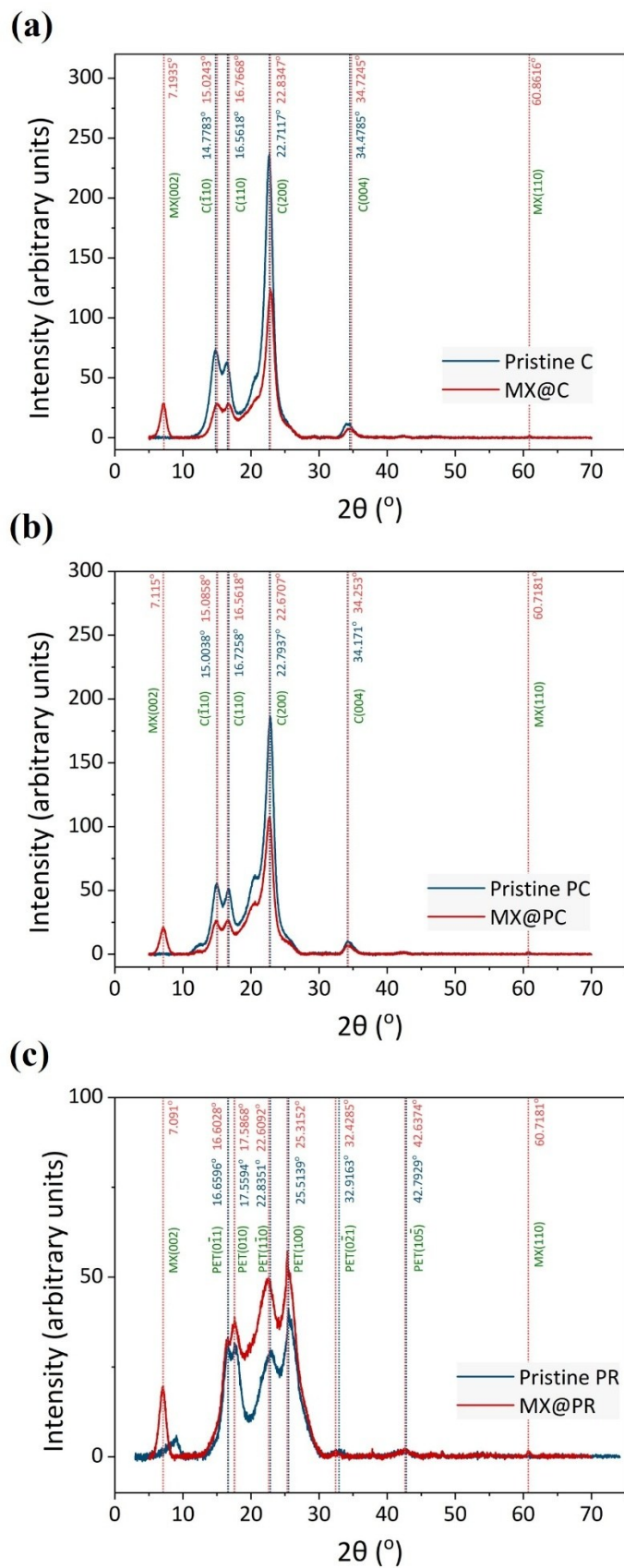


Figure S5: XRD for the crystalline structures of **(a)** pristine cotton (C) with MXene-printed cotton (MX@C), **(b)** pristine polycotton (PC) with MXene-printed polycotton (MX@PC), and **(c)** pristine polyester (PR) with MXene-printed polyester (MX@PR).

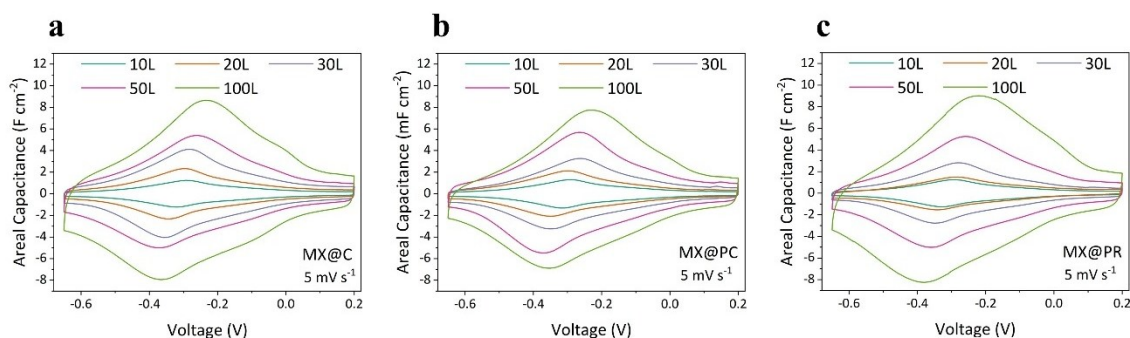


Figure S6: Comparative CVs of MX@Fabric electrodes at a scan rate of 5 mV s^{-1} showcasing the electrochemical behaviour at different mass loadings 10, 20, 30, 50, 100 layers on **(a)** cotton - MX@C, **(b)** polycotton – MX@PC, and **(c)** polyester – MX@PR.

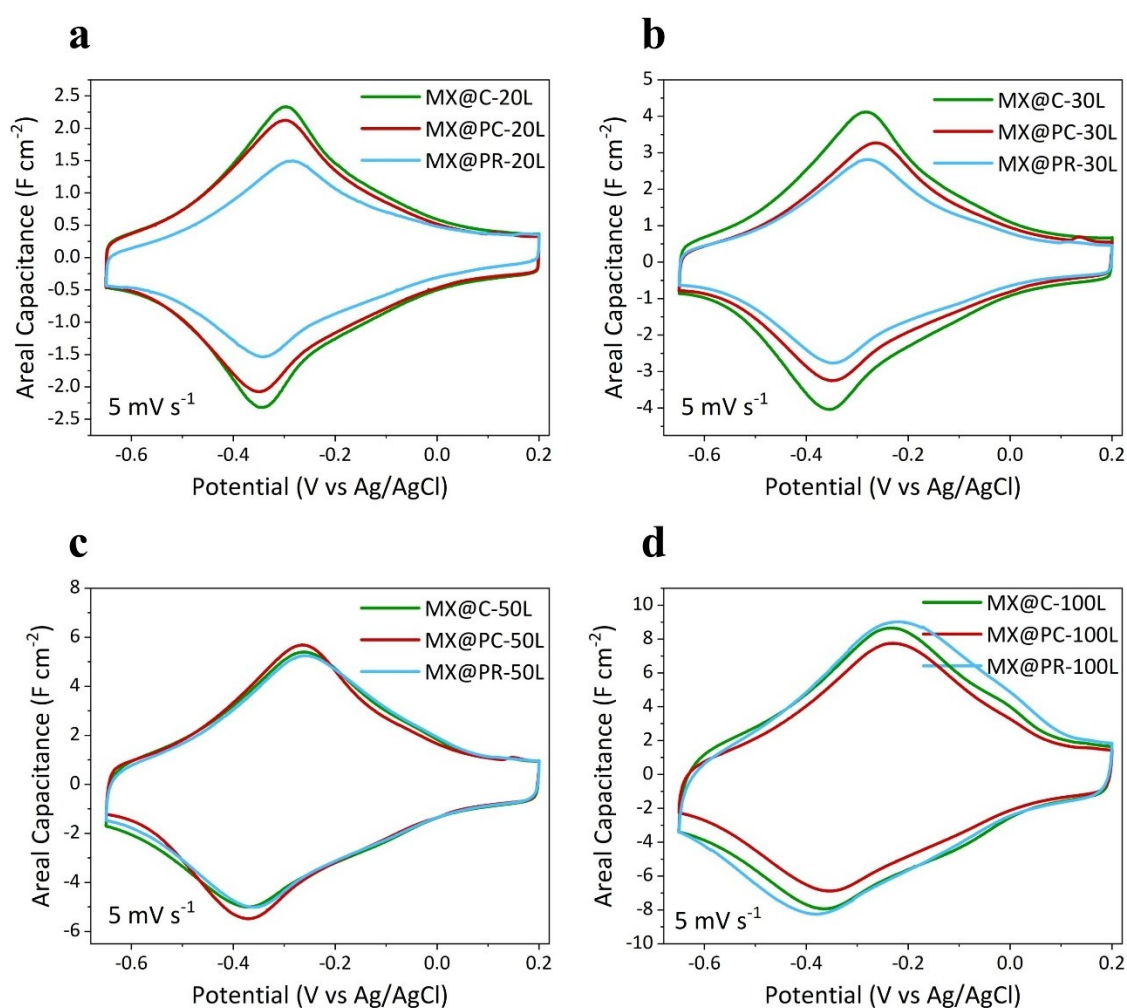


Figure S7: Comparative CVs of the MX@C, MX@PC, and MX@PR electrodes at 5 mV s^{-1} scan rate showcasing the electrochemical behaviour at varying mass loadings: **(a)** 20 layers, **(b)** 30 layers, **(c)** 50 layers, and **(d)** 100 layers.

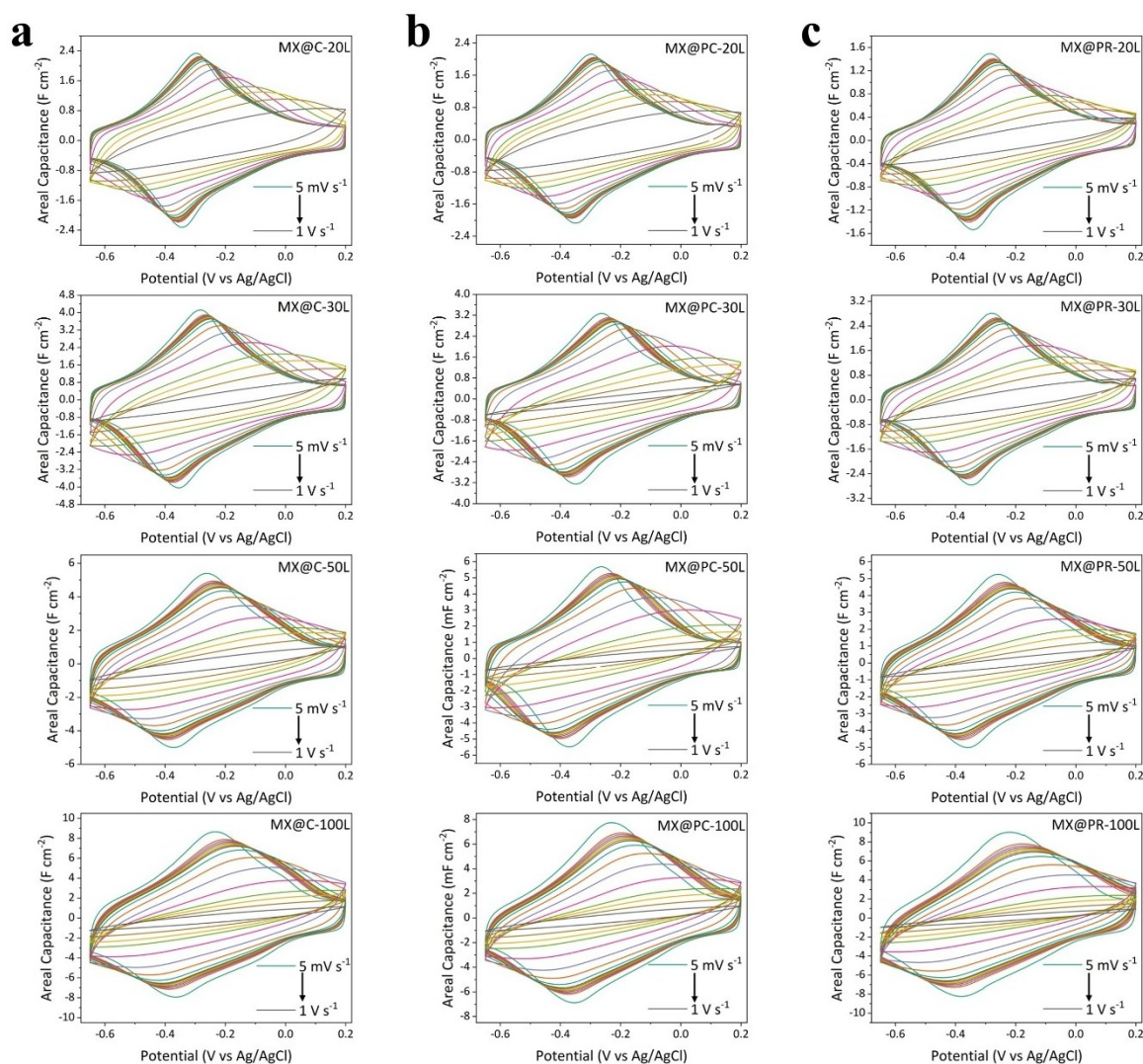


Figure S8: CV characterisation of AJP MX@Fabric electrodes at 5, 10, 11, 12, 13, 15, 16, 20, 30, 50, 100, 200, 300, 500, 1000 mV s^{-1} scan rates at 20, 30, 50, 100 layers mass loadings on (a) cotton - MX@C, (b) polycotton – MX@PC, and (c) polyester – MX@PR.

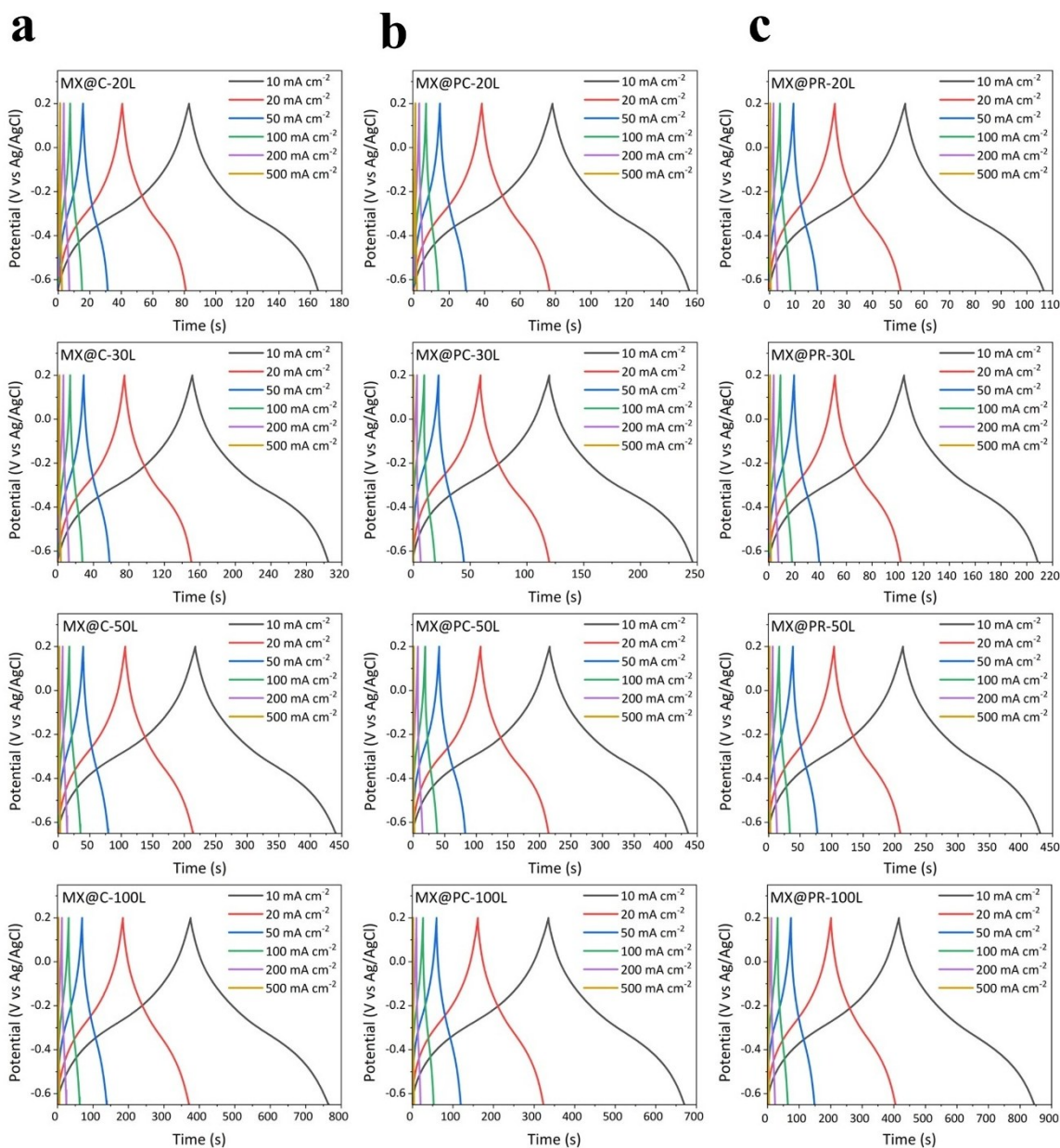


Figure S9: GCD characterisation of MX@Fabric electrodes at 10, 20, 50, 100, 200, and 500 mA cm⁻² current densities with 20, 30, 50, and 100 layers mass loading on (a) cotton - MX@C, (b) polycotton – MX@PC, and (c) polyester – MX@PR.

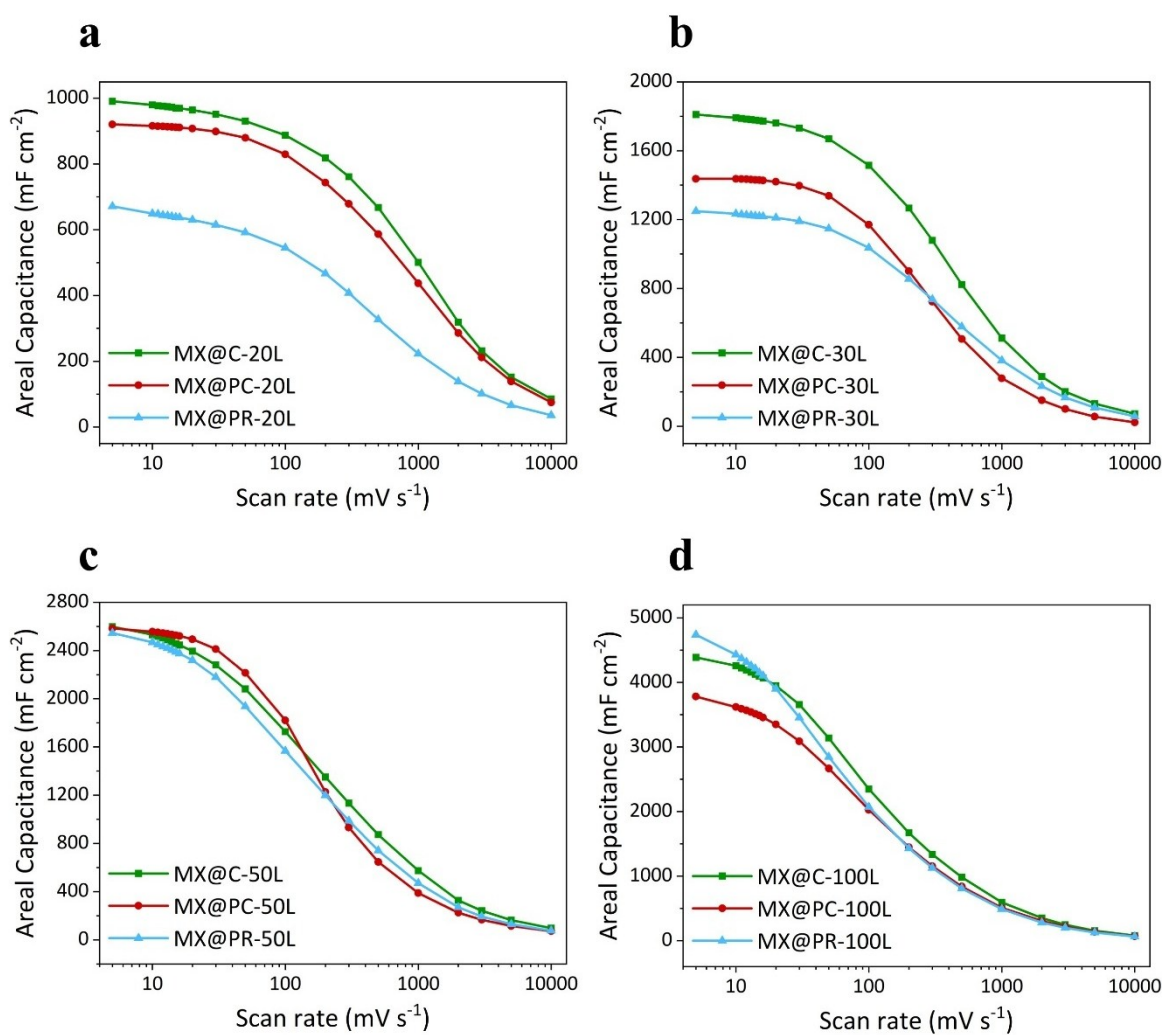


Figure S10: Comparison of rate performance of MX@C, MX@PC, and MX@PR electrodes represented in areal capacitance showcasing the electrochemical behaviour at varying mass loadings: **(a)** 20 layers, **(b)** 30 layers, **(c)** 50 layers, **(d)** 100 layers.

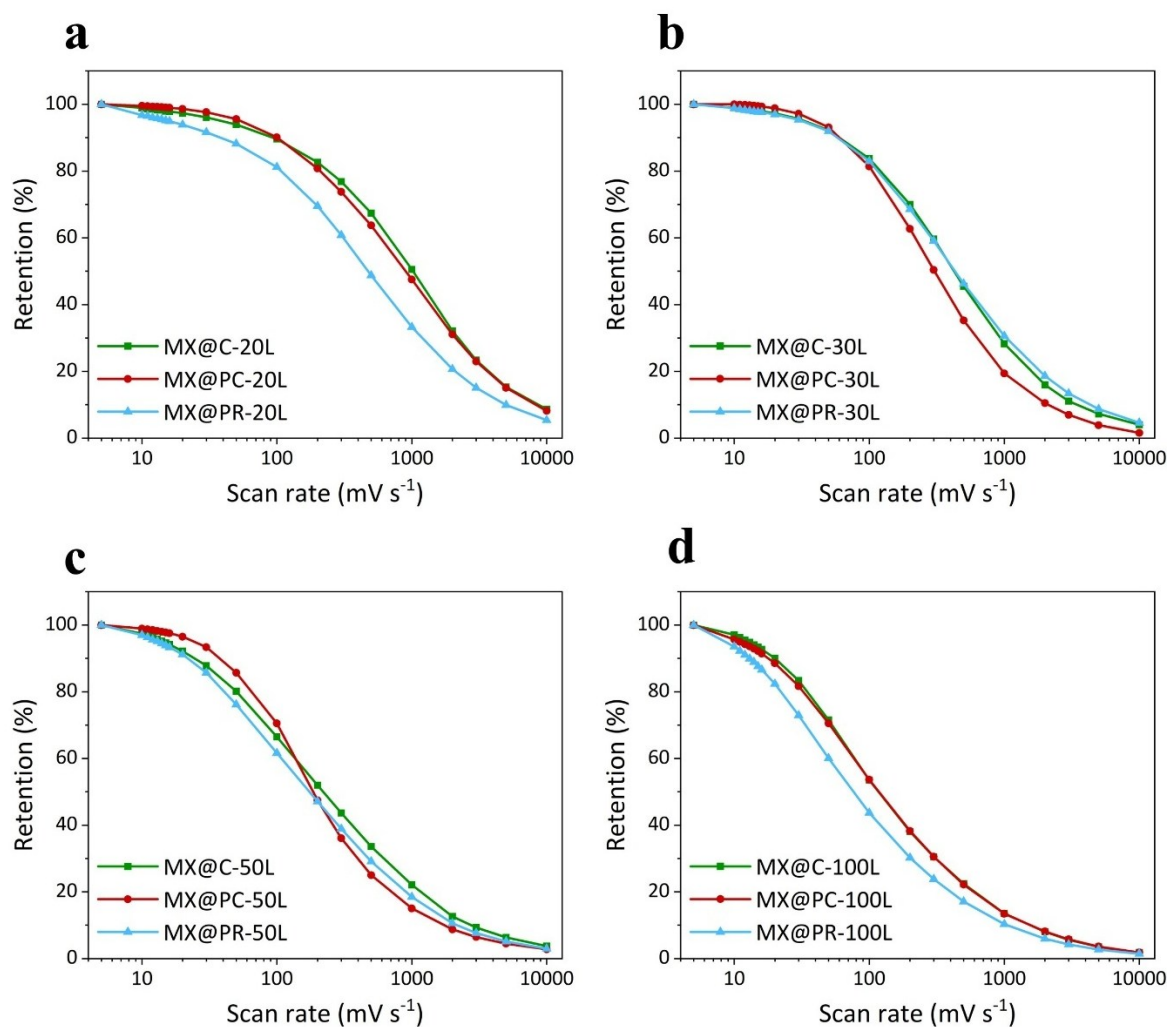


Figure S11: Comparison of areal capacitance retention of MX@C, MX@PC, and MX@PR at varying mass loadings: **(a)** 20 layers, **(b)** 30 layers, **(c)** 50 layers, and **(d)** 100 layers.

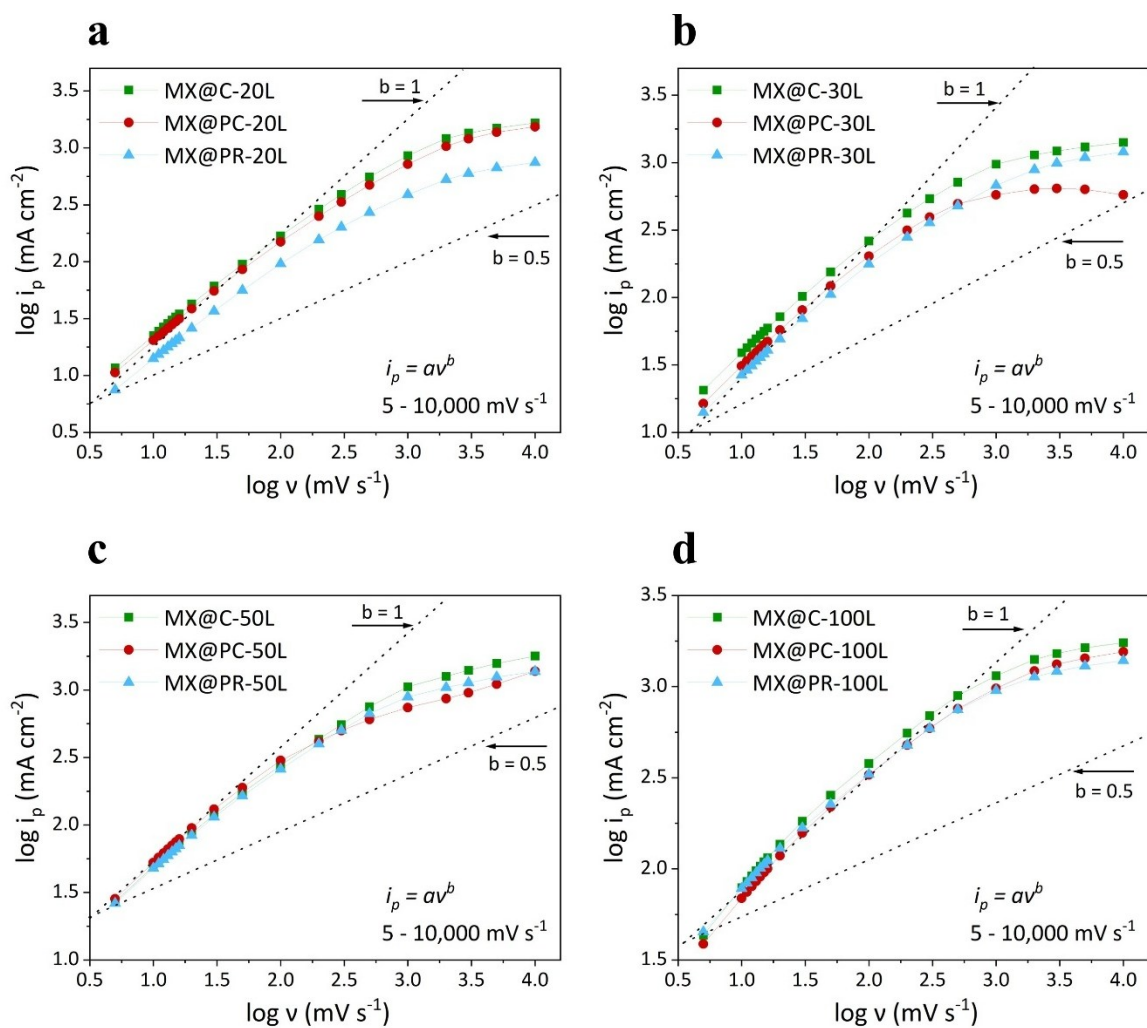


Figure S12: Analysis of the charge storage kinetics via b-values of MX@C, MX@PC, and MX@PR electrodes at varying mass loadings: **(a)** 20 layers, **(b)** 30 layers, **(c)** 50 layers, and **(d)** 100 layers. The dashed line with a slope $b = 1$ indicates the ideal capacitive/pseudocapacitive charging mechanism and fast ion diffusion.

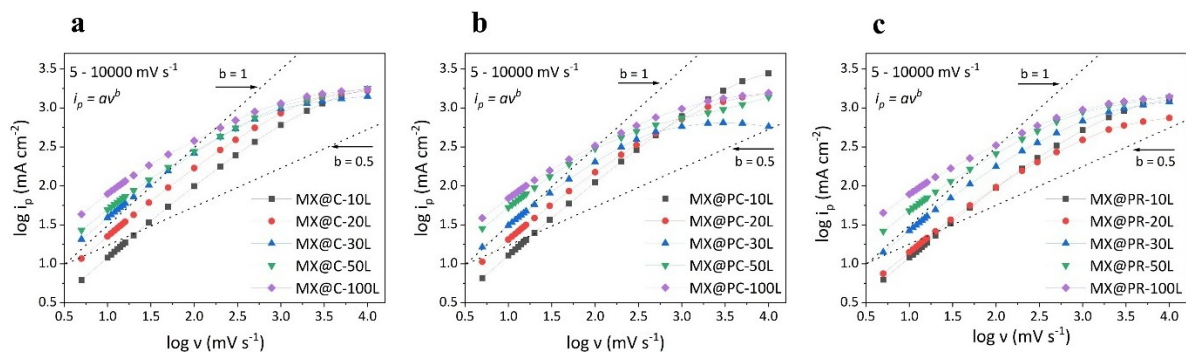


Figure S13: Comparative charge storage kinetics analysis of MX@Fabric-#L electrodes at different mass loadings 10, 20, 30, 50, and 100 layers for **(a)** cotton - MX@C, **(b)** polycotton – MX@PC, and **(c)** polyester – MX@PR.

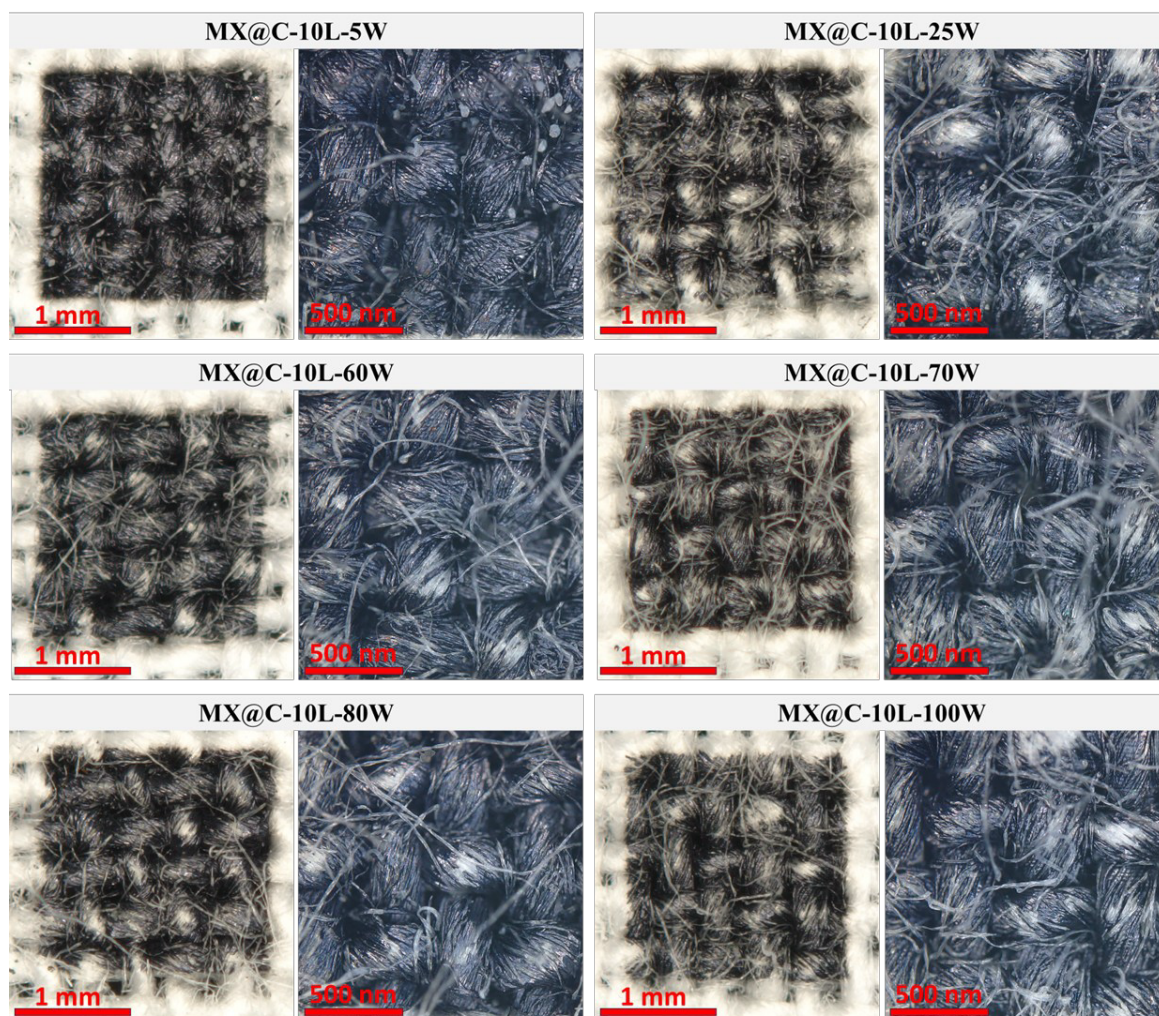


Figure S14: Digital microscope images showcasing the surface evolution of MX@C-10L electrode under different washing cycles: **(a)** 5 washes, **(b)** 25 washes, **(c)** 60 washes, **(d)** 70 washes, **(e)** 80 washes, and **(f)** 100 washes. Each panel presents three representative samples, providing a visual overview of surface changes with increasing washing cycles.

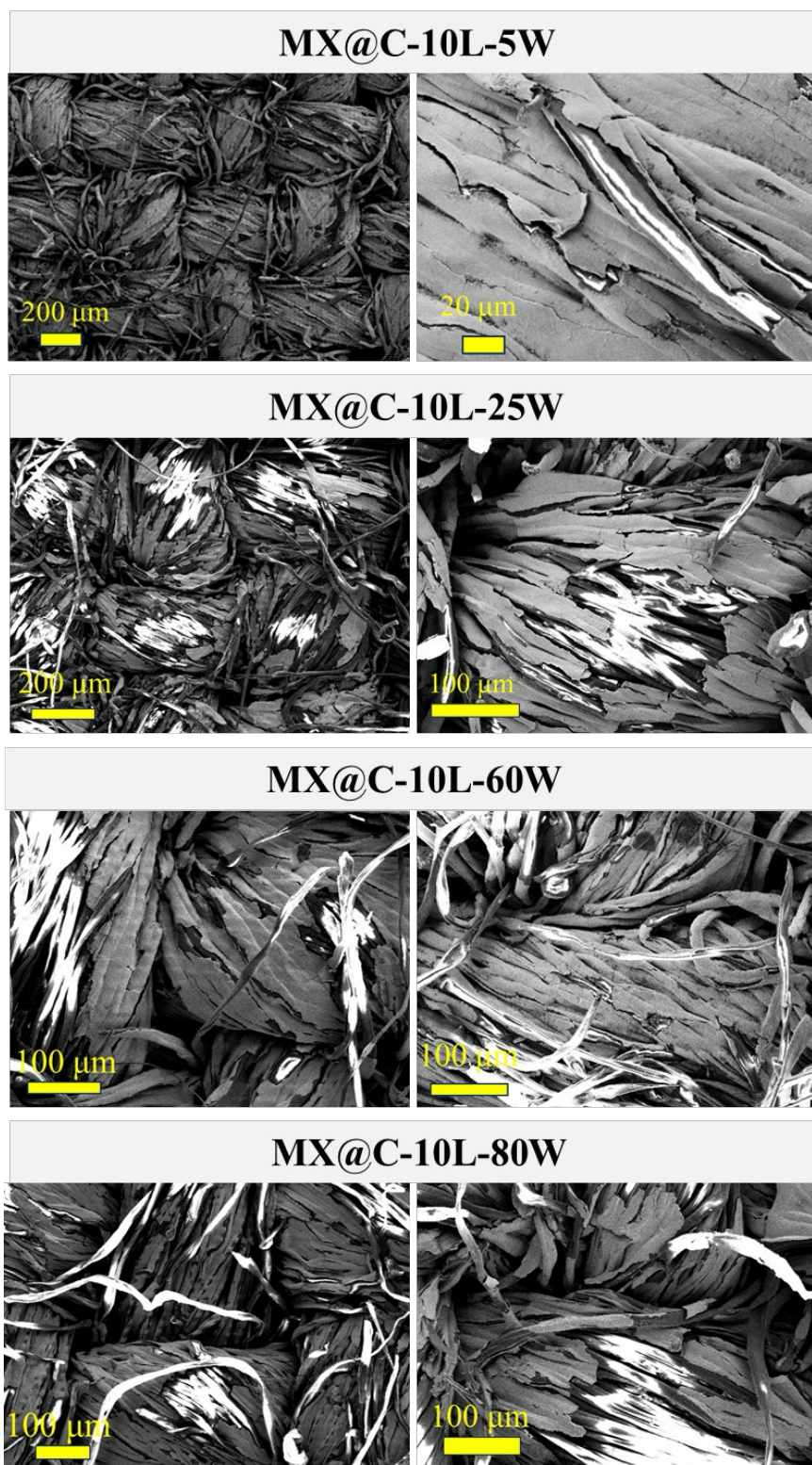


Figure S15: SEM images illustrating the impact of washing cycles on the surface morphology of MX@C-10L electrode at (a) 5 washes, (b) 25 washes, (c) 60 washes, and (d) 80 washes.

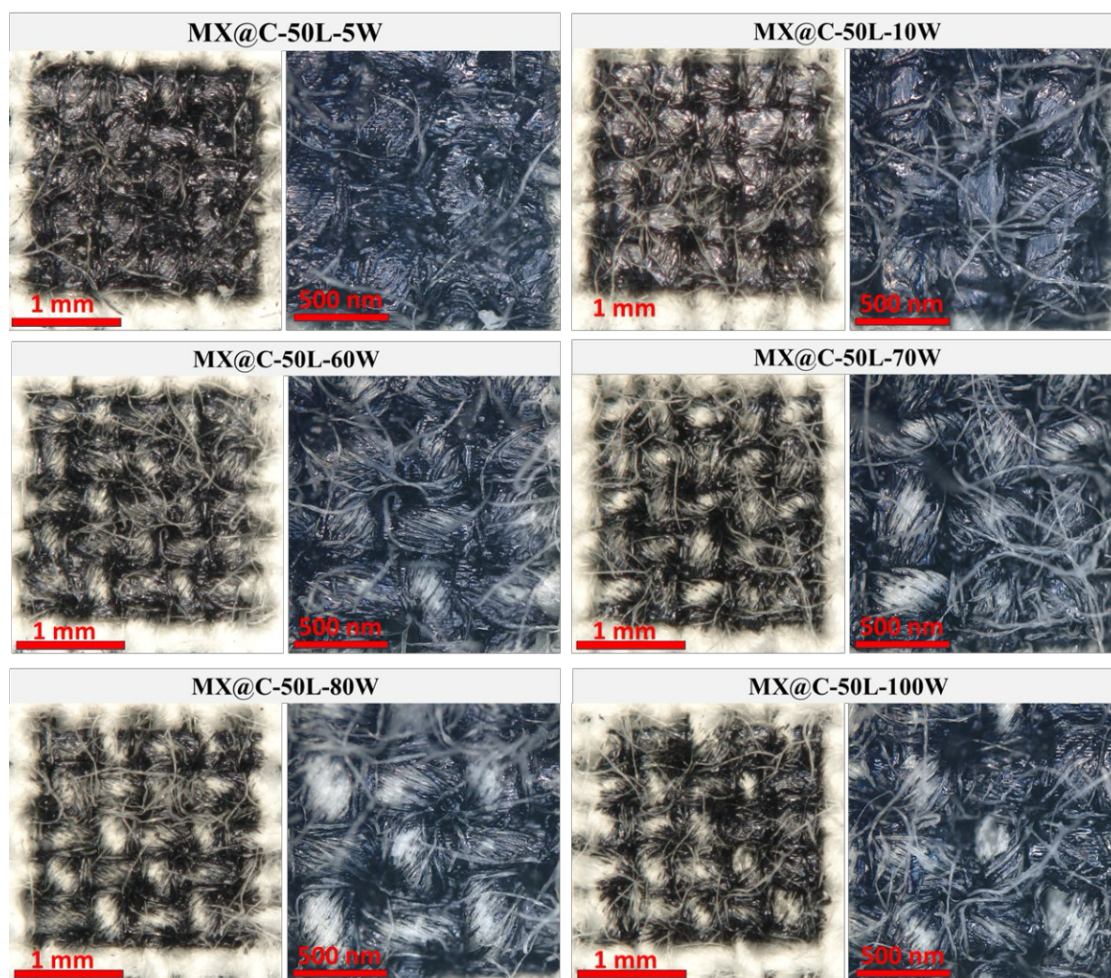


Figure S16: Digital microscope images representing the surface evolution of MX@C-50L electrode under different washing cycles: **(a)** 5 washes, **(b)** 10 washes, **(c)** 60 washes, **(d)** 70 washes, **(e)** 80 washes, and **(f)** 100 washes.

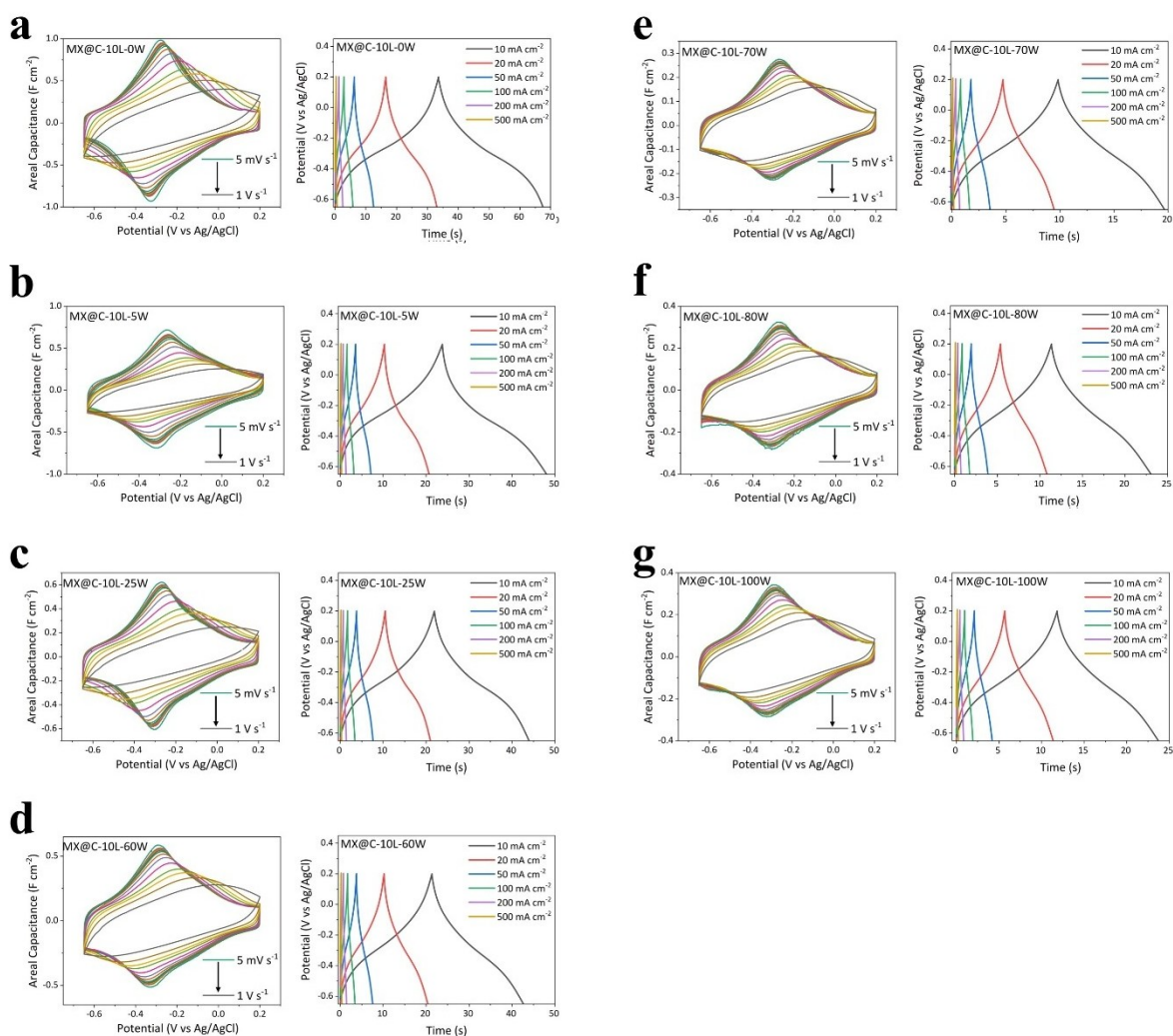


Figure S17: Electrochemical characterization of AJP MX@C-10L electrodes in the washability study, highlighting CVs at scan rates of 5, 10, 11, 12, 13, 15, 16, 20, 30, 50, 100, 200, 300, 500, 1000 mV s^{-1} and GCDs at current densities of 10, 20, 50, 100, 200, and 500 mA cm^{-2} under different washing cycles: **(a)** unwashed, **(b)** 5 washes, **(c)** 25 washes, **(d)** 60 washes, **(e)** 70 washes, **(f)** 80 washes, and **(g)** 100 washes.

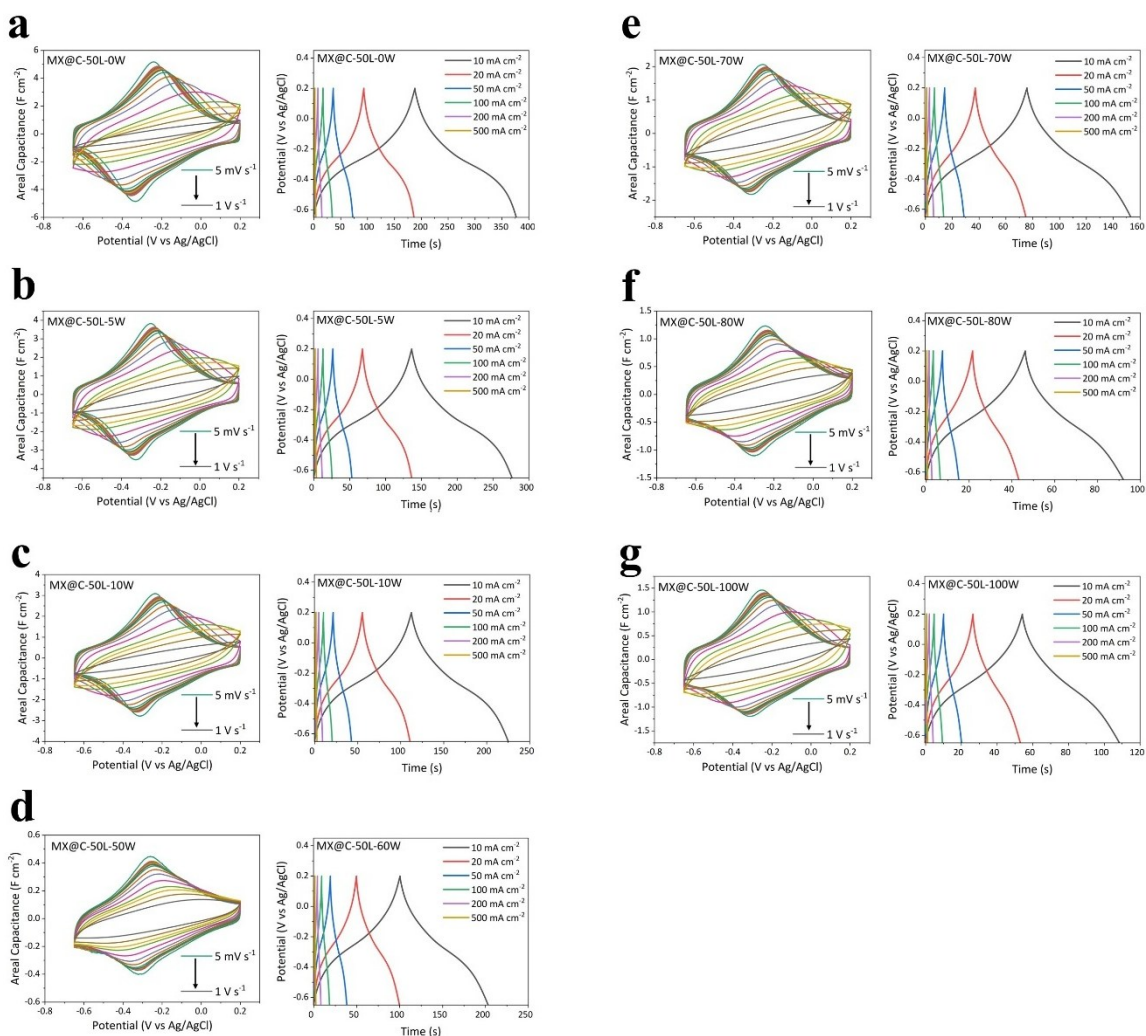


Figure S18: Electrochemical characterisation of AJP MX@C-50L electrodes in the washability study, highlighting CVs at scan rates of 5, 10, 11, 12, 13, 15, 16, 20, 30, 50, 100, 200, 300, 500, 1000 mV s^{-1} scan rates and GCDs at current densities of 10, 20, 50, 100, 200, and 500 mA cm^{-2} under different washing cycles: **(a)** unwashed, **(b)** 5 washes, **(c)** 10 washes, **(d)** 60 washes, **(e)** 70 washes, **(f)** 80 washes, and **(g)** 100 washes.

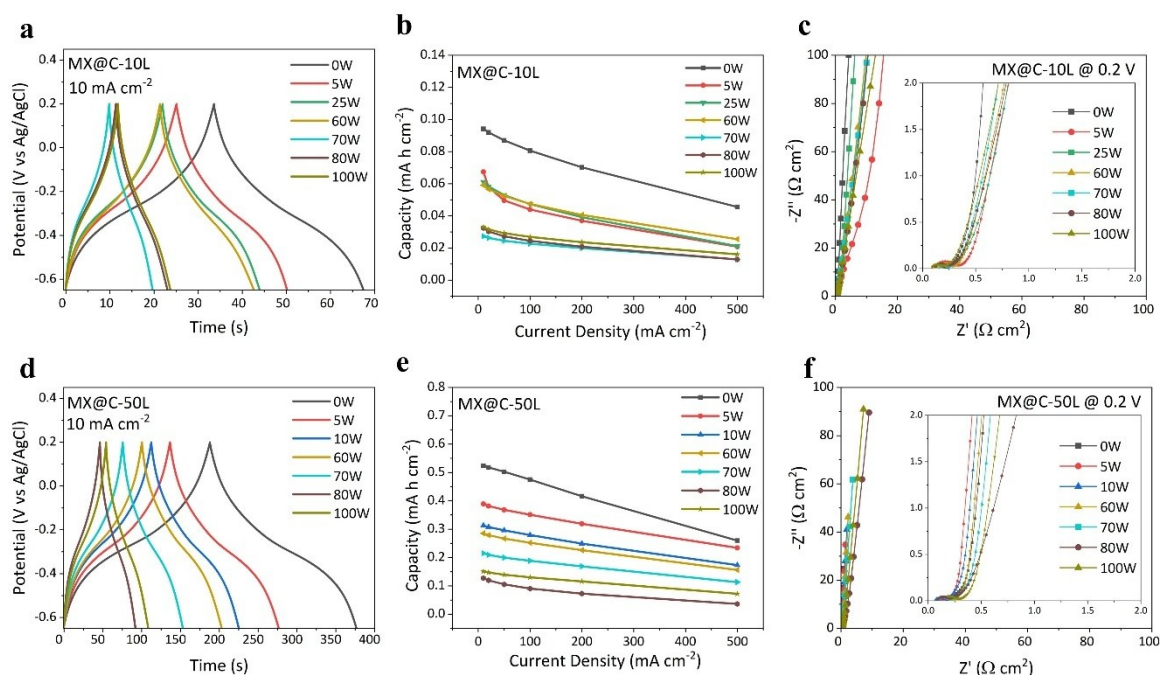


Figure S19: Electrochemical characterisation of AJP MX@C-10L and MX@C-50L electrodes in the washability study, highlighting respectively: **(a, d)** comparison of GCD curves under different washing cycles at 10 mA cm⁻² current density. **(b, e)** Comparative capacity evaluation under different washing cycles. **(c, f)** Comparative EIS of MX@C electrodes recorded at 0.2 V.

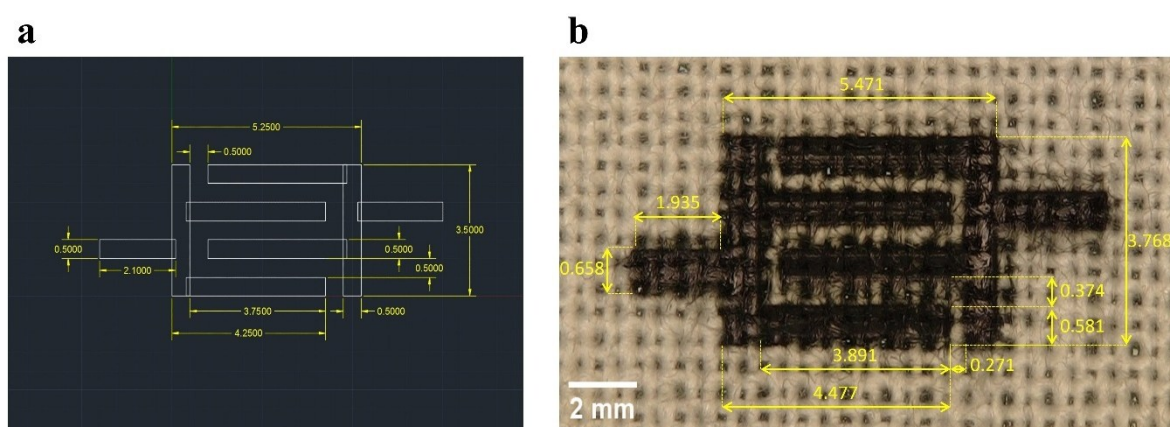


Figure S20: Printed IDD: **(a)** AutoCAD designed vs **(b)** printed pattern.

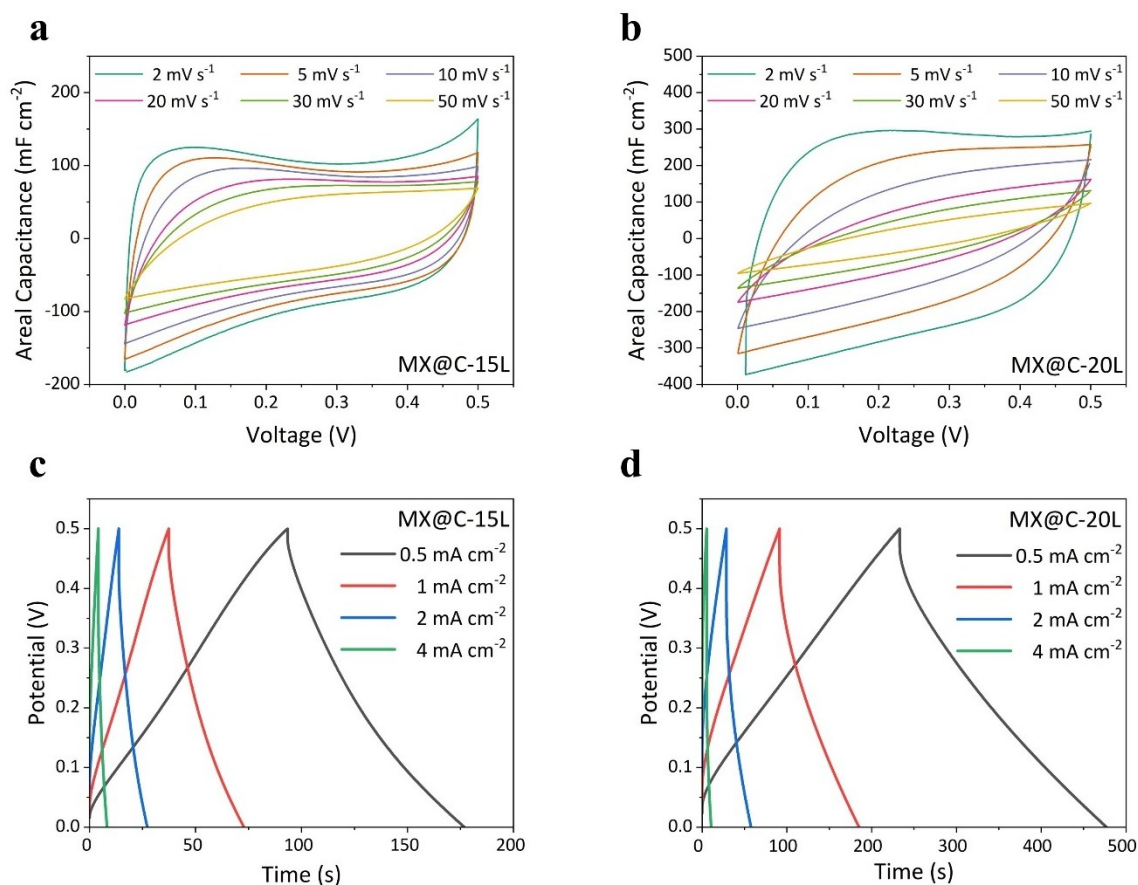


Figure S21: Study of AJP $\text{Ti}_3\text{C}_2\text{T}_x$ MX@Fabric MSCs on cotton fabric (MX@C) with IDD electrode configuration, highlighting: **(a, b)** CV plots of MX@C-15L MSC and MX@C-20L MSC, respectively, at 2, 5, 10, 20, 30, and 50 mV s^{-1} scan rates. **(c, d)** GCD curves of MX@C-15L MSC and MX@C-20L MSC, respectively, at 0.5, 1, 2, 4 mA cm^{-2} current densities, demonstrating symmetrical and linear charge/discharge behaviours with small IR drops.

Comparative Study

Table S3: Areal capacitance comparison in the field of printed MSCs, including samples from this work (MX@C-30L, MX@C-20L, and MX@C-15L) analyzed at a scan rate of 2 mV s⁻¹ and denoted with the asterisk (*) in **Figure 45(a)** in the main text.

Fig. 4(c) Ref.	Areal capacitance @ (Scan rate / current density)	Various printed MSCs	Amount of material deposited	Active material (Ink Conc.) [Additives]	Solvent Substrate Electrolyte	Active Area (AA) Inter-finger Gap (IFG)	Ref
α	381 mF cm ⁻² (2 mV s ⁻¹)	AJP	30L	Ti ₃ C ₂ T _x (10 mg ml ⁻¹) [No additives]	Water Cotton PVA/H ₂ SO ₄	AA: 0.18 cm ² (designed), ~0.21 cm ² (printed) IFG: 500 μm (design), 450 μm (print)	*
β	294 mF cm ⁻² (2 mV s ⁻¹)	Thermal IJP	20L S-Ti ₃ C ₂ T _x + 10L L-Ti ₃ C ₂ T _x	S- Ti ₃ C ₂ T _x (22.4 mg ml ⁻¹) L- Ti ₃ C ₂ T _x (18 mg ml ⁻¹) [No additives]	Water Cotton PVA/H ₂ SO ₄	AA: 1.29 cm ² IFG: 280 μm (optimised)	[106]
γ	249 mF cm ⁻² (2 mV s ⁻¹)	AJP	20L	Ti ₃ C ₂ T _x (10 mg ml ⁻¹) [No additives]	Water Cotton PVA/H ₂ SO ₄	AA: 0.18 cm ² (design), ~0.21 cm ² (print) IFG: 500 μm (design), 380 (print)	*
δ	158 mF cm ⁻² (0.08 mA cm ⁻²)	Screen printing	5L	Ti ₃ C ₂ T _x (NA) [No additives]	Water Paper PVA/H ₂ SO ₄	AA: NA IFG: 200 μm	[639]
ε	151.2 mF cm ⁻² (5 mV s ⁻¹)	3D printing	4L (1.3 μm each)	PPy/PAni coaxial nanotube & rGO (PPCANT/rGO) (NA) [GO stabiliser]	Water Paper PVA/H ₃ PO ₄	AA: NA IFG: NA	[640]

Fig. 4(c) Ref.	Areal capacitance @ (Scan rate / current density)	Various printed MSCs	Amount of material deposited	Active material (Ink Conc.) [Additives]	Solvent Substrate Electrolyte	Active Area (AA) Inter-finger Gap (IFG)	Ref
ζ	135.4 mF cm ⁻² (0.08 mA cm ⁻²)	Screen printing	1.7 mg cm⁻²	PEDOT:PSS@ MnO ₂ (NA) [No additives]	Water Polyester PVA/LiCl	AA: NA IFG: 790 μm	[641]
η	103 mF cm ⁻² (2 mV s ⁻¹)	Thermal IJP	10L S- Ti ₃ C ₂ T _x + 10L L- Ti ₃ C ₂ T _x	S- Ti ₃ C ₂ T _x (22.4 mg ml ⁻¹) L- Ti ₃ C ₂ T _x (18 mg ml ⁻¹) [No additives]	Water Cotton PVA/H ₂ SO ₄	AA: 1.29 cm ² IFG: 450 μm	[106]
θ	100 mF cm ⁻² (2 mV s ⁻¹)	AJP	15L	Ti ₃ C ₂ T _x (10 mg ml ⁻¹) [No additives]	Water Cotton PVA/H ₂ SO ₄	AA: 0.18 cm ² (design), ~0.21 cm ² (print) IFG: 500 μm (design), 380 (print)	*
ι	72 mF cm ⁻² (1 mA cm ⁻²)	EP deposition, EDP	NA	P-TiON/VN AMSC (NA) [Mg(NO ₃) ₂ surfactant]	Multiple NA PVA/LiCl	AA: NA IFG: NA	[642]
κ	61 mF cm ⁻² (25 μA cm ⁻²)	Stamping	1L	Ti ₃ C ₂ T _x (NA) [No additives]	Water Paper PVA/H ₂ SO ₄	AA: NA IFG: 300 μm	[288]
λ	43 mF cm ⁻² (10 mV s ⁻¹)	Extrusion printing	5L	Ti ₃ C ₂ T _x (36 mg ml ⁻¹) [No additives]	Water Paper PVA/H ₂ SO ₄	AA: NA IFG: 89 μm	[258]

Fig. 4(c) Ref.	Areal capacitance @ (Scan rate / current density)	Various printed MSCs	Amount of material deposited	Active material (Ink Conc.) [Additives]	Solvent Substrate Electrolyte	Active Area (AA) Inter-finger Gap (IFG)	Ref
μ	27.29 mF cm ⁻² (0.25 mA cm ⁻²)	Laser printing, vacuum assisted deposition, physical sputtering	thickness of electrode 2.2 μm	Ti ₃ C ₂ T _x (0.1 mg ml ⁻¹) [No additives]	Water Paper PVA/H ₂ SO ₄	finger width 745 μ m IFG: 305 μ m	[643]
ν	23 mF cm ⁻² (0.1 mA cm ⁻²)	Laser cutting, spray coating	4 μm film	Ti ₃ C ₂ T _x NA [No additives]	Water PET PVA/H ₃ PO ₄	Electrodes: 8 mm L 1 mm W IFG: 1000 μ m	[298]
ξ	12 mF cm ⁻² (NA)	IJP	25L	Ti ₃ C ₂ T _x (12.5 mg ml ⁻¹) [No additives]	NMP AlOx-coated PET PVA/H ₂ SO ₄	AA: NA IFG: 410 μ m	[258]
$\circ$	8.8 mF cm ⁻² (0.5 mA cm ⁻²)	Metal deposition, IJP & extrusion printing	NA	ENER-CE800 (active carbon-based) (NA) [No additives]	NA Cotton ENER-EI40W (PVA-based)	AA: NA IFG: NA	[637]
π	1.324 mF cm ⁻² (0.0125 mA cm ⁻²)	Screen printing	1 mg	WJM-graphene:SWC NTs (80 mg ml ⁻¹) [No additives]	NMP, H ₂ O/EtOH, terpineol Polyester PVA/H ₃ PO ₄	AA: 1 cm ² IFG: 600 μ m	[644]
ρ	0.86 mF cm ⁻² (long cycling 50 μ A)	IJP	20L	Ti ₃ C ₂ T _x (1.5 wt.%) [SNC, sodium ascorbate, LDS]	Water TPU coated cotton UV curable LiCl/EG/AM/MB A electrolyte	AA: ~1 cm ² IFG: 600 μ m	[451]

Table S4: Comparative analysis of energy and power density for printed MSCs reported in the literature. The table includes samples from this study, denoted by an asterisk (*). The highlighted entries correspond to the samples in the Ragone plot **Figure 45(b)** in the main text, providing insights into the performance landscape of printed MSCs.

Fig. 4(d) Caption				Ref
AJP MX@C-30L*	Current density (mA cm ⁻²)	Energy density (μWh cm ⁻²)	Power density (mW cm ⁻²)	*
	0.5	10.88693	0.10188	
	1	9.26200	0.19459	
	2	6.86533	0.34846	
	4	3.58583	0.53354	
Thermal IJP MX@C-30L	Current density (mA cm ⁻²)	Energy density (μWh cm ⁻²)	Power density (mW cm ⁻²)	[106]
IJP 20L S- Ti ₃ C ₂ T _x	0.5	12.36000	0.16000	
+	1	7.96000	0.26000	
10L L- Ti ₃ C ₂ T _x	2	6.09000	0.40000	
	4	4.46000	0.58000	
Thermal IJP MX@C-20L	Current density (mA cm ⁻²)	Energy density (μWh cm ⁻²)	Power density (mW cm ⁻²)	[106]
IJP 10L S- Ti ₃ C ₂ T _x	0.5	4.31000	0.06000	
+	1	4.04000	0.13000	
10L L- Ti ₃ C ₂ T _x	2	3.69000	0.24000	
	4	3.30000	0.43000	

Fig. 4(d) Caption				Ref
AJP MX@C-15L*	Current density (mA cm ⁻²)	Energy density (μWh cm ⁻²)	Power density (mW cm ⁻²)	*
	0.5	2.12150	0.09146	
	1	1.70072	0.17234	
	2	1.16674	0.31187	
	4	0.58254	0.51195	
SP MX@P-5L		Energy density (μWh cm ⁻²)	Power density (mW cm ⁻²)	[639]
		1.64000	0.01846	
		1.62000	0.03711	
		1.57000	0.07557	
		1.51000	0.15698	
		1.42000	0.33499	
		1.36000	0.54412	
Stamp MX@P-1L		Energy density (μWh cm ⁻²)	Power density (mW cm ⁻²)	[288]
		0.76000	0.00617	
		0.74000	0.01406	
		0.73000	0.03031	
		0.71000	0.06478	
		0.68000	0.13536	
		0.63000	0.32644	

Fig. 4(d) Caption				Ref
EXTR MX@P-5L		Energy density ($\mu\text{Wh cm}^{-2}$) 0.31660 0.31200 0.30650 0.20860 0.16030 0.10940	Power density (mW cm^{-2}) 0.01140 0.02250 0.04410 0.07510 0.11540 0.15770	[258]
SP WJM-graphene:SWCNTs@PR		Energy density ($\mu\text{Wh cm}^{-2}$) 0.36100	Power density (mW cm^{-2}) 1.13000	[644]
IJP IDD	Cycling at 50 μA	Energy density ($\mu\text{Wh cm}^{-2}$) 0.08000	Power density (mW cm^{-2}) 0.02000	[451]