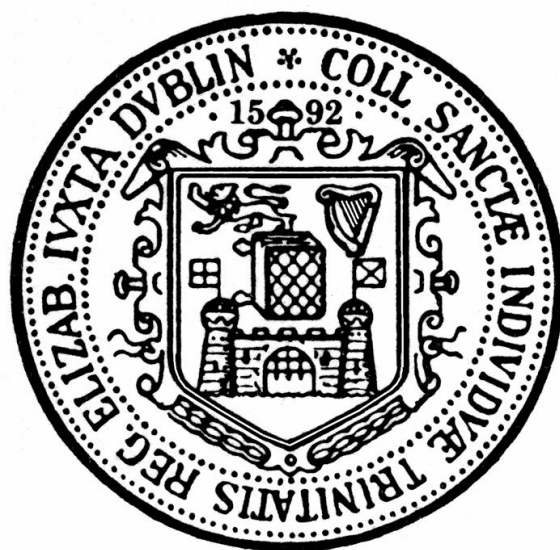


In-situ and Operando (Scanning)
Transmission Electron Microscopy (S)TEM;
a real-time investigation of energy storage
devices and materials at the atomic level



University of Dublin, Trinity College
School of Chemistry
Faculty of Science, Technology, Engineering and Mathematics

A thesis presented to the University of Dublin, Trinity College for the
degree of Doctor of Philosophy (PhD)
Hilary Term, 2021

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DECLARATION

I declare that this thesis has not been submitted as an exercise for a degree at this or any other university and it is entirely my own work.

This thesis includes unpublished work completed in collaboration with others, and have been duly acknowledged in the text wherever included.

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Hilary Term, 2021

Oskar H.L. Ronan

"I'll be honest, we're throwing science at the wall to see what sticks.

No idea what it'll do; probably nothing.

Best case scenario: You might get some superpowers.

Worst case: Some tumours, which we'll cut out."

— Cave Johnson

Dedicated to the loving memory of Tom Leonard,

For my first microscope.

1924 – 2004

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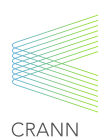
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PUBLICATIONS

- [1] **Oskar Ronan**, Clive Downing, and Valeria Nicolosi. “Novel method for inhibition of vacuum sublimation artefacts for (Scanning) Transmission Electron Microscopy ((S)TEM) of sulphur samples *via* encapsulation.” **Under Preparation** (2021), *Work basis for Chapter 9*.
- [2] Juhan Lee, **Oskar Ronan**, Dahnna Spurling, Clive Downing, Ahin Roy, Valeria Nicolosi, and B. Layla Mehdi. “Real-time Visualisation of MXene Anode *via in-situ* Scanning Transmission Electron Microscopy in a Liquid-sealed Li-ion Battery Cell.” **Under Preparation** (2021), *Work basis for Chapter 8*.
- [3] Nicola Taurisano, Sonia Carallo, Meiyang Liang, **Oskar Ronan**, Dahnna Spurling, João Coelho, Valeria Nicolosi, Silvia Colella, Giuseppe Gigli, Andrea Listorti, and Aurora Rizzo. “Implementation of 2D Transition Metal Dichalcogenides in Inverted Perovskite – Based Solar Cell.” **Under Preparation** (2021).
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ABSTRACT

In the modern age of ubiquitous mobile technology, demand for ever increasing battery capacity and size reduction in such devices is a key driving factor for this sector. Technology is currently striving to improve the power density of batteries and the energy density of supercapacitors. To do so it is imperative to develop new materials, chemistries and manufacturing strategies. However, before all these proposed potential applications can be realised it is crucial to understand the fundamental processes taking place during materials synthesis, processing and device functioning. In real technological applications, a material may in fact be exposed to a variety of stimuli such as mechanical stress, and electric fields. The response of the material to these stimuli often determines their functionality, behaviour and performance in applications.

The aim of this work is to develop a detailed description of the materials under scrutiny in their working states and develop an experimental approach which combines advanced microscopy techniques and electrochemical testing using a specialised *in-situ* liquid-cell holder developed for electron microscopy. This was used to observe and image electrode materials (specifically, Si-based conversion-alloying anode materials) in their working state on the nano-scale. This experimental approach has effectively allowed for a TEM to be used as a “nano-laboratory” for carrying out dynamic electrochemical experiments on a small spatial scale.

Furthermore, in addition to observing materials in their working state, *in-situ* techniques can be used to also capture important intermediate transitional forms, that may be missed by more conventional *post-mortem* methods. To date, we have successfully printed an electrochemical cell consisting of silicon nanoparticles and

LiFePO_4 , and assemble it for *in-situ* observation; this technique is still in the early stages of development, and the experimental issues arising from attempting to perform this type of *in-situ* Transmission Electron Microscopy analysis and solutions are discussed in this work.

Transmission Electron Microscopy (TEM), and Scanning Transmission Electron Microscopy (STEM) have proven to be useful tools for such characterization, allowing structure, composition, bonding and spectroscopic imaging to be followed at the atomic level.

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ACRONYMS AND CONSTANTS

SEI Solid Electrolyte Interphase

CV Cyclic Voltammetry/Cyclic Voltammogram

EC ethylene carbonate ($\text{C}_4\text{H}_6\text{O}_3$)

DMC dimethyl carbonate ($\text{C}_3\text{H}_6\text{O}_3$)

TEM Transmission Electron Microscopy

(S)TEM (Scanning) Transmission Electron Microscopy

EDX Energy-dispersive X-ray Spectroscopy

EELS Electron Energy Loss Spectroscopy

ELNES Electron Energy Loss Near Edge Structure

EFTEM Energy Filtered Transmission Electron Microscopy

SAED Selected Area Electron Diffraction

FEG Field Emission Gun

BF Bright Field

DF Dark Field

HAADF High-Angle Annular Dark Field

MAADF Medium-Angle Annular Dark Field

ABSF Average Background Subtraction Filter

$$h \quad 6.626 \times 10^{-34} \text{ m}^2 \text{ kgs}^{-1}$$

$$c \quad 2.99 \times 10^8 \text{ ms}^{-1}$$

$$m_0 \quad 9.109 \times 10^{-31} \text{ kg}$$

$$e \quad 1.602 \times 10^{-19} \text{ C}$$

I

INTRODUCTION AND THEORY

MOTIVATION AND REPORT OVERVIEW

TEM is widely accepted as one of the most powerful analysis techniques for materials research. Observing materials in their working conditions may provide key insight into the mechanisms by which a variety of materials store charge for emerging energy storage technologies. Such studies into these mechanisms are usually performed as *post-mortem* analysis,¹ using material retrieved from cycled cells (which can be damaged or chemically altered by the process of removing them from their environment), or using a "stop motion" approach (in which material is removed from a cell at regular intervals to analyse its changes). Such methods, while useful, can be very time consuming. Nanoscale variations of individual particles must be explored if a deep understanding of the structure–property relations and critical stages of reactions (such as any short-lifetime intermediate states of these reactions) are to be understood. Such reactions are difficult to capture with the former approach.^{1,2} Furthermore, such *in-situ* techniques can trace the structural and potentially chemical changes of a single isolated part of the material over time,^{3–6} in contrast to the methods described before, where a different sample of material is analysed each time.^{1,7} Liquid cell TEM has only recently become a viable analysis method due to advancements in specimen holder fabrication, and is still a fast-growing area of research.^{8,9} As a result, *in-situ* Liquid Cell TEM is quickly becoming a vital tool for studying the dynamics of nanoscale samples in a liquid environment. It is the aim of this project to utilise this emerging technology to study the electrochemical reactions of Li^+ -ion battery electrode materials in a way that has

not been possible previously.⁹

In order to accomplish this, silicon was selected as a good candidate for *in-situ* experiments due to its high volumetric expansion, which should be extremely evident in the microscope,^{10–14} (and can even be observed with light microscopes with sufficiently large particles¹⁵) unlike some materials studied thus far via this technique whose physical and chemical changes are more subtle (such as MoS₂ nanosheets, FeO₄, and LiFePO₄).^{16–18} Furthermore, the limitations of spatial resolution in liquid cell TEM act in favour of such a material, as the large average size of the Si nanoparticles ($\approx 100\text{nm}$) would not require higher resolutions, and as this material stores energy via a lithium-alloying (a more physical process), chemical changes determined by EELS are less critical for analysis.

Furthermore, Ti₃C₂ MXene was also selected as a candidate material for the *in-situ* experiments presented due to its rising popularity among the energy storage research community.¹⁹ Its promise as a competitor to graphite as an anode material makes studying the dynamic lithiation reactions that may occur during the electrochemical cycling process a subject of great interest, and is also studied here.^{20,21}

Using such novel *in-situ* liquid cell TEM techniques, the aim is to study these surface chemistry reactions in their operating conditions on the atomic scale, and identify the issues surrounding *in-situ* TEM analysis of materials. To date, this is something that has only been successfully achieved in single nanowire observations,^{10,22,23} and not in practical lithium-ion battery technology materials. Electrochemical liquid cell TEM as a technique is still in its infancy and work still needs to be done for it to become mainstream, however it shows great promise for the future of energy storage materials analysis.

Finally, on a separate yet related note, experiments on a method to inhibit imaging condition artefacts on vacuum-unstable samples were conducted. Sulphur, being a material that is both of great interest for lithium-sulphur battery applications in the energy storage research community and one that undergoes sublimation under high-vacuum conditions was chosen for this project.²⁴⁻²⁷ A novel, facile method of inhibiting the sublimation of sulphur to allow for TEM analysis of the material is presented to enable the use of TEM and its robust analysis capabilities for this material where many difficulties were present before. The technique uses a commercial *in-situ* gas holder, which encapsulates the material in a high-pressure (1bar, relative to the vacuum of the TEM) environment to prevent sublimation. This developed method presents new materials analysis opportunities for battery material researchers.

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LITHIUM-ION BATTERIES: AN OVERVIEW

In the following chapter, lithium-ion battery energy storage mechanisms, electrode materials, and electrochemical characterisation techniques are introduced. Three materials are studied (silicon, MXenes, and sulphur), and their respective lithium-ion storage mechanisms, capacity and cyclability benefits over the ubiquitous graphite electrode are introduced here. The main electrochemical characterisation technique used in this work of cyclic voltammetry and the relevance of each material to the state of the art, and commonly used electrode materials is introduced.

2.1 AN INTRODUCTION TO BASIC BATTERY CHEMISTRY

One of the first examples of the modern concept of the battery was developed over 200 years ago in Italy. The Italian physicist and nobleman Alessandro Volta, building on the work of Luigi Galvani, developed the theory that electric current was developed by the contact between two different metals (the anode and cathode). From this, the first “electrochemical pile” was created; this consisted of a series of interchanging zinc and silver (or copper) disks, separated by paper soaked in an electrolyte solution (either sulfuric acid or a salt solution). The tendency of an anode or cathode material to lose or accept electrons respectively is known as its Standard Electrode Potential, and is a characteristic property of a material. The voltage difference between the standard electrode potentials of the two materials

determines the total voltage of the cell.^{1–5} It was realised soon afterward that this potential could be used to do work.¹ Thus, the battery was created.

The two types of batteries of this type in modern use are primary and secondary batteries. Primary batteries are ubiquitous in modern technology due to their low cost, but suffer from the major disadvantage of not being rechargeable.^{1,5} In this work, secondary (or rechargeable) batteries (specifically lithium ion batteries) are studied. In recent years, lithium-ion batteries have been the workhorses of modern consumer electronics, and the subject of much scrutiny for many years due to their high energy density compared to other battery types.^{5–7}

2.2 LITHIUM-ION BATTERIES

A common mechanism by which lithium-ion batteries store energy is via a different mechanism than basic oxidation-reduction reactions. This mechanism, known as intercalation is the reversible migration of Li^+ -ions into interstitial lattice sites in the Li^+ -ion accepting anode material.^{5,8,9} In the charge process, the anode is electrochemically reduced, which results in the uptake of Li^+ -ions into the electrode (intercalation). Electrons move through the external circuit from the cathode to the anode, and the Li^+ -ions travel through the electrolyte to compensate for the negative charge flowing through the external circuit, which results in oxidation of the cathode, and the release of Li^+ -ions (deintercalation). When the cell is discharged, the reverse processes occur (as shown in Figure 1).^{3–6,8,9}

This process is, unsurprisingly, diffusion-based. Under the Einstein–Smoluchowski relation,^{10–12} which can be used to describe the mobility a particle in a medium under Brownian motion:

$$D = \mu k_B T \quad (1)$$

D = Einstein Diffusion constant, μ = mobility of a particle, k_B = Boltzmann's constant, T = absolute temperature (in K).

This equation can be expanded to apply to electrophoresis (the motion of a charged particle in a fluid acting under an applied uniform electric field^{2,13}). The mobility (μ) of a particle is defined as the velocity a particle can move through a medium when an external force is applied:

$$\mathbf{v_d} = \mu \mathbf{F} = \mu \mathbf{E} \quad (2)$$

μ = mobility, $\mathbf{v_d}$ = drift velocity, $\mathbf{F}$ = Force applied, $\mathbf{E}$ = Electric Field applied

In the case of a parallel plate electrochemical cell configuration, this applied force is the electric field across the cell, and the Einstein–Smoluchowski relation becomes:

$$D = \frac{\mathbf{v_d}}{\mathbf{E}} k_B T$$

or:

$$\mathbf{v_d} = \frac{D}{k_B T} \mathbf{E} = \frac{D}{k_B T} \frac{dV}{ds} \quad (3)$$

ds = incremental distance travelled by the charged particle to the electrode, dV = voltage applied across the electrodes, as $V = \int_{V_1}^{V_2} \mathbf{E} \cdot d\mathbf{s}$

As we can see in Equation 3 the drift velocity of the charged particle (or Li^+ -ion in this case) is directly related to the applied voltage across the electrochemical cell (dV). Thus, the rate of diffusion, or Li^+ -ion intercalation is also directly related to the applied voltage across the cell. One of the most common Li^+ -ion intercalation materials is graphite. Due to its layered structure, graphite can accommodate large amounts of Li^+ -ions, or charge between its layers(Figure 1); this capacity for charge storage, along with its low toxicity is what makes graphite a popular energy storage

material for Li^+ -ion batteries. Despite its advantages, graphite is limited by its low theoretical maximum capacity and much of the effort of the lithium ion battery research community has been focused on exploring new materials with higher capacities for energy storage.⁵ Intercalation is not the only mechanism by which Li^+ -ions can be stored by a material; other mechanisms are explored in the next sections. Alloying (a similar process to intercalation but less reversible over time) is demonstrated by silicon nanoparticles, intercalation is demonstrated by MXene flakes, and redox storage reactions are demonstrated by sulphur.

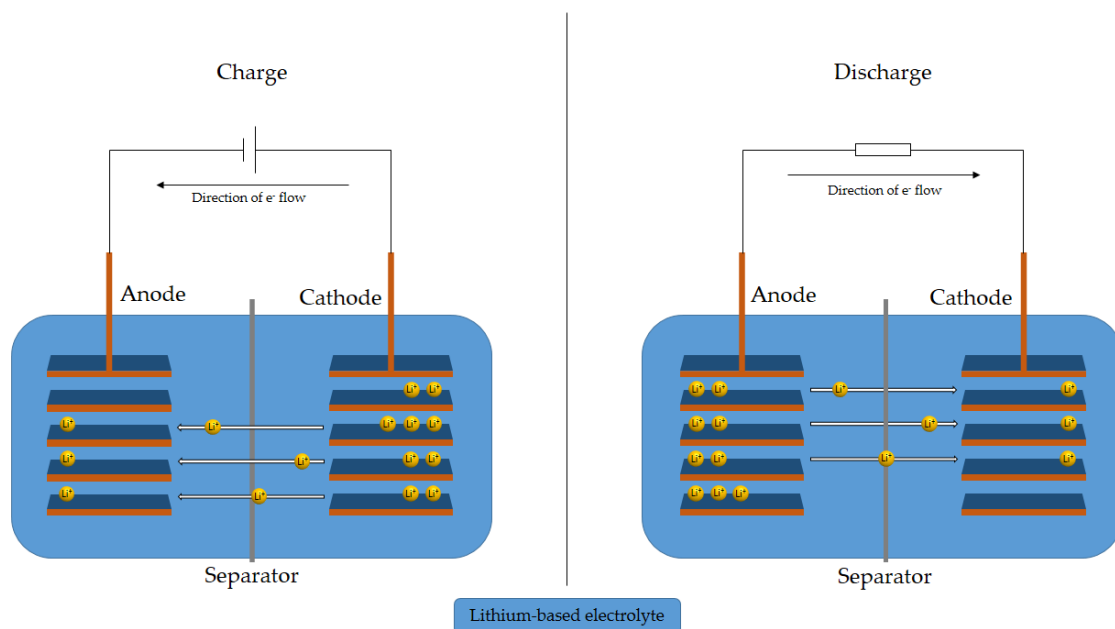


Figure 1: Schematic of Li^+ -ion intercalation in layered materials. Li^+ -ions are stored between the lattice planes of these materials. Electrons move through an external circuit to balance the charges. Li^+ -ion migration through the electrolyte is also shown.

2.3 SILICON AS A LITHIUM-ION BATTERY ANODE MATERIAL

As an anode material, silicon has been gathering increasing attention as an alternative material to graphite used in most modern Li^+ -ion energy storage devices and

has been the subject of much research in our group.¹⁴ This is due to its much higher theoretical capacity for charge storage (3579 mAhg^{-1} for silicon^{14–17} (Li_xSi ; highest capacity phase: $\text{Li}_{15}\text{Si}_4$) compared to 372 mAhg^{-1} for graphite¹⁸ (LiC_6)¹⁹). This almost 10-fold increase in capacity over graphite makes it an extremely attractive alternative in this age of ubiquitous, power-hungry, battery-powered electronics.^{20,21} Unfortunately, one of the drawbacks of Si as an anode material is its low mechanical stability upon cycling. High cyclability is necessary for consumer electronics. The mechanism by which Si stores Li^+ -ions is different from the traditional intercalation described earlier in Chapter 2, and in Figure 1. Li^+ -ion insertion in Si proceeds via an amorphisation of the surface of the Si. As the Li^+ -ions diffuse into the surface, the crystal structure of Si is broken down. The Si particles can increase in volume by up to 300% during this process,^{15,17,20,22–25} as shown in Figure 2; this is what leads to the pulverisation of the Si surface, and thus its low mechanical stability and cyclability.^{15,23–25} Materials that store charge carriers in this way are known as conversion-alloying anode materials, and show great promise as high capacity Li^+ -ion battery materials.^{26–28}

Generally speaking, lithium conversion-alloying reactions can be divided into two types; insertion reactions, and displacement reactions.^{15,20,29} In insertion reactions, the Li^+ -ions combine with the host anode material to create the alloy. It is possible for this reaction to take place with or without a phase/structural change to the anode material (known as addition and solid-solution reactions respectively). In displacement reactions, the Li^+ -ions take the place of a component (thus displacing it) of the host anode material. Displacement alloying tends to be less reversible than insertion alloying, and since Si is an addition insertion alloying material, displacement reactions will not be discussed further.^{15,20,29}

As Si undergoes addition insertion alloying, the crystal structure is changed (in this case amorphised) during charge and discharge cycles. As subsequent cycles occur the reaction changes from an addition to a solid-solution reaction, as Si has

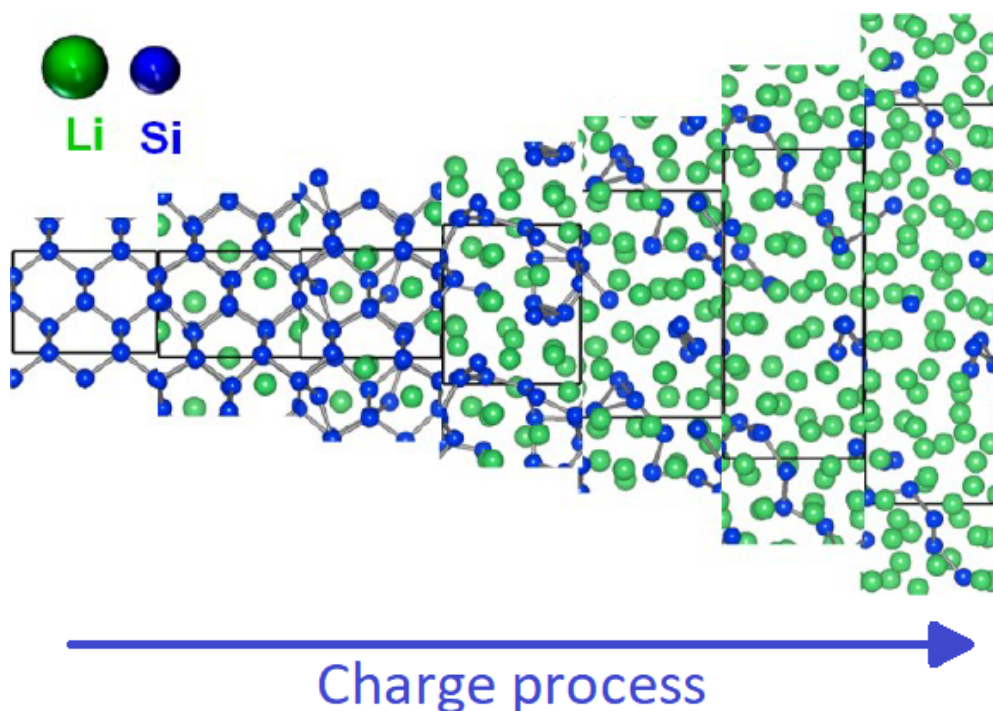


Figure 2: Showing the amorphisation of crystalline silicon (cSi) upon Li^+ -ion insertion. The volumetric expansion of Si is also depicted from pristine cSi (left) to fully amorphised (right); the cell expansion can be seen as the black boxes increase in volume from left to right.^{22,25} (Image reprinted with permission from Reference [22]. Copyright 2012 American Chemical Society.)

become amorphised and no subsequent phase/crystallinity change occurs.^{15,29} Si cannot be re-used many times due to this destructive process of Li^+ -ion storage; this pulverisation mechanism has been studied *ex-situ*, but the exact mechanism by which the silicon is destroyed has yet to be exactly determined.^{22,30,31}

2.4 Ti_3C_2 MXENE AS A LITHIUM-ION BATTERY ANODE MATERIAL

Another material that has gained much attention over recent years for possible energy storage applications is a family of layered materials known as MXenes. MXenes (layered, 2-dimensional metal carbides/nitrides) are obtained from a family of layered materials known as MAX phase. The MAX phases have a general formula

of $\text{M}_{n+1}\text{AX}_n$ ($n = 1-3$), where M is a transition metal ($\text{M} = \text{Ti}, \text{Sr}, \text{V}, \text{Cr}, \text{Ta}, \text{Nb}, \text{Zr}, \text{Mo}, \text{Hf}$), A is a main-group element (mostly group III or IV, $\text{A} = \text{Al}, \text{Ga}, \text{In}, \text{Ti}, \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$), and X represents C or/and N.³²⁻³⁷ MXenes are obtained by selectively removing the A component *via* etching, leaving a delaminated mono-layer material of general formula M_{n+1}X_n . Ti_3C_2 MXene has been studied as an anode material for lithium-ion batteries, and is used here. The Ti_3C_2 MXene used in this work is obtained from Ti_3AlC_2 MAX phase, with the aluminium etched away.

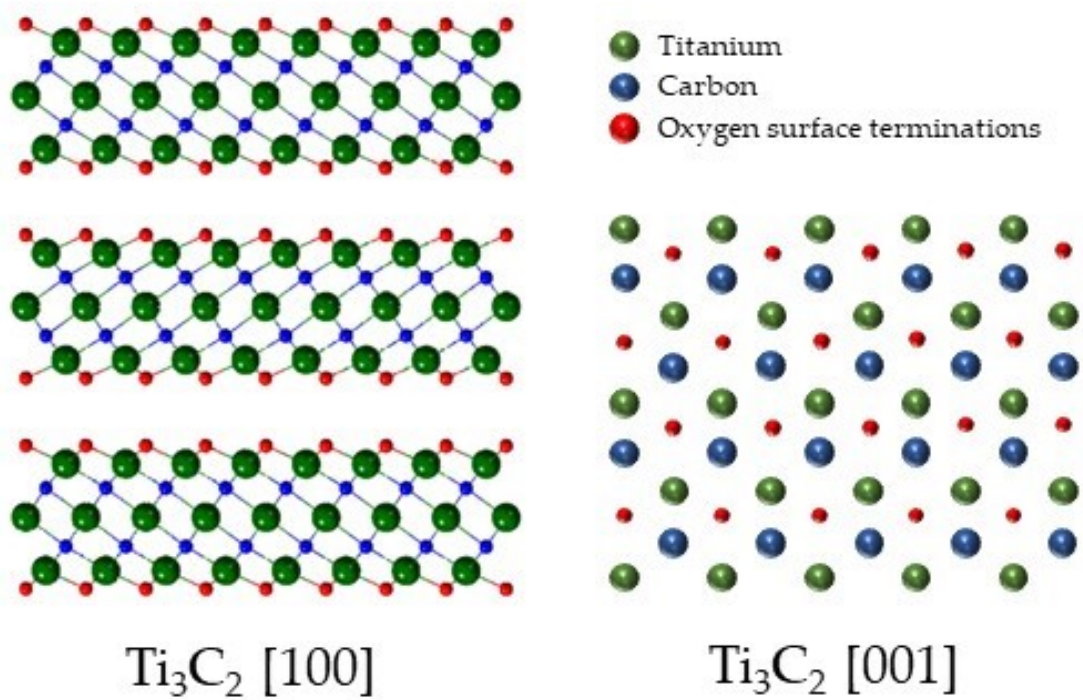


Figure 3: Schematic showing the layered, hexagonal structure of Ti_3C_2 MXene. Inter-layer spaces provide large surface area, and potential for Li^+ -ion charge storage.

Being a two-dimensional layered material, MXenes can store charge *via* the intercalation method described above. Similar to graphitic carbon anodes, MXene can accept Li^+ -ions into interstitial lattice sites between each layer.⁸ With a theoretical capacity comparable to currently used graphite (320 mAhg^{-1} compared to 372 mAhg^{-1}) MXenes seem like a promising anode material due to this comparable capacity, but with a greater cyclic stability. Being a highly conductive material,

anodes could also be constructed from MXenes without the need for conductive additives, which can lower the total capacity of the completed anode compared to a pure material. This could lead to less performance degradation over repeated charge-discharge cycles compared to graphite, which is highly desirable in an age where one of the major limiting factors of our mobile devices is the short service life of the batteries that power them.

2.5 SULPHUR AS A LITHIUM-ION BATTERY ANODE MATERIAL

Sulphur has also been widely studied as a potential electrode material for Li^+ -ion batteries. Its relatively high theoretical capacity of $\approx 1650 \text{ mAhg}^{-1}$, potential to provide greater energy storage density, and elemental abundance³⁸ has attracted a lot of attention within the Li^+ -ion battery research community.^{39,40} Certainly, sulphur presents an attractive possible high capacity alternative to commercial graphite for Li^+ -ion battery applications.

Sulphur, much like carbon, has a tendency to undergo catenation (that is, the binding of an element to itself through covalent bonds to form chain or ring molecules) and exists in different allotropes. While sulphur can exist in rings or chains of almost any size,⁴¹ the most stable allotrope (and most common) is S_8 , an octagonal orthorhombic ring of sulphur.⁴² When these sulphur rings undergo reduction during the discharging of a Li-S battery, the rings open and form long chain lithium polysulfides. As the discharge process continues, the initial long chain lithium polysulfides are continually broken down into smaller chains, until at the end of the process, Li_2S is formed. For the reverse process, S_8 is reformed via intermediate lithium polysulfide chains, resulting in a theoretically reversible electrochemical reaction.^{39,40}

As with all things, there are other reactions in the system to consider that hinder

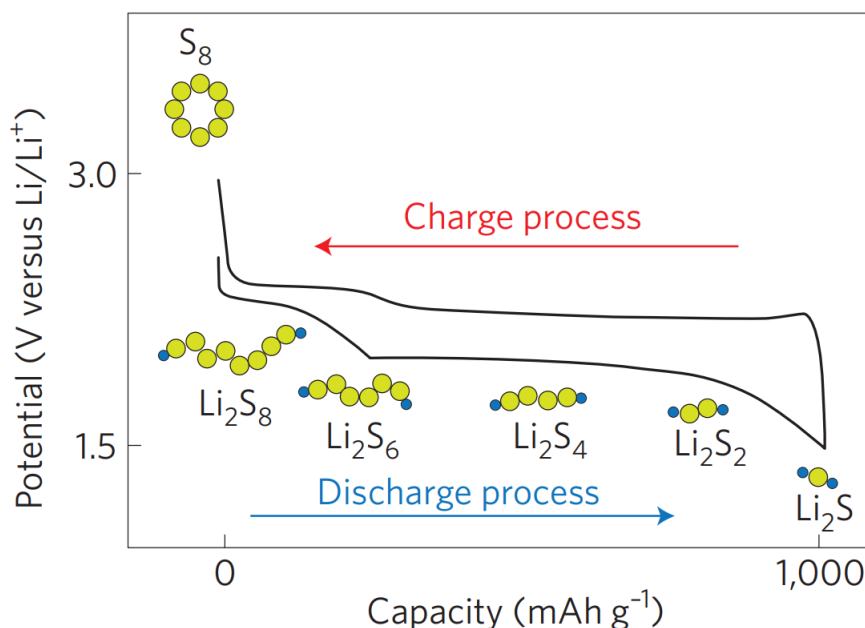


Figure 4: Schematic showing the mechanism of formation of lithium-polysulfide chains from octagonal orthorhombic S_8 rings during Li-S battery discharge process. (Image reprinted with permission from Reference [40] and Reference [43]. Copyright 2012 Nature Publishing Group.)

the performance of such battery materials. The continual structural changes required to break and re-form the polysulfides and sulphur tend to break down the electrode over time, resulting in a loss in performance. However, this is not the primary cause of poor performance in Li-S batteries. A phenomenon known as the "shuttle effect" causes the most capacity loss in the system. The so-called "higher order" polysulfides (between 6 and 8 S-atoms in the chain) are highly soluble in the organic electrolytes used in Li^+ -ion batteries. These initial intermediate polysulfides migrate toward the lithium anode and react with the lithium metal. They are reduced to lower-order (fewer than 6 S-atoms per chain) polysulfides and migrate back to the cathode, where they form higher-order polysulfides again. This cycle repeats continuously.³⁹ In severe cases, this can lead to a huge loss in lithium from the anode, along with an infinite recharge loop. The shuttle effect also induces deposition of solid Li_2S_2 and Li_2S on the lithium anode and loss of the sulphur

active material from the cathode. This greatly reduces the Coulombic efficiency of the cell and shortens cycle life, and leads to unstable cycling.⁴⁴

There have been many methods employed to attempt to circumvent this polysulfide shuttling effect, with many of them employing some form of encapsulation of the sulphur inside a carbon or conductive matrix, modification of the electrolyte properties, or the addition of interlayers to prevent polysulfide migration away from the sulphur electrode.^{39,40,44,45}

2.6 THE SOLID ELECTROLYTE INTERPHASE (SEI)

Common to every battery electrode material, regardless of the mechanism of Li^+ -ion storage is the formation of the Solid-Electrolyte Interphase (or SEI) layer during electrochemical cycling. Apart from electrode material degradation as a result of the physical processes of Li^+ -ion storage mechanisms, one of the main common mechanisms of capacity loss in the Li^+ -ion battery systems is the loss of Li^+ -ions from the electrolyte to a reaction within the cell which forms a solid layer on the surface of the anode. This layer is known as the Solid-Electrolyte Interphase (or SEI) and is formed by reaction of intercalated Li and the electrolyte.⁴⁶ It will be present in concert with any observable swelling in the silicon system, and thus is of interest to this work.

The SEI forms during the first charging stages of battery operation as most electrolyte solutions are thermodynamically unstable at the operating voltages of rechargeable batteries.^{47,48} Upon the first charge of the cell, the electrolyte degrades and deposits a variety of organic and inorganic electrolyte decomposition products on the negative electrode,⁴⁹ forming the SEI. Typically, this layer is approximately 10-100nm in thickness,⁵⁰ and in an ideal scenario, the SEI selectively allows Li^+ -ions to pass through, while hindering electron transport.

The exact compounds formed as the SEI are thought to vary depending on a va-

riety of factors, including operating conditions, electrolyte composition and anode material.^{48,51} It is a complex surface layer, but it is believed that the inorganic components arise from salt degradation products, while the organic components arise from solvent degradation products (see Figure 5). While Figure 5 shows the schematic SEI of a lithium surface, the SEI of a silicon surface should be somewhat similar as the SEI is formed from the breakdown and deposition of the electrolyte; however some of the components will differ and contain Si-Li compounds also. In previous studies of the commonly utilised electrolyte 1M LiPF₆ in EC/DMC 1:1, components of the SEI have been found to contain LiF, LiOH, Li₂CO₃, polyethylene oxides, lithium-oxide-polycarbonates, and a variety of other lithium-based organic molecules.⁴⁷⁻⁵³ However, these studies were carried out on a graphitic anode, and the Si-based system studied here will differ. Previous studies have also shown the presence of SiO_xF_y and Li_xSiO₂ species on Si surfaces indicate that the anode material itself may play a role in the species formed as the SEI.^{54,55} This is still a widely debated topic, as the exact composition of the SEI is still not fully understood.^{48,56}

All of this generally results in an enormous capacity drop after the first recharge due mostly to lithium loss to the SEI. Fortunately, the growth of the SEI is a self-limiting process, as once the initial layer has formed, no further electrolyte can reach the anode, and the SEI suppresses further SEI growth.⁵⁷ The SEI, while electronically insulating and impermeable to electrolyte solution, is still permeable to Li⁺-ions. This allows for many charge-discharge cycles without further lithium loss to the SEI.⁴⁸

However, if the SEI was not present, the generally corrosive electrolyte solution would gradually erode the anode, thus making the battery useless after a short time,⁵⁸ and Li⁺-ions would be continually lost from the system to the SEI. Thus while the SEI contributes to an initial capacity loss, it is an essential passive component of the Li⁺-ion cell to maintain its capacity over time.

Due to the fact that the SEI is quite thin by comparison to the overall size of most



Figure 5: Schematic depiction of the SEI at an anode interface, and ionic transport within the SEI.

Figure gives an impression of the complex and still not fully understood composition of the SEI formed by typical battery electrolyte decomposition. (Image adapted with permission from Reference [50]. Copyright 2017 Elsevier.)

anode materials,⁵⁰ a technique with high spatial resolution must be used if one wished to analyse this layer in its working state; thus TEM is employed to enable such studies due to its high spatial resolution and simultaneous imaging and spectroscopic capabilities.⁵⁹ Liquid cell TEM is particularly appropriate for this task, as the SEI is sensitive to air, moisture and other contaminants, and so *ex-situ* and *post mortem* studies cannot perform a proper analysis.⁶⁰

2.7 CYCLIC VOLTAMMETRY AND ELECTROCHEMICAL CHARACTERISATION

In order to study the electrochemical properties of each of the materials described above, a suitable electrochemical characterisation technique must be used. The pri-

mary electrochemical characterisation method used in this work is Cyclic Voltammetry (CV), which is a type of potentiodynamic voltammetry (voltage applied is varied over time) used to study electron transfer reactions. This technique is similar to a linear sweep voltammetry, whereby it applies a linear sweep potential between the working and counter electrodes between a pre-defined voltage window and measuring the current between them, but differs by reversing the sweep to return to the initial potential. This is then repeated as many times as desired (in a cyclic fashion).^{2,5,61} This reversible cyclic linear sweep waveform can be visualised in Figure 6. The current response of the electrode is measured as the voltage is swept. If reducible/oxidisable agents are present in the system, the current between the working and counter electrodes will rapidly increase as the redox potential is approached, then rapidly decrease as the quantity of reducible/oxidisable agents are depleted. This is typically visible in CV curves as peaks. If the reaction is reversible, a corresponding oxidation/reduction peak can be observed on the reverse sweep (dependant on the initial sweep direction). If the reaction is irreversible, no corresponding peak will be present.^{5,61–63} Such peaks can be used to qualitatively determine the reversibility of a redox reaction, or show the presence of any intermediate compounds or secondary reactions in the system.

In the case of Li^+ -ion battery materials, this technique can be used to visualise Li^+ -ion intercalation. As Li^+ -ion intercalation proceeds, Li^+ -ions from the electrolyte are reduced to lithium atoms during the charge cycle in the anode, as shown in Equation 4 below.



During discharge, the lithium atoms are oxidised and taken up into the electrolyte once again. This results in a pair of Li^+ -ion intercalation peaks in the CV of a Li^+ -ion battery electrode material.^{5,19,62}

Importantly for the setup used in this work, CV can be used in a two-electrode

system, and does not require the presence of a reference electrode. A reference electrode is not always necessary for such battery systems as this work is not an isolated study of the characteristics of the working electrode independent of the counter electrode, and a two electrode system will suffice for these experiments.²⁰

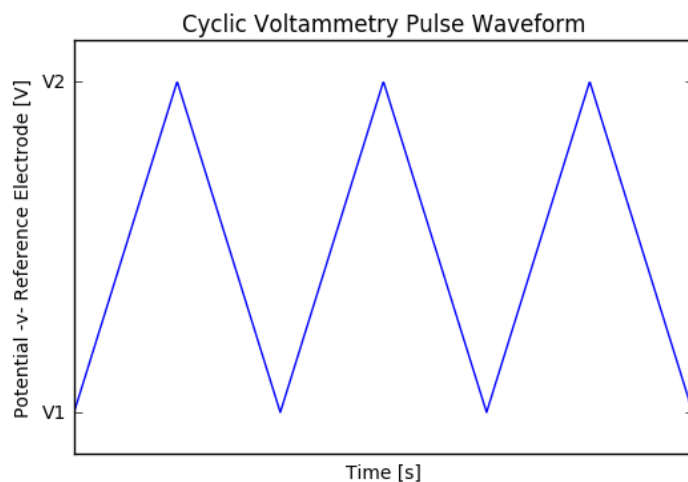


Figure 6: Sample sawtooth-type waveform of applied potential over time used in the Cyclic Voltammetry electrochemical characterisation technique. Voltage is ramped at a constant rate within a defined potential window between the initial (V_1) and final (V_2) potentials.

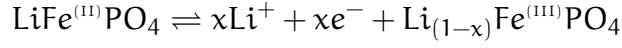
This simple technique is used for the *in-situ* setup, as this work is not concerned with the performance of the materials, but rather simply needs a voltage to be applied to drive Li^+ -ion intercalation, and corresponding data measurement confirming reversible electrochemical reactions.

2.7.1 Theoretical Capacity of Materials

The following materials are used in this work; silicon nanoparticles, Ti_3C_2 MXene, and sulphur as an anode (as described earlier in this chapter), and lithium iron phosphate (LFP) as the cathode and source of Li^+ -ions in the full systems due to

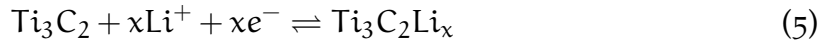
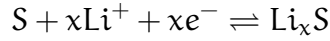
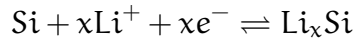
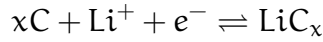
inherent fabrication limitations of using a pure lithium foil in TEM experiments (which will be described later in Chapter 7). The following half-cell equations describe the reversible redox reactions the materials undergo:⁶⁴

cathode oxidation (charging anode):



where $0 < x \leq 1$

anode reduction (charging anode):



It is important to state that these reactions are not spontaneous, and require an external applied potential to drive the reactions.

The electrical capacity of a material is defined as the amount of charge the material can store. Therefore, it has the unit of the Coulomb.

Via dimensional analysis:

$$\eta F = C \quad (6)$$

Where η = number of moles of electrons (mol), F = Faraday constant (96485 C/mol), and C = charge (Coulombs = C)

Applying a simple conversion factor to change the dimensions to standard:

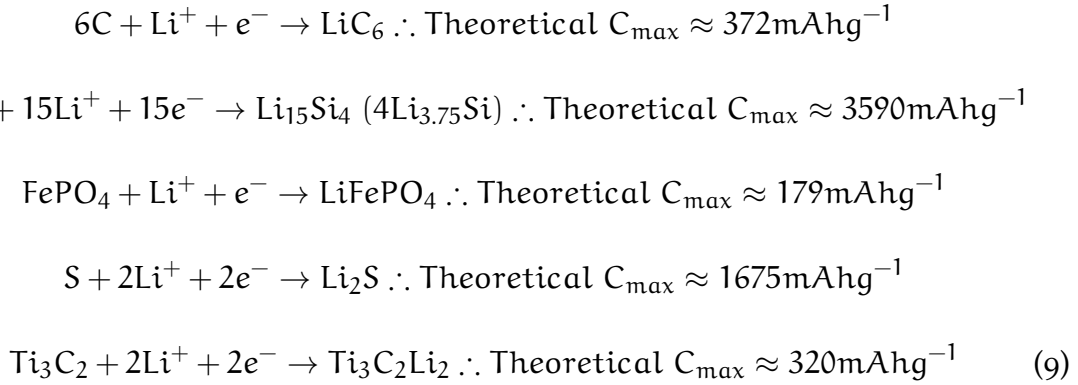
$$1C = \frac{1}{3600}\text{Ah} = \frac{5}{18}\text{mAh} \quad (7)$$

The specific capacity is defined as electrical capacity per unit mass. Therefore, the equation for the theoretical specific capacity of a given material becomes:²⁰

$$\text{Specific Capacity } (C_{\text{max}}) = \frac{\eta}{M} \left(\frac{5}{18}F \right) = \text{mAhg}^{-1} \quad (8)$$

Where M = molar mass of the material (in grammes).

To acquire the value for η , one must analyse the chemical equation for the reaction in the battery cell; η can be extracted directly from such equations,⁶⁵ as outlined below:



Using Equation 8, we can make a crude approximation of the Specific Electronic Capacity of any electrode material. However, a full determination that takes into account the structure of a material requires complex DFT calculations, as well as the determination of each material's Density of States.^{37,66} Such calculations were not undertaken here as they were beyond the scope of this work.

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TRANSMISSION ELECTRON MICROSCOPY

The main characterisation technique used in this work is Transmission Electron Microscopy (TEM). TEM was chosen due to its high spatial and real-time temporal resolution when imaging samples, as well as combining a variety of spectroscopic and chemical analysis techniques into a single instrument. Depending on the system, spatial resolutions down to $1\text{\AA}$ and with a CCD camera refresh rate of 400 frames per second (Gatan K2, Gatan Inc.) are typical of many TEM setups. Simultaneous spectra acquisition can be performed during imaging, which can allow for chemical analysis of the materials under scrutiny as we observe changes occurring. This makes it a suitable candidate for *in-situ* analysis of the battery materials discussed under working conditions. While *in-situ* analysis such as this is the goal of this work, work must still be done to develop techniques for reliable image acquisition in a liquid environment.

3.1 AN INTRODUCTION TO TEM: THE ELECTRON WAVE

Fundamentally, TEM is based on the concept of wave-particle duality;¹ that is that particles such as electrons can exist as both a particle and a wave. Using the de Broglie wave^{1,2} relation, Ruska and Knoll developed microscopes³ using electron optics, rather than visible-light optics. These microscopes quickly surpassed the resolution limits of visible-light microscopes, and are to this day still limited by

imperfections in the electron optics, rather than by diffraction limits, as can be shown using Equation 10 below.

$$\lambda = \frac{h}{\sqrt{2m_0eV}}$$

or, with relativistic corrections:

$$\lambda = \frac{h}{\sqrt{2m_0eV \left(1 + \frac{eV}{2m_0c^2}\right)}} \approx 1.97\text{pm} \quad (10)$$

Where λ = wavelength, h = Planck constant, m_0 = rest mass of electron, e = electron charge, V = accelerating voltage (usually 300kV), c = speed of light in vacuum, p = momentum.¹

Following on from this, the theoretical resolution of an electron based optical system such as a TEM operating at a typical operating voltage of 300keV can be approximated by the Rayleigh criterion for a circular aperture as shown in Equation 11. It can be seen that the resolution is highly dependent on the wavelength of the source, thus a high energy electron source is highly suitable for resolving sub-nanometre features.

$$d = 1.22 \frac{\lambda}{\sin\theta} \quad (11)$$

Where d = resolution, λ = wavelength, θ = the angle of collection of the magnifying lens¹

From these simple equations, TEM has a theoretical diffraction limited resolution in the pm range, however most modern TEM technology can only resolve details approximately 100 times larger than this ($\approx 0.5 - 1\text{\AA}$) due to imperfections in the lens systems.^{2,4,5} These lens imperfections (such as slight asymmetry in the shape of the polepieces, or atomic defects in the polepieces) give rise to geometric and chromatic aberrations, which are the primary limitation factors to achieving the diffraction limit of the microscope. Other lens defects limit resolution also, but these two are the most pervasive and limiting.

Geometric aberrations are caused due to inconstancies of the magnetic field of the

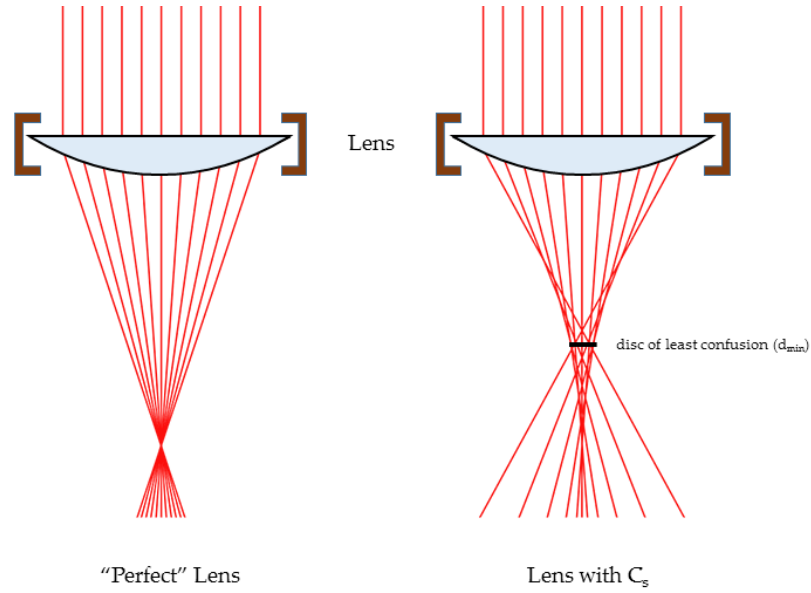


Figure 7: Ray diagram demonstrating Geometric Aberration. Multiple focal points can be observed in the focused beam and the disc of least confusion is shown.

lens off the central optic axis. As a result, the further away from the central optic axis an electron is, the more it is deflected back toward the axis by the lens. This results in multiple focal points of the focused beam, thus, imaging a point object as a disk and blurring the image (see Figure 7).

Chromatic aberrations result from the lens deflecting electrons of differing energies (or wavelengths) as they pass through the lens, causing different focal points for each electron energy (see Figure 8). The comparison is often made to colour separation in light-lenses. This can be shown in the Lorentz equation^{1,6} (Equation 12):

$$\mathbf{F} = q\mathbf{E} + (q\mathbf{v} \times \mathbf{B}) = q\mathbf{v} \times \mathbf{B} \quad (12)$$

Where $\mathbf{F}$ = force acting on the electron due to the lens, q = electron charge, $\mathbf{E} = 0$ (no static electric field in lens system), $\mathbf{v}$ = relativistic velocity of the electron, $\mathbf{B}$ = magnetic field.

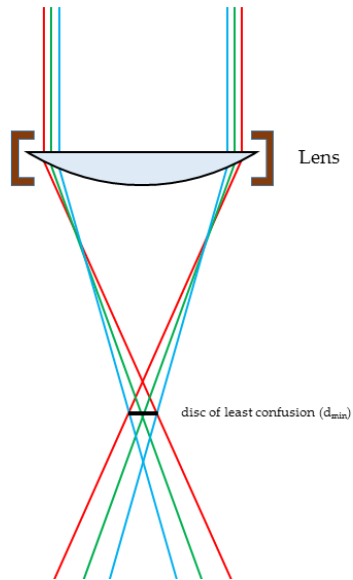


Figure 8: Ray diagram demonstrating Chromatic Aberration. Each colour represents a different electron energy (wavelength). Multiple focal points can be observed in the focused beam as a result of different electron energies.

As the velocity of the electron is determined by its energy, electrons of differing energies will not have the same transverse force applied in the same magnetic field.

3.2 IMAGE FORMATION

A TEM image is formed due to the interaction of high energy electrons with a sample. When the electron beam passes through a sample, it can undergo a number of different scattering events and interactions with the sample (see Figure 9). Aside from the forward scattered deflections such as elastic and inelastically scattered electrons, a number of backscattered electrons, secondary electrons and Auger electrons can be detected from the sample by the detectors in the microscope. A number of X-ray emissions can also be detected, and allow for simultaneous characteristic EDX spectra to be acquired.

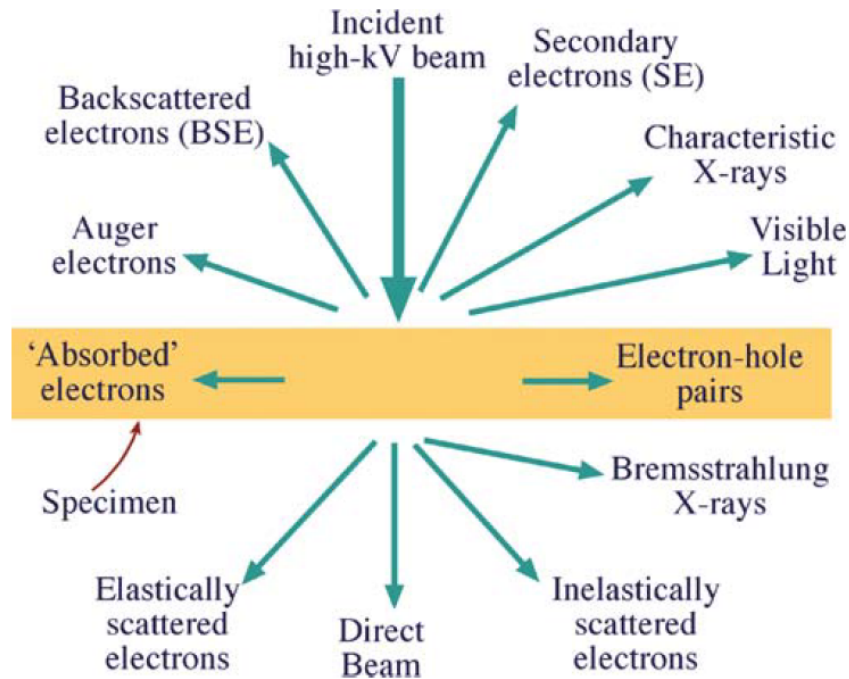


Figure 9: Diagram showing various types of electron scattering and X-ray emission from sample in TEM. (Image reproduced with permission from Reference [2]. Copyright 2009 Springer-Verlag US.)

A TEM image may be formed from either the direct beam (known as Bright Field imaging), or from a diffracted beam (known as Dark Field imaging).^{2,7} This can be visualised using the ray diagram shown in Figure 10.

In TEM mode, the beam is focused with the condenser lenses so that it is parallel at the sample plane, illuminating the entire region within the beam. Image contrast arises as a direct result of scattering interactions of the incident electron beam with the sample. There are a number of ways the electron beam can be altered as it passes through the sample, and both the amplitude and the phase of the wave can be altered by the sample. This leads to a number of different types of contrast that form the image.²

Amplitude contrast, which is subdivided into mass-thickness contrast and diffraction contrast, is the more intuitive of the contrast mechanisms. Mass-thickness con-

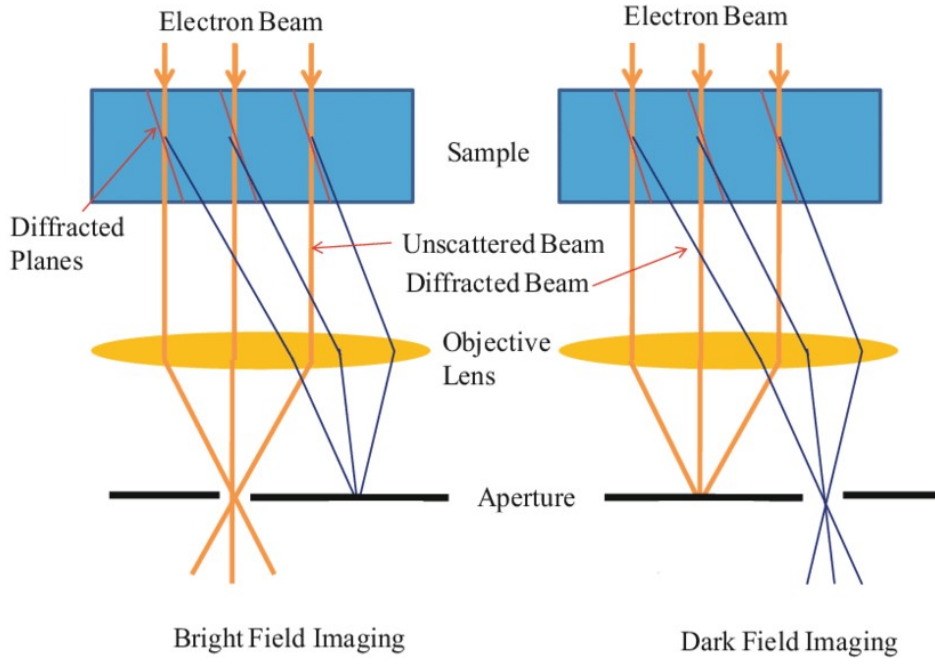


Figure 10: Ray diagram showing the selection of Bright Field (BF) or Dark Field (DF) imaging modes from the direct beam and diffracted beam respectively using appropriate objective apertures. (Image reproduced with permission from Reference [7]. Copyright 2018 Springer US.)

trast arises from incoherent elastic scattering (Rutherford scattering) of electrons. The cross section for Rutherford scattering events depend strongly on the atomic number (Z) and the thickness of the sample (see Equation 13). Therefore, mass-thickness contrast will form an image where regions of the sample that are thicker or are composed of higher mass atoms will appear darker in a bright-field (BF) image or brighter in a dark-field (DF) image because more of the beam is incoherently elastically scattered away from the optical axis.²

$$\sigma_R = \frac{e^4 Z^2}{16(4\pi\epsilon_0 E_0)^2} \frac{d\Omega}{\sin^4 \frac{\theta}{2}}, \quad N(\theta) = n t \sigma_R \quad (13)$$

Where σ_R = Rutherford scattering cross section, e = electron charge, Z = atomic number, ϵ_0 = permittivity of free space, E_0 = kinetic energy, $d\Omega$ = solid angle, θ = scattering angle, $N(\theta)$ = number of electrons scattered at a specific angle, n = number of atoms per unit

volume in sample t = sample thickness

Phase contrast arises due to differences in the phase of the electron waves scattered by the sample. The differing phases of the scattered waves post-sample interfere, and give rise to fringes. If the sample contains a high degree of periodicity (such as a single crystal sample) these fringes give contrast corresponding to lattice spacing in the sample, and can be frequently seen in high resolution (HRTEM) images as lattice planes.² Phase contrast is limited by the contrast transfer function (CTF) of the TEM system, which is determined by the mathematically described geometric aberration coefficients. The resolvable spatial frequency by phase contrast is determined by the frequency at which the first CTF crossover occurs, and the contrast reverses (see Figure 11).^{2,8} This point in the CTF is determined by the aberration coefficients of each microscope, and is often referred to as the "instrument resolution limit" as no contrast is produced at 0 and no information can be acquired at this point.² However since this work does not consider any phase contrast HRTEM due to sample limitations discussed in Chapter 4 and Chapter 7, further discussion is beyond the scope of this thesis.

Periodicity in the sample can also be used to image a diffraction pattern from the sample. Diffraction patterns form in the back focal plane of the objective lens as a result of constructive interference of the electron wave satisfying Bragg's law (Equation 14).

$$n\lambda = d_{hkl}\sin\theta_B \quad (14)$$

Where n = diffraction order, d_{hkl} = lattice spacing for the hkl crystal plane, θ_B = Bragg angle

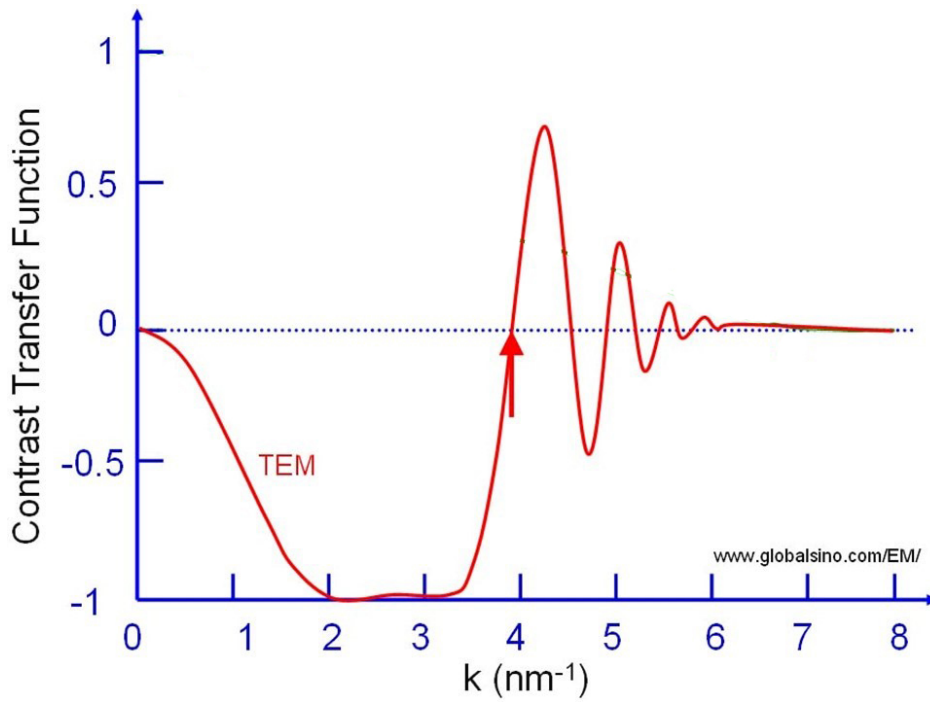


Figure 11: *Example CTF of TEM imaging system. Arrow marks first crossover point, and spatial frequency of information limit of phase contrast. (Reproduced with permission from Reference [8])*

The back focal-plane image can then be projected onto the screen to form an image of spots for all planes meeting the Bragg criterion. The spots form a characteristic diffraction pattern with symmetry that is related to the symmetry of the crystal.

3.3 SCANNING TRANSMISSION ELECTRON MICROSCOPY

In STEM mode, a convergent electron beam (or electron probe) produced by an electron gun and a series of condenser lenses is focused and rastered across the specimen and using x and y axis deflection scan coils. It differs from standard TEM imaging as the resolution is determined by the probe size (typically of the order $2\text{\AA}$), and not by the diffraction limit.⁵ It is thus a direct imaging method, and

its images are more intuitively interpreted.

A number of signals can be collected post sample, and the most typical ones include transmitted electrons that have been scattered at low angles (known as Bright Field (BF) imaging) and that have been scattered at high angles (known as Annular Dark Field (ADF) imaging) with respect to the central optic axis. In this case image contrast is derived from scattering angle, which is directly related to the atomic mass of the atoms in the sample (known as Z-contrast). Higher Z atoms scatter the incident electron beam to higher angles on the ADF detector, which is seen as brighter regions in an ADF image.² For a larger scattering angle ($>50\text{mrad}$) (higher Z), High Angle Annular Dark Field (HAADF) imaging is commonly used to give contrast in STEM imaging. For a lower scattering angle ($>10\text{mrad}$) (lower Z), Medium Angle Annular Dark Field (MAADF) imaging can also be employed if equipped in the microscope's ADF detector to give more contrast. A large amount of spectroscopic data can also be acquired simultaneously with imaging, specifically from characteristic X-rays emitted by electron-sample interactions (Energy Dispersive X-ray Spectroscopy (EDX/EDS)) and from transmitted electrons that have lost a measurable amount of energy from interactions with the sample; this measured energy loss gives rise to Electron Energy Loss Spectroscopy (EELS), a powerful quantitative tool used to probe chemical data at the local atomic scale.⁵

3.4 IMAGING OF THICK SAMPLES

While scattering events are the key to imaging with electrons (without which no image could be formed), too many can cause resolution and contrast issues. This is of particular importance to this work, due to the inevitably thick nature of the samples used for the *in-situ* holder suite described in the next chapter.

In a standard TEM setup, samples are prepared to be approximately 100nm thick,

or thinner. If the sample is too thick, the electrons scattered by a feature in the material (such as an atom, plasmon, phonon, or a dislocation *etc.*) have a finite probability of being scattered again. If scattering is considered as independent random events, the probability of n -fold scattering will follow a Poisson distribution⁶ as long as the inelastic mean free path of a scattered electron remains in the sample.

$$P_s = \left(\frac{\left(\frac{t}{\lambda_e} \right)^n}{n!} \right) e^{-\frac{t}{\lambda_e}} \quad (15)$$

Where P_s = probability of scattering, t = sample thickness, λ_e = inelastic mean free path of electrons in the sample (sample dependent value), and n = number of scattering events ($n \in \mathbb{N}$).

As can be seen in Equation 15 the probability of a larger number of scattering events increases with the ratio of sample thickness to mean free path of electrons in the sample⁹ (See Figure 12). This phenomenon (known as plural scattering, for between two and twenty scattering events²) reduces the possible resolution of the image and makes spectra extremely difficult to interpret, as the electrons have been scattered by more than just the feature one wishes to observe and the contrast mechanisms described above are forming an image that is derived from more than a single scattering event. Typical inelastic mean free path of electrons in a material can be calculated by the relativistic full Penn algorithm to be approximately 100nm - 150nm between 40keV - 300keV, the typical incident electron energy range of most TEM systems.¹⁰⁻¹²

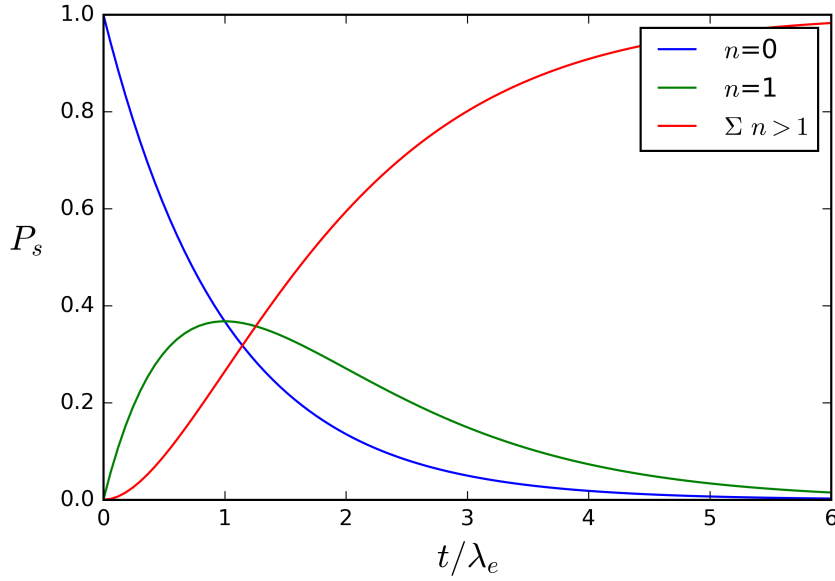


Figure 12: Poisson distribution for different values of n (scattering events). Blue line depicts probability of no scattering events (exponentially decreases with sample thickness), the green line depicts the probability of a single scattering event, and the red line depicts the sum of the probability of a finite number multiple scattering events (increases with sample thickness) as a function of t/λ_e . (Finite number of events specified as $\sum_0^\infty P_s = 1$)

3.5 SPECTROSCOPY IN TEM

One of the major appealing factors of using (S)TEM as an imaging technique is it's ability to acquire simultaneous quantitative spectra from the material under scrutiny during imaging. The two most common types of spectroscopy possible in (S)TEM are Energy Dispersive X-ray Spectroscopy (EDX/EDS) and Electron Energy Loss Spectroscopy (EELS), although more specialised setups can also perform techniques such as Auger Electron Spectroscopy or Raman Spectroscopy using *in-situ* lasers.

EDX is a technique used to identify elemental composition of the sample. When a high energy electron interacts with an atom, it has a probability to undergo two possible events that can emit an x-ray; a significant change in momentum due to interaction with the Coulombic field of the nucleus, or eject an inner-shell core elec-

tron from the atom. If the electron is "slowed" by interacting with the field of the nucleus, it loses its excess energy in the form of emitted high energy photons (or x-rays). As the energy released can be any value up to the energy on the incident electron, this is seen as a continuous exponential decay spectrum, with no defined peaks. This is known as the *Bremsstrahlung* or "braking radiation". Some of this lost energy is re-absorbed by the sample, which gives rise to the characteristic "hump" at the lower end of the *Bremsstrahlung* background. This part of the x-ray spectrum contains no useful quantitative data about the sample. The other possibility is that the incident electron will eject a core electron. If this occurs, the atom is now said to be in an "excited" state. An electron from a higher energy level in the atom can then relax to the now empty lower energy state, and release its excess energy as an x-ray. As this energy difference is unique to each element the x-rays emitted are also characteristic to each element; by measuring their energies, the elemental composition of the sample can be determined.²

The characteristic x-rays are grouped according to which electron shell transition generated the x-ray. The innermost shell is known as the K shell, with the next shells designated the L and M shells, and so on. Each characteristic peak is named based on the shell it relaxes to; a relaxation from L to K is known as the K_{α} peak, from M to K is the K_{β} peak, from M to L is the L_{α} peak etc. Technically, one can have transitions between sub-shells within each shell (provided it isn't a forbidden transition under the rules of quantum mechanics) but the probabilities of such transitions occurring are much lower, and their energies so low that they are usually not considered in EDX spectroscopy in the TEM. This nomenclature is based on a simple Bohr-model of the atom and its electronic structure, and doesn't take into account the shapes of atomic orbitals or more complicated explanations of electronic structure theory.²

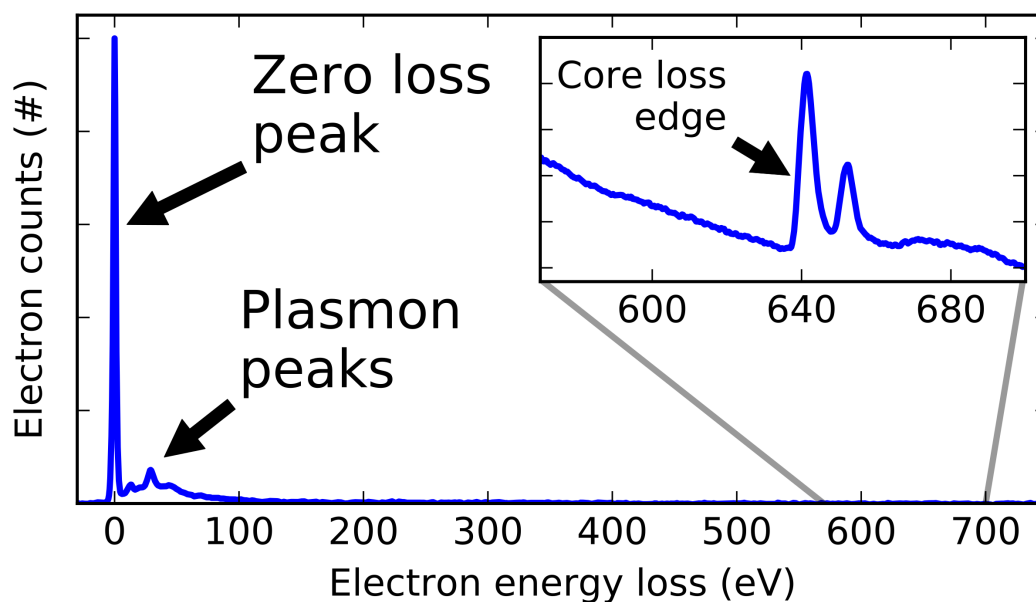


Figure 13: Example EELS spectrum showing the Zero-loss, Low-loss, and Core-loss regions of the spectrum. Peaks arise as a result of energy losses from inelastic electron interactions with atoms in a sample. (Image reproduced with permission under Wikimedia Creative Commons Licence. Original author: Magnunor. Available at <https://commons.wikimedia.org/wiki/File:Electron-energy-loss-spectrum-feature-overview.svg/media/File:Electron-energy-loss-spectrum-feature-overview.svg>)

EELS can also be used to determine elemental composition, but it is a much more powerful technique capable of determining chemical bonding states of different elements, along with certain optical properties of materials. When an electron interacts inelastically with atoms in a sample, the electron may lose energy and momentum to the sample. This energy loss is measurable, and can be interpreted as an energy loss spectrum. A typical EELS spectrum is composed of a number of distinct regions. The Zero Loss Peak (or ZLP), the Low Loss region, and the Core Loss region. (see Figure 13)

The ZLP contains no usable spectroscopic information, it is the result of electrons that have not experienced a change in energy or momentum as a result of inelastic interactions with the sample.^{5,13}

The low loss region ($\leq 100\text{eV}$) typically contains information about the optical properties of the sample, with plasmon peaks located in this region. Such losses are not considered in this work.

The core loss region of the energy loss spectrum ($\geq 100\text{eV}$) contains information on the elemental composition, electronic structure, and concentration of the sample. Characteristic electronic transitions can be used to determine a sample's elemental composition, similar to EDX; however EELS can detect elements that cannot be detected *via* EDX, such as low-Z elements like lithium and hydrogen.¹⁴ Low-Z elements like lithium have lower probabilities of x-ray emission, and produce soft x-rays which are absorbed by many detectors when they do. Hydrogen and helium do not produce characteristic x-rays at all.¹⁵ EELS can be a useful technique for detecting such elements where EDX falls short. The information that can be obtained can be much more detailed, with near edge characteristics (ELNES) of the elemental peak yielding data on valence state of the element, local bonding information, and density of states to name a few.^{5,13,16}

In STEM, EELS and EDX provide powerful spectroscopic tools for localised measurement across a sample, with atomic resolution possible in the right conditions. These techniques can be taken a step further in STEM, as a spectrum can also be acquired for each pixel of the image as the probe is rastered across the region of interest (creating the so-called "datacube" image). This can then be used to generate a spectrum image, showing the distribution of different elements throughout the sample.⁵

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IN-SITU LIQUID CELL TRANSMISSION ELECTRON MICROSCOPY

As mentioned previously, due to the environmental requirements of an electrochemical cell, this work primarily focuses on liquid cell TEM. In its most basic form, liquid cell TEM involves encapsulating a specimen in a liquid environment between two thin electron transparent membranes, thus isolating the liquid environment from the TEM vacuum and allowing imaging. Such a technique is very useful for the study of various wet-chemistry or electrochemical reactions. In this work, electrodes for electrochemical testing are also included in the viewing region of the membrane (See Figure 14).

4.1 LIQUID CELL TEM

TEM imaging in liquid environments can be traced back to the early days of the technology,^{1,2} however technical challenges prevented its widespread use.^{3,4} Liquid cell electron microscopy poses some unique challenges different from more conventional electron microscopy techniques such as isolating the liquid environment from the high vacuum required ($\sim 1 \times 10^{-6}$ Torr $\approx 1.3 \times 10^{-9}$ atm) to minimise scattering from sources other than the sample in the column.³⁻⁵ In order to maintain a balance between the strength required for liquid isolation and electron transparency, most commercial solutions use thin membranes of SiN_x to encapsulate the liquid (Figure 14). Some first generation and in-house solutions using single-layer graphene has also been used as a viewing window.^{2-4,6-14} While higher resolutions

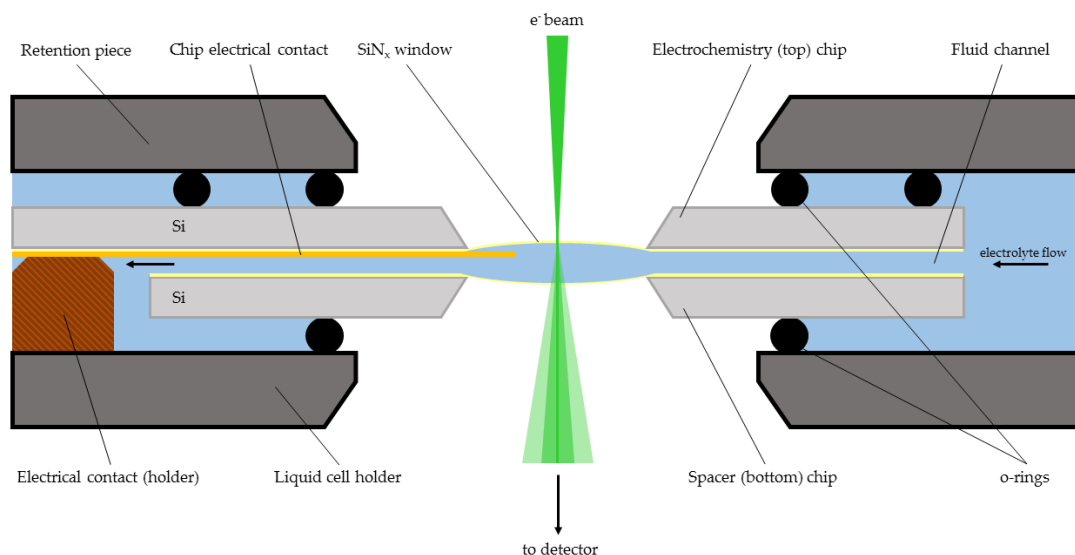


Figure 14: Cross-sectional schematic (not to scale) of the Hummingbird liquid cell electrochemistry microfluidic chip setup used in the experiments. Schematic demonstrates bowing of the SiN_x viewing window under fluid pressure. Electrode materials are positioned on the electrical contact electrode on the viewing window.

are possible with graphene windows (being atomically thin), an external stimulus such as electrical bias or heat could not be applied; thus the commercial solution is used here, which has been successfully used to study similar systems.^{2,4,10,15–29}

Many previous studies have used an open-cell electrochemical configuration, where a low vapour pressure ionic liquid was used in the column, and a biasing holder used to cycle the material under scrutiny.^{30–39} Such setups do not require the isolation of the liquid from the column vacuum, and the lack of membrane windows provides the ability to perform HRTEM imaging. While these experiments provide

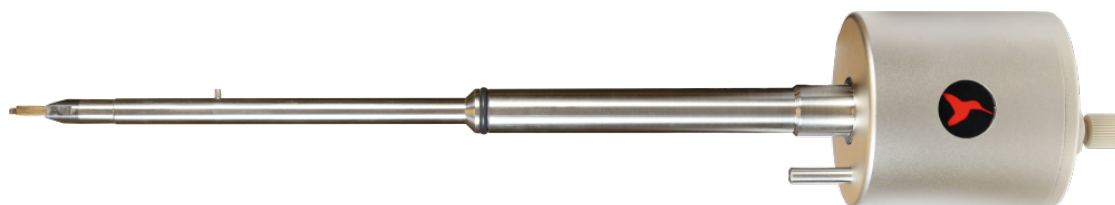


Figure 15: Hummingbird Specimen Holder for Liquid Cell TEM. (Courtesy of Hummingbird Scientific, Lacey, WA, USA.)

some insight into the reaction kinetics of the systems, they diverge by such an extent from a real-world environment that the conclusions may be inapplicable to any battery technology. In experiments consisting of open-cell nanowires with a solid or ionic liquid electrolyte, the experiment is inherently anisotropic as the lithium ions can only travel along a single crystallographic axis. Under normal operating conditions, lithium ions may be able to insert from any surface, so these types of experiments are flawed only if they wish to make any conclusions pertaining to real-world electrochemistry as the reaction kinetics would differ.⁴⁰

Recently, there have been breakthroughs in *operando* imaging of battery materials with simultaneous electrochemical characterisation.^{41,42} Such advances have been made possible through major improvements and redesigns to the sample holders used, and show how far the field has come in such a short time.

There are some shortcomings that occur in liquid-cell TEM which cannot be neglected. Electron beam damage is a technical challenge of particular importance to liquid cell TEM. For organic and some inorganic compounds, the damage mechanism is radiolysis: the breaking of chemical bonds and ionisation as a result of inelastic scattering. Considerations for e^- beam damage must be taken into account for any TEM work⁵ (particularly at higher voltages for HRTEM), but extra thought must be given to *in-situ* experiments as the liquid environment is far more susceptible to heating damage and radiolysis^{4,20,43-45} than more traditional solid-state thin samples. This is a direct result of the thickness of the liquid layer present in a closed liquid cell sample. The >300nm thick liquid layer provides a large interaction volume and scattering cross-section for radiolysis events to occur, and the easily breakable bonds of many organic compounds (compared to crystal structures) allow for quick degradation of the liquid environment in the presence of the electron beam.⁴⁶

A final consideration for the liquid cell setup must be made for the maximum possible image resolution one can achieve with this method. As discussed previously

in Chapter 3, image resolution in TEM mode is limited in thicker samples by plural scattering events, and in STEM mode by a similar process known as beam broadening. As the electron beam passes through a sample, the probability of an electron scattering event increases as the beam passes through more and more material (see Figure 12 and Equation 15 in Chapter 3), and a focused electron probe in STEM is thus broadened.⁴⁷ Probe broadening thus becomes the resolution limiting factor for nanoparticles deeper in the sample (*i.e.* immersed in a liquid, in this case) for STEM imaging.^{48–50} This can be thought of mathematically as a point spread function obscuring the image. The thicker samples also introduce more C_c in the post-sample lenses, further limiting the resolution.

Traditionally, TEM samples are prepared to be thinner than 200 nm.^{5,51} In the liquid cell setup used in this work, the samples are much thicker than the traditional setup, and due to the thickness limited resolution as a result of plural and multiple scattering of a TEM, the resolution of materials in a liquid environment is expected to be lower than solid-state TEM.^{4,5,24}

When imaging with thick samples, more consideration must be taken to choose the best imaging mode. For samples loaded on the upper window, STEM can obtain a better image, while for material located deeper within the liquid layer, TEM can provide higher resolution.^{50,52,53} In the case of the liquid cell setup, the material is deposited on the electrochemistry chip, which is oriented on the topside of the liquid layer, thus (S)TEM would be the most appropriate choice for imaging. A secondary benefit of STEM over TEM for imaging in liquid layers is the circumvention of the image contrast portion of the plural scattering problem. Contrast on a HAADF detector is highly dependant on scattering angle (see Chapter 3, Equation 13), as liquid layers only scatter at low angles due to being typically low atomic number (Z) elements. Provided the sample is of a sufficiently high Z -number (and thus high scattering angle), the contrast in the image will be dominated by the sample rather than the liquid environment when using a HAADF detector.⁴⁸ This

will practically result in a higher contrast sample relative to the background. This is obviously less relevant when using a BF detector. These effects are schematically shown in Figure 16.

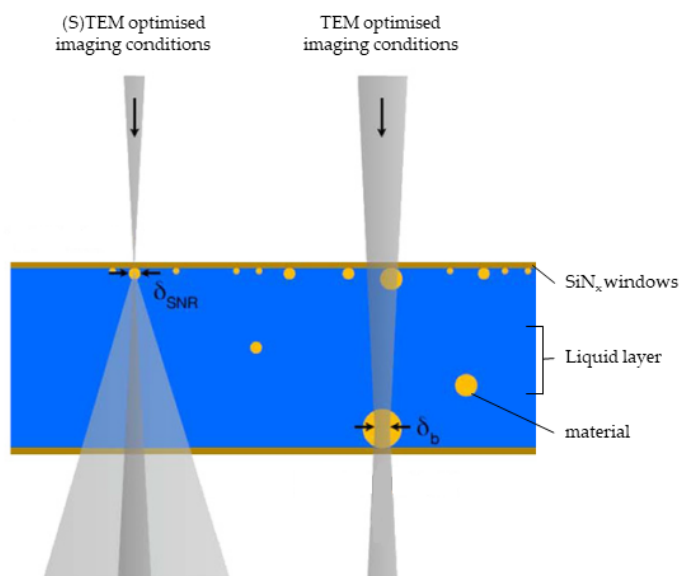


Figure 16: Schematic showing optimised liquid cell imaging conditions for (S)TEM and TEM respectively. (Adapted with permission from reference [50]. Copyright 2014 Elsevier.)

The SiN_x windows encapsuating the liquid are 50nm thick each, and so the addition of material and electrolyte begins at a thickness that is larger than conventional sample thicknesses used in TEM. This is of particular concern in this work, as the sample thickness can approach 1 μ m or greater in thickness due to window bowing out from the pressure difference between the column and the sample. This is beyond conventional sample thickness, and so plural and multiple scattering events as described in Chapter 3 become significant. The possibility of atomic resolution HRTEM in a liquid cell remains difficult to achieve and special care must be taken when interpreting any electron energy loss spectra (EELS) collected as a result of this sample limitation.^{4,5,54} However recent reports by Liao *et al.* have resolved lattice planes in Pt nanoparticle growth in a 100nm liquid cell similar to the one used in these experiments, so such resolution is not impossible to achieve under

the right conditions.^{27,55–57} (For example; high atomic number (Z) nanoparticles like Pt,⁷ α – Fe₂O₃,⁵⁸ and Pt – Pd nanoparticles.⁵⁹)

In spite of such drawbacks, *in-situ* liquid cell TEM is a powerful technique that can provide essential experimental spectroscopic and imaging data for mechanisms and phenomena that are not yet fully understood that has been lacking in the field of electrochemical characterisation thus far.²⁹

It has also been noted that the presence of the electron beam in the liquid cell can set up a static electric field orthogonal to the SiN_x membrane surface (parallel to the beam, similar to two negatively charged parallel plates) as a result of emission of secondary and Auger electrons from the sample which cannot be neutralised due to the inherent electrical impedance (but high ionic conductivity) of an electrochemical cell, complicating matters further.⁶⁰ The presence of a static electric field can lead to a number of issues such as altering the diffusion of charged ions in solution (perhaps inhibiting electrochemical performance), inducing bubble formation due to charging of the SiN_x windows. The induced electric field can also modify the parameters of the system by lowering the Gibbs Free energy of the system,⁶¹ thus spontaneous precipitation of materials from the electrolyte may become possible. This is far from desirable in a system set up to study a facsimile of a battery cell, and may alter the conditions of the cell beyond those of a real-world analogue.

Obtaining spectroscopic data from the liquid cell holder remains one of the great challenges of this work. In fact, the most common chemical analysis technique of energy-dispersive X-ray spectroscopy (EDX) is near impossible in the current setup. However, unlike the limitations seen in EELS, this is not due to sample thickness or composition but rather the design of the holder itself. Once generated, characteristic X-rays will not suffer from as great a signal loss with increasing liquid thickness, and spectra can be resolved.²⁹ The design of the specific holder used in this work

is an early design, (not optimised for spectroscopy) and blocks the line-of sight between the sample and the detector, even at high tilt angles (20°) (See Figure 17). As a result, any X-rays generated from electron interactions with the sample are absorbed by the titanium of the holder, and the spectra collected contain only Fe, Co, and Ti peaks from the pole pieces and holder.^{62,63} This, combined with the relatively inefficient 30mm^2 EDX detector equipped on the microscope make acquiring statistically significant x-ray data almost impossible. This is not an issue with newer holder designs.⁶⁴

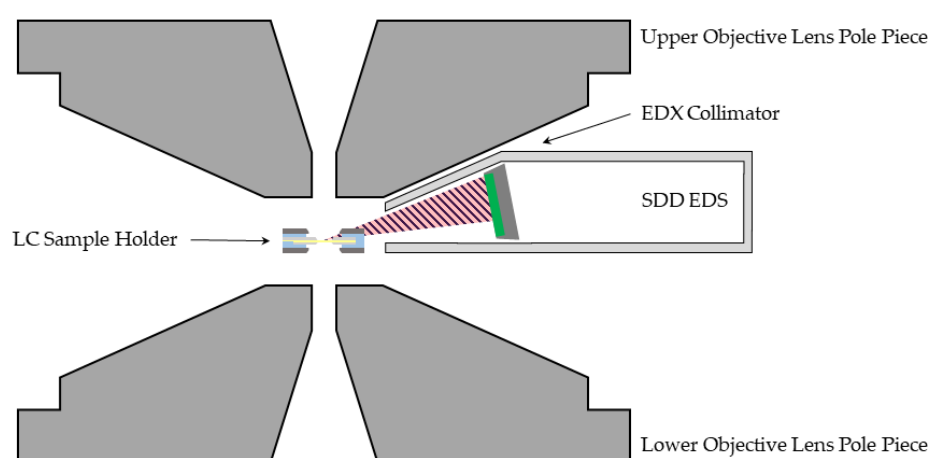


Figure 17: Schematic diagram of the relative positions of the sample holder and the EDX detector inside the TEM. The detector is shadowed by the holder, and is thus unable to detect X-rays being emitted by the sample.

It is possible to remedy this issue and obtain useful data from EDX, however it requires major modifications to the sample holder. Zaluzec *et al.* used micro-machining methods to modify the angle of the chamfer angles of the bore countersink in the holder, thus allowing for a line of sight between the sample and the detector.⁶³ This method has proven effective, as elemental analysis and spectroscopy was possible with the holder post-modification.⁶³

It may also be possible to design and manufacture a new top plate *via* additive manufacturing methods, such as 3D metal printing, with a larger chamfer angle

countersink to accommodate EDX; this method may prove to be better, as it does not destroy the original top plate for the holder.⁶⁵ While this may be possible, an attempt made to create such a secondary top plate during the course of this work failed due to insufficient resolution of the metal 3D printer available.

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IN-SITU GAS CELL TRANSMISSION ELECTRON MICROSCOPY

A sample immersed in a liquid is not the only native environment in which samples can be observed. Gasses can also be introduced to the sample during TEM imaging and spectroscopic measurements. One may want to do such an experiment to study catalytic activity of materials in the same gasses in which they are active, or observe oxidation of materials in a gaseous environment.

5.1 GAS CELL TEM

Placing a sample in a local gas environment inside a TEM is not a new technology. This concept has been in existence since the development of one of the first Environmental TEMs (ETEM) in the mid-1960s by Hashimoto.¹ These early modifications to the TEM column led to the differentially-pumped ETEMs that are available today. These systems use a series of turbo-molecular pumps and diffusion limiting apertures around the specimen chamber to maintain a gaseous environment between the pole pieces of the TEM, while also maintaining the high-vacuum required by other parts of the system, primarily surrounding the electron gun.² This solution required costly (and usually prohibitive) and extensive modifications to the column and polepieces of the TEM, as shown in Figure 18. The advantage of this type of system being that one could continue using standard sample holders with this type of setup.^{3,4} The disadvantages of these is that the experiments are pressure limited as most differential pumping systems can only maintain a pressure of about 50 torr

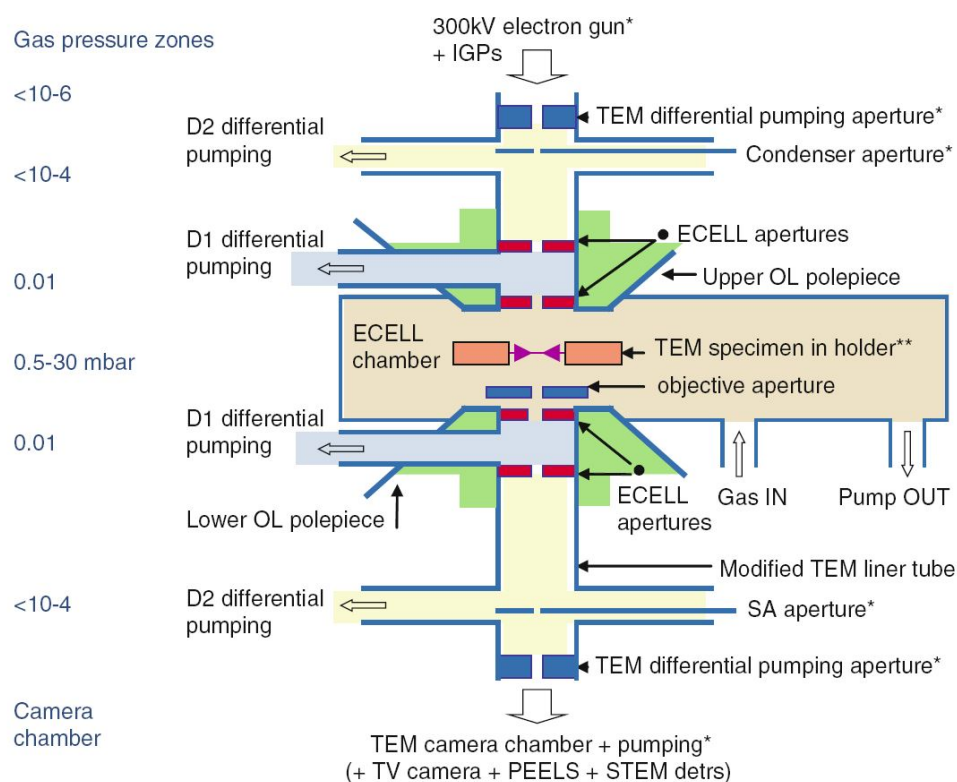


Figure 18: Schematic diagram of typical column modifications required for an ETEM setup. The differential pumping apertures on either side of the polepieces, and the additional gas inlet and pumping surrounding the specimen chamber are shown. (Image reproduced with permission from Reference [3]. Copyright 2016 Springer International Publishing Switzerland.)

(about 6% of atmospheric pressure), and many are incompatible with EDX detectors, as a gaseous environment would contaminate the window of the detector.^{3,4} Until recently, most experiments involving gas-solid interactions in the TEM required the use of these differential pumping systems built into the column of the TEM. But the setup used in the experiments described in this work is similar to the Liquid Cell TEM sample holder described in Chapter 4, with the gas enclosed between two SiN_x windows. The advantage of this system being that it can be used in any TEM (of the appropriate model). Such a design is much more cost efficient, as a gas-cell sample holder is much cheaper than the extensive column modifications needed for an ETEM. The setup used is a DENS Solutions Climate Holder, shown in Figure 19 and Figure 20.

Gas Cell Transmission Electron Microscopy, by contrast to Liquid Cell TEM, possesses fewer limitations in terms of quantitative imaging and analysis. Of course, the presence of a gas surrounding the sample will disrupt the imaging capabilities of the microscope, but to a far lesser extent than that of a liquid. Plural scattering in a gas cell is far less of an issue, as the density of material to interact with is orders of magnitude lower than that of a liquid (which is comparable to that of a solid). In turn, EELS spectroscopy in such a sample environment is much simpler, and not obscured by a large background signal like with a liquid sample.^{3,5-9} These holders are also compatible with EDX spectroscopy, unlike many ETEMs as the gas is contained within a cell.

Also, the issues arising from beam-sample interactions with the liquid environment are not present in the gas cell as a direct result of this lower density of material.

As a result, sample resolution in Gas Cell TEM is somewhat comparable to standard imaging (albeit, with a loss of electron intensity on the detector) with HRTEM and atomic resolution STEM easily achievable.^{3,5,10-13} Only having the sample under scrutiny determine the maximum intensity of the beam (rather than the environment it is immersed in) results in much higher signal from the sample when compared to liquid-phase imaging.



Figure 19: *DENS Solutions Climate Specimen Holder. (Courtesy of DENS Solutions, Delft, Netherlands.)*

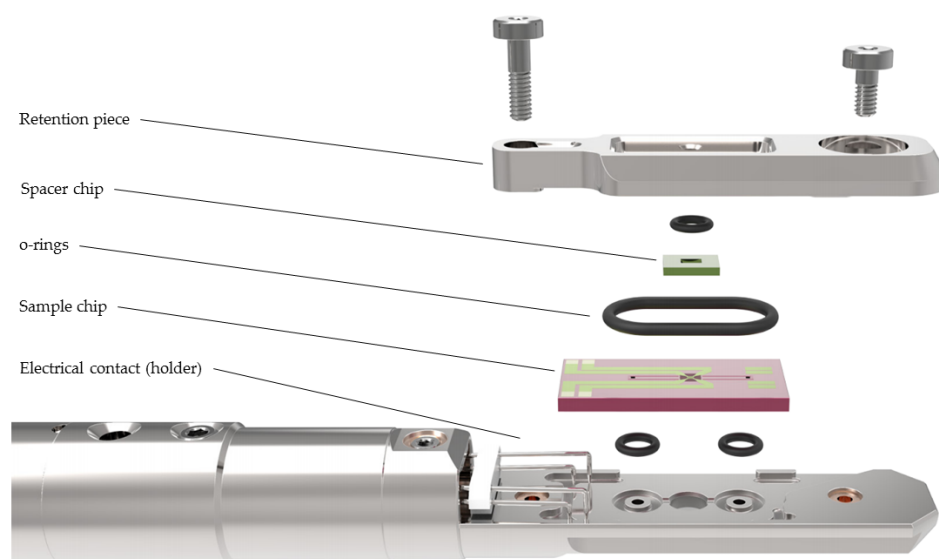


Figure 20: Schematic diagram of the DENS Solutions Climate Holder tip for Gas Cell Transmission Electron Microscopy. The sample is sandwiched between 2 silicon chips, and sealed with o-rings. (Courtesy of DENS Solutions, Delft, Netherlands.)

The ability to observe materials in atmospheric conditions provides an interesting avenue for the characterisation of certain energy storage materials. Previous reports completed by members of our group have shown how materials can degrade over time when exposed to atmosphere,¹⁴ however these studies were unable to observe phenomena in real time and did not extend to the effect of elevated temperatures on this process. Such a study is possible with the use of a closed Gas Cell experiment on a Micro Electro-Mechanical System (MEMS) heating chip, such as the DENS Climate chips as shown in Figure 21. Heating is achieved on the chip by virtue of the Joule effect when current is forced through the conductive heating coil on the chip. The temperature can then be measured from the changing resistance of the coil (similar to a thermistor), which can be accurately measured by using the four-point-probe built right into the chip. Each chip is factory calibrated to ensure

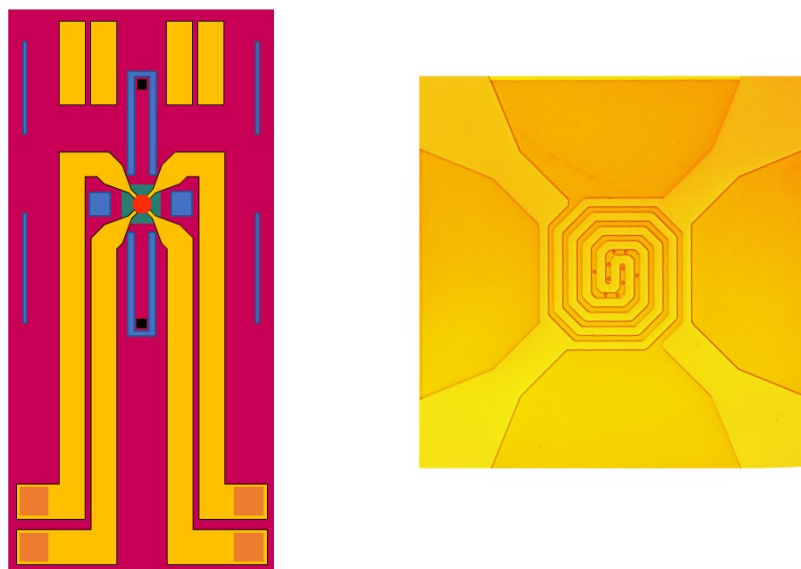


Figure 21: Schematic diagram of the DENS Solutions Climate Holder Heating Chip. MEMS chip contains a four point resistive heating setup for closed loop feedback heating control over the SiN_x window specimen support. Also shown is optical image of the resistive heating coil and contacts located over the central SiN_x windows.

an accurate measurement.¹⁵

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II

EXPERIMENTAL METHODS

EXPERIMENTAL SETUP

In the following chapter the techniques common to all of the results chapters are described. The formulation of printable inks for use in electrochemical reactions, the process of inkjet printing of those inks, the electrochemical testing of the inkjet printed electrodes, and assembly of the *in-situ* sample holders is described.

6.1 MATERIALS AND INK PREPARATION

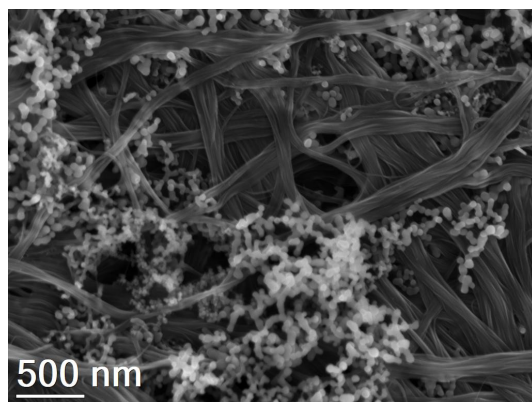
For these experiments, both a working and counter electrode material is required for the two electrode cell setup being used on the electrochemical chips.

Polycrystalline silicon nanoparticles (<80nm, synthesised via gas-phase laser ablation methods) used as purchased from US Research Nanomaterials Inc, Houston TX, USA, dispersed in 2-propanol (IPA) were chosen as the working electrode for the setup. The dispersion was produced by preparing a 10mg/ml stock solution of SiNP and dispersing in IPA via liquid phase dispersion methods (as described by Nicolosi *et al.*¹) using a sonic bath for 30 minutes. The resulting dispersion was diluted as required with IPA, and deposited directly using the inkjet printer. For coin cell electrochemical testing, a slurry of 90% SiNP (the active material), 5% CNT (as a conductive additive), and 5% poly(1,1-difluoroethylene) (PVDF) (as a binder) dissolved in n-methyl-2-pyrrolidone (NMP) was used, deposited on copper foil and spread to a nominal thickness of 30µm with a doctor blade before air-drying. SEM images of the SiNP/CNT composite and SiNP ink electrodes are shown in Figure 22.

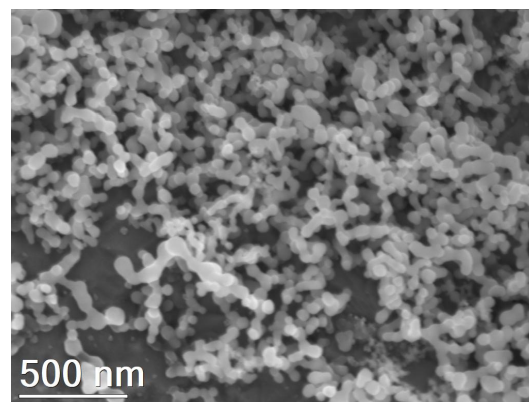
LiFePO_4 was used as the counter electrode, and source of Li^+ ions in the electrochemical system.² The LiFePO_4 was prepared as a slurry of 85% LiFePO_4 (the active material), 10% Carbon Black (as a conductive additive), and 5% poly(1,1-difluoroethylene) (PVDF) (as a binder) dissolved in n-methyl-2-pyrrolidone (NMP) deposited on aluminium foil and spread to a thickness of 30 μm with a doctor blade for *ex-situ* electrochemical tests. An inkjet-printable ink was prepared *via* methods similar to previously reported formulations.³⁻⁵ The LFP ink was composed of 80% LiFePO_4 (the active material), 20% Carbon Black (as a conductive additive), dispersed in a solution of 94.9% H_2O , 5% Ethylene Glycol (as a viscosity modulator), and 0.1% Triton X-100 (as a surfactant). The solids and solvent mixture were combined with a mass loading of 10mg/ml in a ball miller, and left to mix for 12 hours. The resulting dispersion was placed in a centrifuge at 2000rpm for 10 minutes, and the supernatant collected as the final printable ink. The sediment of larger particles was discarded. SEM and EDS analysis show the composition of the inks in Figure 23 and Figure 24, showing the presence of the expected elements.

6.2 INKJET PRINTING

Primarily, high-precision drop-on-demand (DoD) inkjet printing is used for placement of materials onto the electrodes on the chips for *in-situ* experiments. It is an attractive method for materials deposition as it is versatile in terms of the materials and solvents that can be used, there is very little waste of material, does not contact the substrate, and can be scaled to larger devices. The scalability of this method can allow the same ink and printer to be used for the small-scale *in-situ* experiments here, as well as for the printing of macroscale devices for more commercial uses.⁶

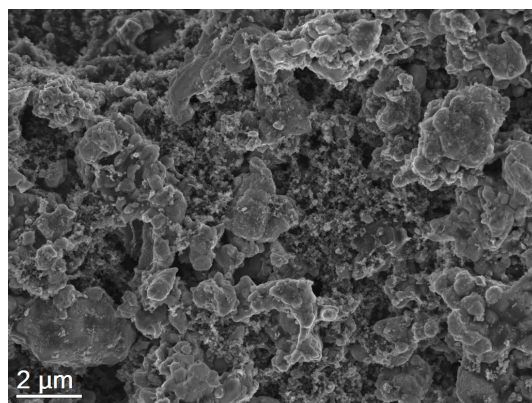


(a) SiNP-CNT Slurry

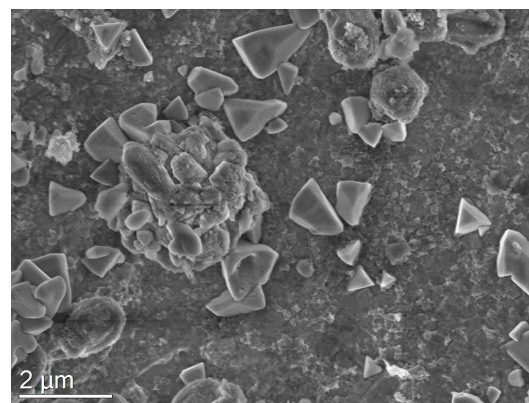


(b) SiNP Ink

Figure 22: SEM images of Silicon Nanoparticle working electrode material, prepared via both a) slurry casting for ex-situ electrochemical coin cell testing with CNT and PVDF binder, and b) inkjet printing as used to deposit pure material to the in-situ chips. The agglomerated SiNP are seen to decorate the CNT-PVDF network in the slurry electrode, and the pure ink shows an agglomerate of SiNP. Images acquired @4keV with a Zeiss Gemini Ultra using In-Lens detector.



(a) LFP Slurry



(b) LFP Ink

Figure 23: SEM image of LFP/Carbon Black counter electrode material, prepared via both a) slurry casting for ex-situ electrochemical coin cell testing, and b) inkjet printing as used to deposit material to the in-situ chips. With the slurry method, a higher mass loading is observed, and a higher amount of amorphous Carbon Black. The lower concentration ink shows more separation between the amorphous Carbon Black and the crystalline LFP. Images acquired @4keV with a Zeiss Gemini Ultra using In-Lens detector.

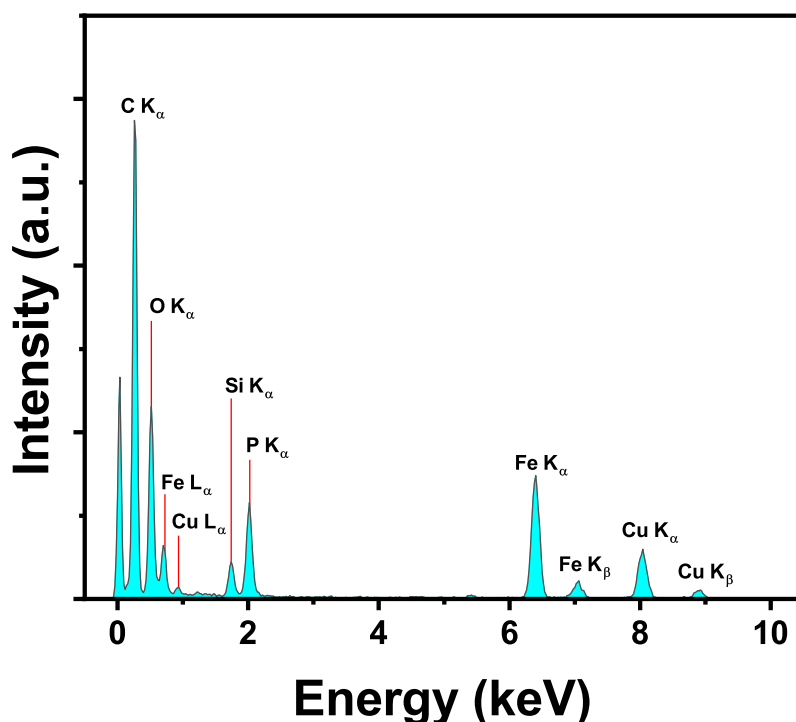


Figure 24: EDX spectrum of the LFP/C ink. Spectra acquired on Jeol2100 @200keV equipped with an Oxford Instruments 80mm² silicon drift detector with 10° holder tilt (ROI shown in Supplemental Information, Figure 53). Iron (Fe), phosphorus (P), and oxygen (O) peaks clearly present from the LFP component of the ink mixture. Lithium component not resolvable with EDX. Carbon (C) peak also clearly identifiable from both the Carbon Black conductive additive and the lacey carbon grid. Copper (Cu) peaks arise from the Cu TEM grid. Silicon (Si) peak due to an EDX spectral artefact; an internal fluorescence peak from the silicon window on the silicon drift detector is a likely culprit.

The DoD deposition is controlled by the printer with a piezoelectric element in the printhead (Dimatix Materials Printer DMP-2850). This piezoelectric element creates a droplet by moving a diaphragm in a very precisely controlled manner. Initially, the printhead is primed and the unbiased piezoelectric crystal is in a neutral position. An electric potential is applied to the piezoelectric crystal and the crystal contracts to draws more ink in from the reservoir to the nozzle head. An opposite bias is then applied, and the piezoelectric crystal expands into the nozzle head forcing the ink out of the nozzle. The piezoelectric crystal then returns to a neutral

position, the ink from the reservoir refills the chamber, and the process is repeated many times per second (up to 20kHz on the Dimatix). This is shown in Figure 25. The applied bias across the piezoelectric crystal is correlated to the energy needed to form and break off a droplet of ink at the nozzle. A time series of this process is shown in Figure 26. As a result inks with higher surface tensions and viscosities require a larger voltage to be applied to create a stable droplet for printing. This varies wildly from solvent to solvent and thus from ink to ink. This means the signal waveform that drives the piezoelectric crystal must be customised for each material and ink. These waveforms can be tuned to control droplet size and shape, and reduce the occurrence of satellite droplets. Finally, any particles suspended in the ink must not be any larger than $\frac{1}{50}$ the size on the printhead nozzle, to prevent clogging.⁶

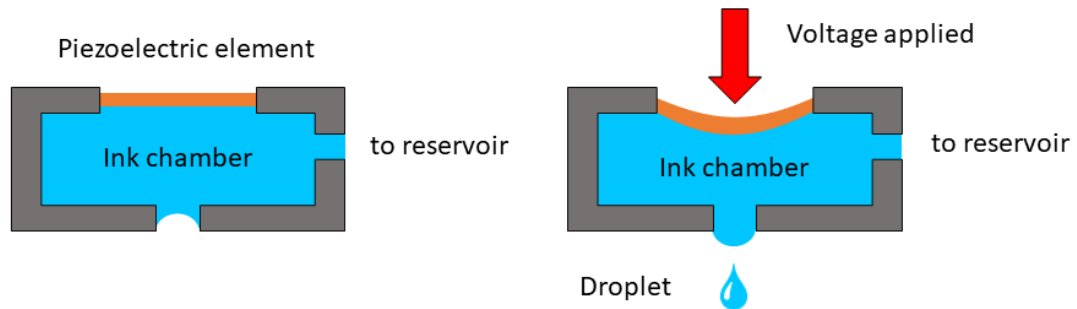


Figure 25: *Schematic of a typical piezoelectric printhead droplet formation. Application of a voltage deforms the piezoelectric element, forcing the diaphragm to eject a droplet from the nozzle. The ink chamber is then refilled from the reservoir, and the cycle begins again.*

Each material was used as an ink for piezoelectric inkjet-printed electrodes onto the electrochemical chips described in Section 6.4 below, and the active materials extend to the electron-transparent SiN_x membrane region to enable the imaging of the materials. The inkjet printing method of material deposition is particularly



Figure 26: Time series photographs of the ejection of a pristine droplet from the printhead nozzle.

Under the ideal applied bias waveform parameters for the specific ink, the droplet is initially pushed out of the nozzle by the piezoelectric element. When the reverse bias is applied, the droplet breaks free, and the process begins again. (Image reproduced with permission from Autodrop Gantry system AD-P-9000 manual. Copyright 2016 Microdrop Technologies GmbH.)

useful for this work, as the printer allows for small droplet size ($\approx 10\text{pl}$) and precision placement of material which will be shown in the next chapter.^{6,7} In this particular case, other high precision placement methods (such as micromanipulation tweezers (Kleindiek Nanotechnik GmbH)) are ineffective due to the porosity of the silicon material. The ratio of material between the counter and working electrodes was kept at $>25:1$, to ensure full cell capacity matching and also allowing for inefficiencies in Li^+ extraction from the cathode material.⁸ The chips were then plasma-treated after deposition of the SiNP ink using a Fischione model 1020 plasma cleaner using a 25% oxygen/argon mix for 5-10 seconds for further cleaning and to improve their surface hydrophilicity at allow for easier wetting of the LiFePO_4 water-based ink on the substrate.⁹

6.3 ELECTROCHEMICAL CHARACTERISATION

Ex-situ electrochemical testing of coin cells was carried out with a BioLogic VMP-300 potentiostat.

While using a half-cell setup would be simpler and more reliable, using lithium metal was out of the question for this system due to concerns about placing lithium metal in the liquid cell holder and how quickly lithium metal will degrade. As such, LiFePO_4 was chosen as the counter material as a suitable alternative source of lithium in the system.² A 0.1M stock solution of LiClO_4 dissolved in 1:1 (v/v) ethylene carbonate (EC) and dimethyl carbonate (DMC) was used as the electrolyte in most of the experiments. The standard 1M LiPF_6 EC:DMC electrolyte was not considered for the liquid cell *in-situ* setup, due to concerns about LiPF_6 degradation that will be discussed in Chapter 7.

6.4 *in-situ* HOLDER ASSEMBLY

The setup for implementation of the *in-situ* liquid cell microbattery to study the electrochemical reactions with liquid electrolyte is schematically illustrated in Figure 14 in Chapter 3, and for the gas cell experiments is schematically illustrated in Figure 20 in Chapter 5. This electrode geometry was implemented using a SiN_x membrane deposited on Si chips as illustrated previously.

The microbattery was built on basis of the *in-situ* TEM liquid-electrochemistry holder purchased from Hummingbird Scientific (Lacey, WA, USA) (Figure 27). Two silicon chips with the dimensions of 2.6mm x 3.4mm x 200 μm , and 2.6mm x 2.6mm x 200 μm were used as the electrochemical chip and spacer chip, respectively. Each

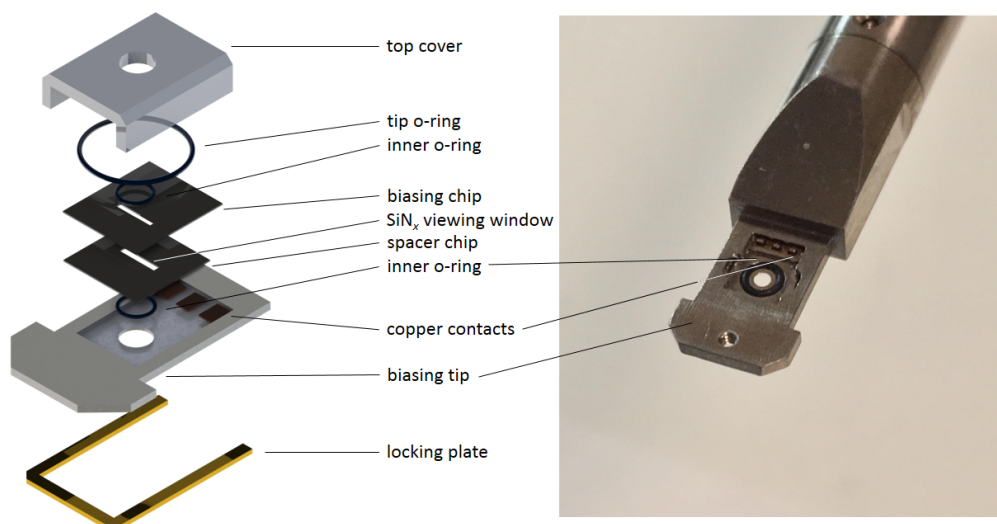


Figure 27: Schematic of liquid electrochemical tip assembly process. The biasing chip and spacer chip are sandwiched and sealed using 3 o-rings, then secured using the top cover and locking plate.

chip contains a $50\mu\text{m} \times 200\mu\text{m}$ viewing window with a 50nm-thick low-stress SiN_x membrane, allowing transmission of the high energy (300kV) electrons for imaging, while still sealing the electrolyte between the chips.¹⁰ Three electrodes (either gold (Au) or platinum (Pt)), 100nm in thickness) are patterned onto the electrochemical chip by the manufacturer with a mutual spacing of $20\mu\text{m}$ on the SiN_x window, as shown in Figure 28. The electrodes extend from the SiN_x window to the edge of the chip, therefore allowing the connection of the electrodes to an outside circuit. A polymer (SU-8, a cross-linked photoresist based on bisphenol A (4,4'-(propane-2,2-diyl)diphenol)) is coated on the spacer chip to create a microchannel; polymer thicknesses ranges from 100nm-1 μm , depending on the experiment.¹⁰ These chips were again plasma treated in the 25% oxygen/argon mix for 5-10 seconds before experiments to make their SiN_x membrane surfaces hydrophilic, so that liquid can easily wet the interior of the liquid cell.⁹

A droplet of electrolyte was applied to the top surface of the spacer chip, and the microchannel was formed by face-to-face stacking of two chips and was used to

accommodate flowing electrolyte, and to seal the electrolyte (fully immersing all of the electrodes and active materials). The assembled cell in cross-section is schematically illustrated in Figure 14 in Chapter 4. The normal thickness of the liquid layer being approximately the thickness of the microchannel (depending on which spacer is used); however, upon loading the cell into TEM column, the membrane will bulge outward due to the pressure differences (see Figure 14 in Chapter 4). Therefore, this thickness is not precisely known.^{11–21} Membrane bulging will be dependant on the shortest side length of the window, as well as the window's mechanical properties and thickness.^{22,23} For a SiN_x window, it has been calculated that the window could bulge up to approximately 500–700nm, drastically increasing the sample thickness.^{23,24}

The sealing is completed based on a three-O-ring technique (as shown in Figure 27), and the whole device is implanted in the Hummingbird biasing *in-situ* liquid TEM holder. Once assembled, the liquid cell holder was leak-tested in a vacuum-pump station to ensure that the electrolyte was safely contained and not leaking.

The liquid electrochemical cell is connected through the specimen holder to a Gamry Reference 600 potentiostat (Gamry, Warminster, PA, USA), allowing electrochemical testing of the active materials during imaging under the TEM.²⁵ A cyclic voltammetry technique (as described in Chapter 2) was used *in-situ*. The materials are cycled between appropriate voltage windows similar to those cited in literature,^{26–28} and as shown in *ex-situ* testing of the electrochemical system seen in Chapter 7. The voltage was swept at a rate of 0.2mVs^{-1} to generate a cyclic voltammogram (CV) curve for the setup.

The electrolyte was fed into the liquid cell *via* PEEK (polyether ether ketone) tubing through an external screw driven syringe pump operated at a low pumping rate of no more than $2\mu\text{l}/\text{min}$ to prevent window breakage.

The SiN_x sample chips for the gas cell holder were assembled in a similar manner.

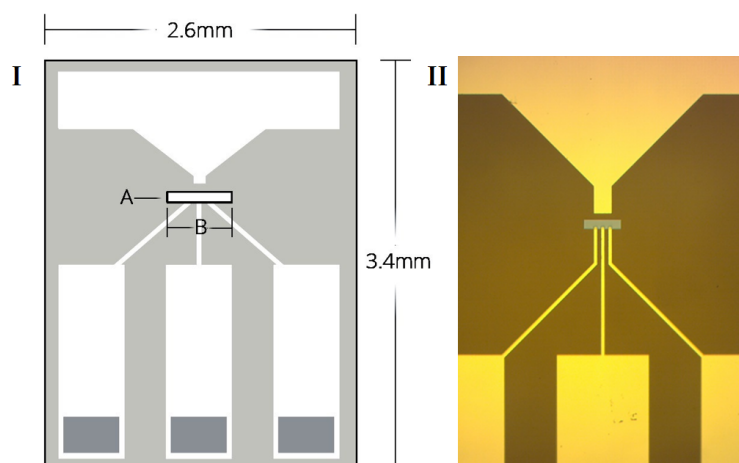


Figure 28: (I) Schematic layout of standard 3-pin Electrochemical chip for Hummingbird Liquid Electrochemistry Holder; total dimensions shown, and SiN_x window dimensions of $50\mu\text{m} \times 200\mu\text{m}$ (AxB). (Courtesy of Hummingbird Scientific, Lacey, WA, USA.) (II) Corresponding optical microscope image of the chip.

The chips, purchased from DENS Solutions (Delft, Netherlands)(Figure 21) were used to isolate the gas flow in the holder from the microscope using a 30nm layer of SiN_x , similar to the Hummingbird setup. The sealing of the holder is completed based on a three-O-ring technique (as shown in the diagram in Figure 20) similarly to the liquid cell holder. Once assembled, the gas cell holder was leak-tested in a vacuum-pump station to ensure that the gas flow was safely contained and not leaking. The holder can be connected to a proprietary external gas flow controller *via* PEEK tubing while in the microscope to introduce gas to the sample.

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III

RESULTS AND DISCUSSION

"Remember kids, the only difference between screwing around
and science is writing it down."

— Adam Savage

IN-SITU TEM OBSERVATIONS OF ELECTROCHEMICAL CYCLING OF SILICON NANOPARTICLES

7.1 ANALYSIS OF SILICON NANOPARTICLE LITHIATION

Before any *in-situ* experiments can be undertaken, experiments must be carried out to determine the expected response from the setup. To this end, *ex-situ* electrochemical cycling of the chosen material (silicon nanoparticles), and *post-mortem* analysis of cycled cells was carried out to determine electrochemical activity, and material response to normal conditions. The results of these experiments are described below.

7.1.1 *Ex-situ Analysis of SiNP Lithiation*

Ex-situ experiments were carried out to determine the voltage window in which to cycle the silicon nanoparticles; from these tests, the nanoparticles are cycled between 0-1.5V in 2032 coin-type half-cell (schematic shown in Figure 29) tests with a lithium counter electrode as demonstrated in Figure 30, and in literature values.^{1,2} It is clear that the Si-nanoparticles are electrochemically active in this voltage window, with a pair of reversible intercalation peaks revealed at an onset of ~ 0.25 V vs a lithium counter electrode as a result of increased current as the electrochemical reaction proceeds.^{3,4} However, as lithium metal cannot be used in the *in-situ* setup, due to practical limitations of lithium storage capabilities at the microscopy

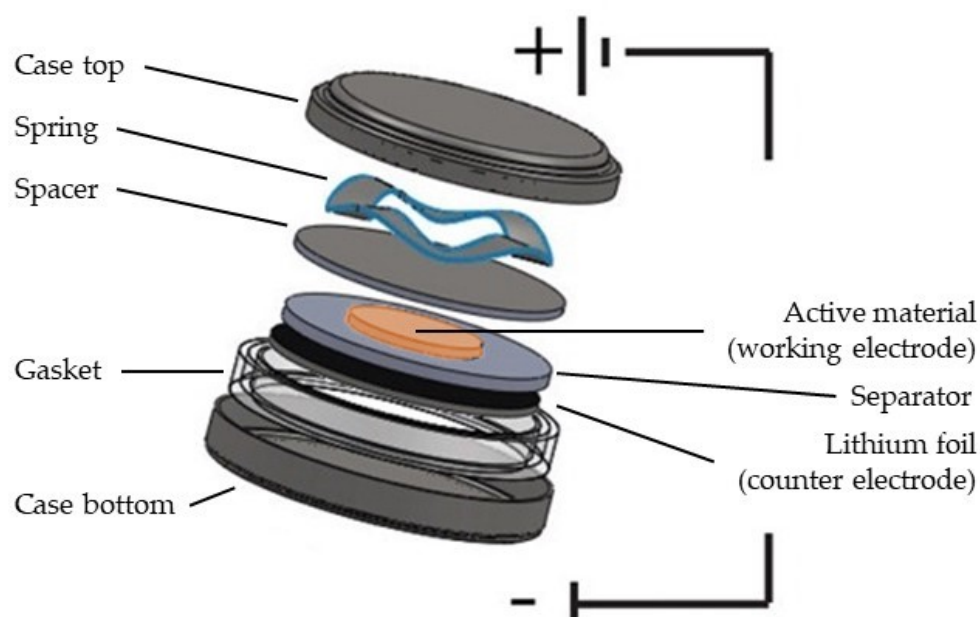


Figure 29: Coin cell schematic, showing arrangement of components of the 2032 type coin cell for *ex-situ* half cell, and full cell electrochemical testing. The spring and spacer disc act as a current collector for the anode. The separator prevents electrodes contacting, while being permeable to electrolyte for ionic conductance. The lithium foil acts as its own current collector and reference electrode. (Image adapted with permission from Reference [6]. Copyright 2016 ACS.)

facility. LiFePO_4 is used as an alternative cathode material.⁵ Both the SiNPs and LiFePO_4 were tested in half-cell configurations with lithium foil used as the counter/reference electrode to verify electrochemical activity and locate relevant reaction peaks. These are shown in Figure 30 and Figure 31.

The *ex-situ* CV data on both the traditional slurry electrodes and the inkjet printed electrodes are also compared to ensure electrochemical activity is not affected by the deposition method. It can be clearly seen that there is little difference between the reversible electrochemical reaction peaks in both Figure 30 and Figure 31. The current response is much lower for the inkjet printed electrodes, however this is easily attributable to the mass loading difference between the two methods, as far

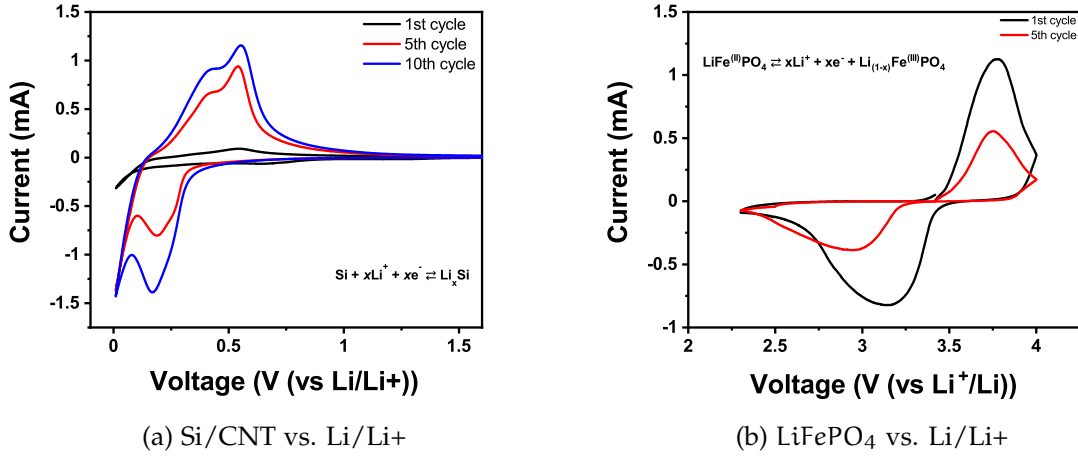


Figure 30: Cyclic Voltammogram at 0.1 mVs^{-1} of a) SiNP/CNT slurry vs. Lithium counter electrode, and b) LiFePO₄/C slurry vs. Lithium counter electrode. A pair of reversible peaks can be seen in each CV, indicating a lithiation-delithiation reaction. (1M LP30 electrolyte)

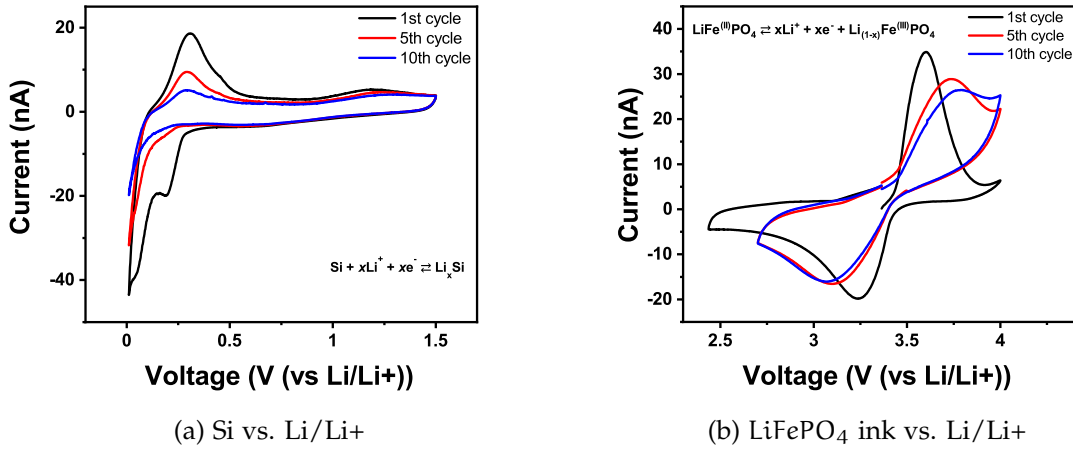


Figure 31: Cyclic Voltammogram at 0.1 mVs^{-1} of a) SiNP IPA based ink vs. Lithium counter electrode, and b) LiFePO₄/C water based ink vs. Lithium counter electrode. A pair of reversible peaks can be seen in each CV, indicating a lithiation-delithiation reaction. (1M LP30 electrolyte)

less material was used for the inkjet printed electrodes than the slurry cast electrodes. There also appears to be an additional peak located at $\sim 0.55 \text{ V}$ vs Li/Li⁺ in the SiNP/CNT slurry when compared to the pure SiNP material, which is a small

irreversible intercalation peak arising from Li^+ -ion insertion into the CNT component, and can be ignored. The two components were combined into a full cell, and subsequently tested as both slurry cast and inkjet deposited electrodes in the same fashion as the half cells. In the full cell, the voltage window for Li^+ -ion insertion shifts to 2.5-4V for this material combination, which has been demonstrated in literature values and in Figure 32.^{7,8} The reversible redox peaks in this region onset at $\sim 3.45\text{V}$ indicate where intercalation and deintercalation events should be observed during the course of cycling within the TEM.

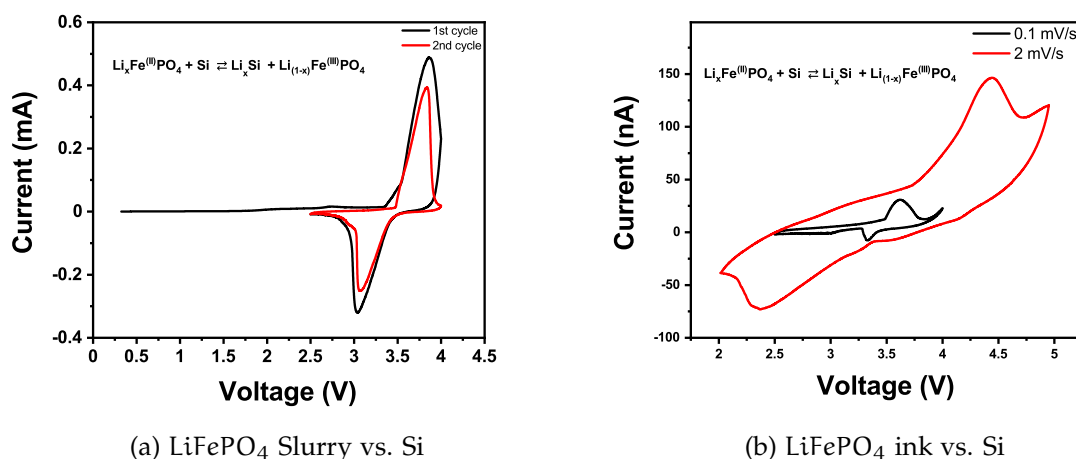


Figure 32: Cyclic Voltammogram of full cell reversible Li^+ -ion intercalation reaction of a) Si vs. LiFePO_4/C at 0.1mVs^{-1} , b) Si vs. LiFePO_4/C inks at 0.1mVs^{-1} and 2mVs^{-1} showing the effect of scan rate on intercalation peak position and current response; peak onset location remains the same at $\sim 3.45\text{V}$ for both scan rates. (1M LP30 electrolyte). This system is being replicated within the microscope.

The motivation behind *in-situ* experimentation and imaging is derived from missing critical steps *via* simpler *post-mortem* analysis. To this end, a sample of SiNP electrode was extracted from one of the cells used in Figure 31. The *post-mortem* sample was obtained by removing the electrode from a cycled coin cell, and washing it in IPA with the assistance of an ultrasonic bath. The resulting dispersion of cycled

material was prepared on a TEM grid by dropcasting, along with a pristine fresh sample prepared *via* the same method. TEM and STEM characterisation and analysis was carried out using an FEI Titan (S)TEM operated at 300keV. The particles are assumed to be spherical for simplification of analysis, and individual nanoparticle diameters were measured using ImageJ over several image sets for each analysis. As can be seen in Figure 33, The difference between the randomly sampled average particle sizes pre- and post- cycling are not very noticeable at first glance. Upon completing a two-tailed t-test on the normal log-transformed dataset⁹⁻¹¹ (see Equation 11.3.1, Supplementary Information Section 11.3), a t-statistic of 2.47 was obtained. This statistical analysis is described in further detail in the Supplementary Information, Section 11.3. From this analysis it can then be stated that there is a statistically significant difference in the means of the two datasets, formally indicating an average particle size increase post-cycling.¹²

Upon further examination of the images shown in Figure 33, only a small proportion of SiNPs can be observed to have increased in size by 300% as the theory discussed in Chapter 2 would suggest for the formation of the Li_xSi alloy nanoparticles. While nanoparticles of diameters $\geq 250\text{nm}$ were observed in the post-cycling sample (and only that sample), the average nanoparticle diameter increase was only measured to be $\approx 10\text{nm}$; an increase from 72nm to 83nm ; this corresponds to $\approx 53.2\%$ increase in volume (again, assuming spherical nanoparticles), on average. Further evidence of Li^+ -ion insertion is provided by the EELS spectra in Figure 34. EELS was chosen for this analysis due to the difficulty of detection of low-Z elements such as lithium by EDX. Upon loss of a core electron, lithium is much more likely to emit an Auger electron than an x-ray; in the low probability than a photon emission occurs (which can occur), the photon will be of such a low energy that it would be absorbed by the window of the EDX detector before it is detected.

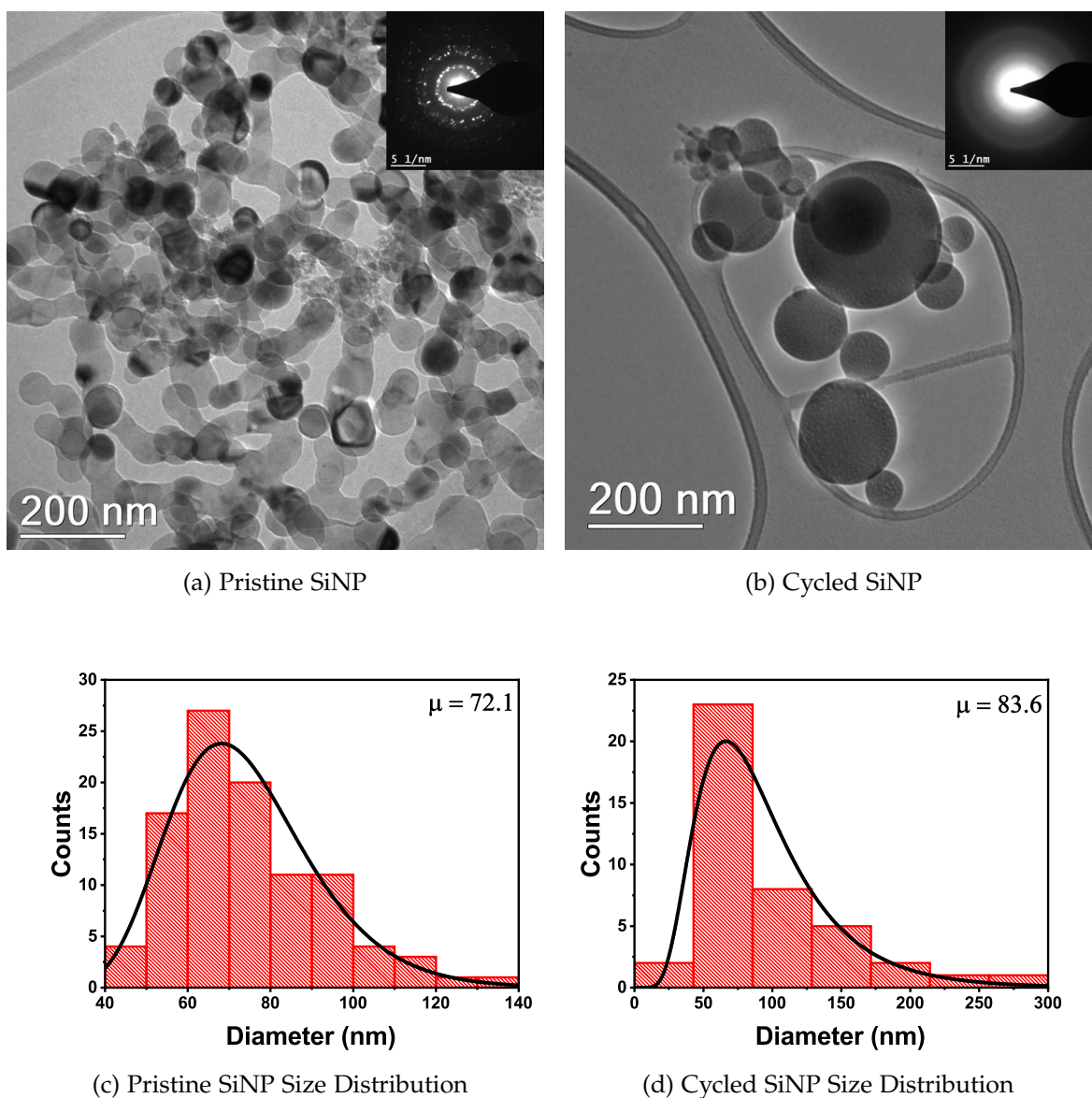
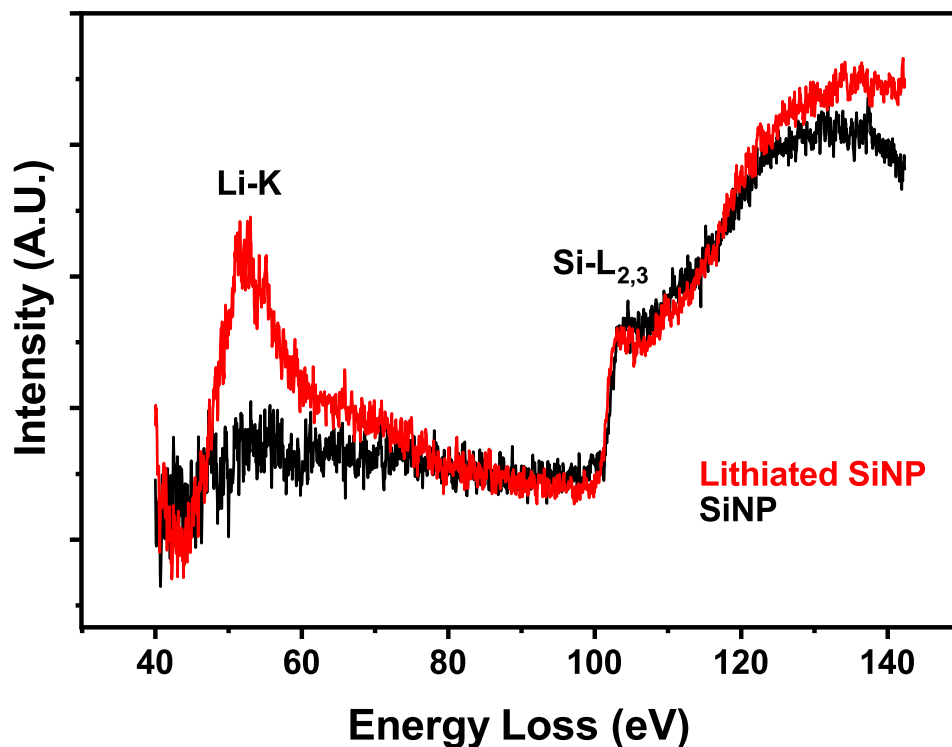


Figure 33: Statistical analysis of SiNP pre- and post-cycling. BF TEM images captured at 300keV of individual SiNPs a) pre-electrochemical lithiation and b) post-electrochemical lithiation. Individual particle swelling can be seen, as well as phase change from highly polycrystalline (from multiple particles) to completely amorphous as evidenced by the inset SAED in each image.

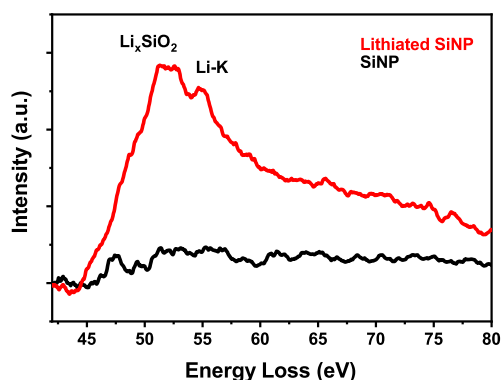
Size distribution histograms of individual particle diameters for c) pre-electrochemical lithiation and d) post-electrochemical lithiation. Nanoparticle diameter determined using ImageJ image analysis software over several images (shown in Supplemental Information, Section 11.3, Figure 56).

A windowless EDX detector has been shown to detect the Li-K_α peak at 55eV (well below the absorption threshold for windowed detectors) according to literature sources,¹³ however the microscopes available are neither equipped with windowless EDX detectors nor Auger electron spectrometers. For these reasons, EELS is utilised to detect lithium in the sample.

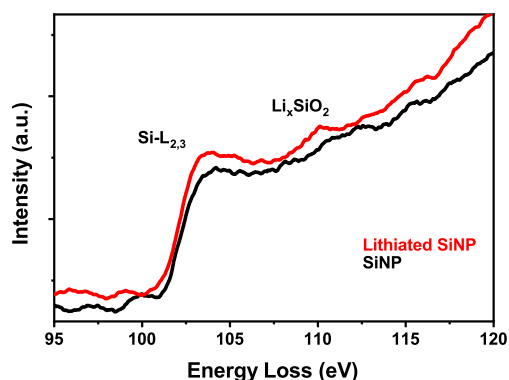
Spectra were collected from single points on the SiNPs (shown in Supplementary Information Section 11.3) to reduce knock-on beam damage to the sensitive amorphous particles. The spectra were acquired in FEI Titan (S)TEM operated at 300keV with an energy dispersion of 0.05eV/Ch, drift tube bias of 40V, nominal energy range of 40-140eV, and a collection semiangle of 7.8mrad. Lithium is clearly present in the particles after cycling as evidenced by the Li K-edge peak at approximately 55eV.¹⁴ Upon post-processing application of an adjacent averaging filter to the spectra to decrease signal noise, the fine structure of the signal becomes more evident. Near-edge fine structure (ELNES) similar to previously reported literature spectra in both the Li-K and Si-L_{2,3} edges confirm the presence of Li_xSiO_2 in the lithiated SiNP, and the formation of the SEI.¹⁴⁻¹⁶ Combined with the volumetric expansion and amorphisation shown in Figure 33, lithiation of the SiNP is confirmed. Regions from which spectra were acquired are shown in the Supplementary Information, Section 11.3.



(a) Raw EELS spectra of pristine SiNP and lithiated SiNP



(b) Li-K edge



(c) Si-L_{2,3} edge

Figure 34: a) STEM EELS spectra showing presence of lithium within a SiNP after electrochemical cycling shown in Figure 31. Lithium is confirmed by Li-K edge at 55eV. (Spectra were collected from single points on the SiNPs to reduce knock-on beam damage, and have been corrected to remove background. Spectra acquired @300keV in FEI Titan (S)TEM with an energy dispersion of 0.05eV/Ch, drift tube bias of 40V, nominal energy range of 40-140eV, and a collection semiangle of 7.8mrad.) Adjacent averaged near-edge fine structure (ELNES) of b) Li-K edge, and c) Si-L_{2,3} edge. Secondary Li-K pre-edge feature (at $\approx 52\text{eV}$) and Si-L_{2,3} post-edge feature (at $\approx 110\text{eV}$) confirming presence of Li_xSiO_2 and SEI in the lithiated SiNP.^{14,16}

While evidence from the larger particles and EELS remain, clearly the dynamic volume expansion during the formation of the Li_xSi alloy has been almost completely missed by such a *post-mortem* method. The sample has also been washed and exposed to various environments in the process of being transferred to a TEM grid. Such exposures are difficult to avoid with *post-mortem* analyses and may introduce or remove critical components of the cycled electrode materials. This only further highlights the need for dynamic observation of the materials in their operational state.

Once this *ex-situ* work to determine the experimental conditions to be used in the *in-situ* setup was completed, the *in-situ* liquid cell was then assembled and cycled in the microscope. The materials and electrochemical conditions have been confirmed to work, and that electrochemical lithiation has occurred in the SiNP. Upon imaging the liquid cell setup, a number of phenomena arising from e^- beam interactions with the lithium-based electrolytes^{17,18} were observed. While these phenomena were unexpected, the technology is still relatively new to the field, and so such issues are inevitable. Limiting or eliminating the effects of these interactions is key to prolonged observation of battery materials, as Li^+ -ion insertion is a slow process, and must be observed over the course of several hours. These phenomena are discussed in detail in the next section.

7.2 DEVELOPMENT OF *in-situ* AND *operando* TEM IMAGING TECHNIQUES

In this section, the development of techniques for effective observation of battery materials (specifically SiNP) in a liquid electrolyte environment within a TEM are explored. A number of effects intrinsic to liquid cell electron microscopy, and methods for overcoming them to achieve the most stable imaging conditions are discussed here.

7.2.1 Cell Fabrication

The first step in electrochemical liquid cell experiments is fabrication of the battery on the electrochemical chips, which relies on accurate deposition of the materials onto the liquid cell electrodes. Much work has been done by previous members of the Nicolosi group on the development of the material deposition via inkjet printing,^{19,20} used here to deposit materials onto electrochemical chips. Any material of a suitable size dispersed in a suitable solvent can be printed onto the electrodes with sufficient contact to be electrochemically cycled (see Figure 35); this process is well understood, provides extreme precision in material placement, and reliably reproducible. This inkjet printing deposition method is described previously in Chapter 6, Section 6.2.

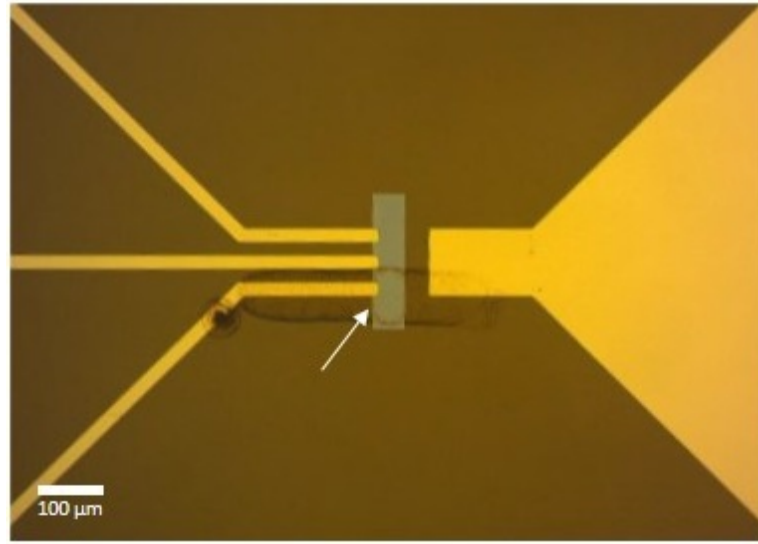


Figure 35: Optical microscope image of silicon ink (indicated by arrow) deposited on electrochemical chip via inkjet printing methods. High degree of precision using this method is demonstrated by the scale bar. All three electrodes (working, counter, and pseudo-reference) are located symmetrically over the SiN_x window.

7.2.2 Data Acquisition

The first issue that was noticed in the setup upon *operando* cycling in the microscope is the inherently low-current electrochemical response of the cell (on the order of nA as measured by the potentiostat),^{21,22} and associated signal noise.

This can be simply explained by the Randles–Sevcik equation,^{23,24} which describes the current response on a redox reaction in an electrochemical cell in cyclic voltammetry.

$$I_p = \left((2.69 \times 10^5) n^{\frac{3}{2}} C D^{\frac{1}{2}} v^{\frac{1}{2}} \right) A \quad (16)$$

I_p = anodic peak current, n = number of electrons involved in redox reaction, C = concentration (mol/m³), D = lithium ion diffusion coefficient, v = potential scan rate (Vs⁻¹), A = electrode area

As can be seen in Equation 16, with a constant potential scan rate, the current response of an electrochemical system in cyclic voltammetry heavily depends on the area of the electrode. Thus we can expect a current response in the picoampere range with the appropriate constants²⁵ and dimensions of this setup.

It has been reported that electrochemical data can be influenced by the inherently small quantities of material used in the setup, and even from the e^- beam presence near the electrical contacts in the cell.^{26–28} This is to be expected, as the volume of electrolyte and electrode placement is critical in thin-layer electrochemistry.^{28,29} While it can be difficult to detect,²² it is not impossible, as we have measured electrochemical reactions at this scale.

Another issue that has recently come to light is the technical issue of instrument-induced signal noise in the data recorded by the potentiostat. It has been suggested that by using a potentiostat to perform electrochemical experiments in a TEM, a ground loop can be set up due to the now electrically-coupled instruments, and induce a large amount of noise to the measurements.²⁸ If the potentiostat, controlling computer, and TEM are all individually grounded (which is the case by default), and there are small differences in the potential between the different ground points, this can influence measurements by obscuring peaks in noise. A solution to this issue is to ground the potentiostat to the chassis of the TEM, thus reducing a potential source of noise.²⁸ This should make any intercalation peaks in any CV data collected much easier to distinguish from the background signal.

In a further attempt to enhance the signal from the potentiostat, the stock cable connecting the tip to the potentiostat was replaced. A new cable was developed with a stronger electrical contact to the tip, and each wire was electromagnetically shielded to reduce crosstalk and further improve the signal-to-noise ratio³⁰ to the potentiostat.

The use of a low-current potentiostat with an integrated transimpedance amplifier may also help solve these particular issues, and has been used for microfluidic electrochemistry in other applications.³¹ Improving the signal-noise ratio for the equipment is crucial to the success of the experiment, as if the signature peaks for the reaction are obscured by noise, it will be difficult to definitively state that any reactions observed are caused by electrochemical cycling.

7.2.3 Window Stability

Upon initial imaging of the cell, it was observed that the two 50nm SiN_x membranes sandwiching the electrolyte demonstrated a tendency to rupture, as the SiN_x membranes are extremely delicate when dealing with macroscopic forces. It is not uncommon for the membrane windows to break, causing rapid evaporation of the volatile electrolyte solvent into the TEM column.

There are a number of steps one can take to reduce the risk of membrane rupture by tailoring the conditions of the experiment. One possible cause of membrane rupture during the experiment is from the flow of electrolyte, as the electrolyte is fed from an external syringe. This acts as an external source of hydrodynamic pressure in the system, and acts to increase the already large pressure differential across the membrane (≈ 10 orders of magnitude larger than TEM vacuum pressure).

While eliminating the external hydrodynamic force from the system will decrease the pressure difference, it will also have the advantage of eliminating the possibility of turbulence in the liquid cell. Turbulent flow is characterized by random and rapid fluctuations of swirling regions of fluid (eddies) and pressure throughout the flow.³² A "back of the envelope" calculation can determine the Reynolds Number (a ratio of the inertial and viscous forces used to quantify whether or not fluid flow will be turbulent; see Equation 17) for the fluid flow in the window region (making

the assumption the flow in the tubing is laminar as a best-case scenario) and give an indication as to whether or not the flow is indeed turbulent.

$$Re = \frac{\text{inertial forces}}{\text{viscous forces}} = \frac{\rho v D_h}{\eta} \quad (17)$$

Re = Reynolds Number, ρ = fluid density, v = average flow velocity, D_h = hydraulic diameter³² = $\frac{4A}{p}$ (A = Cross sectional area, p = internal wetted perimeter), η = dynamic viscosity

Also, using the Kendall equation (which is derived from earlier work by Arrhenius)³³⁻³⁵ (Equation 18) for the viscosity of a binary mixture of ideal fluids, we can roughly calculate the dynamic viscosity of our electrolyte.

$$\ln \eta = x \ln \eta_1 + (1 - x) \ln \eta_2 \quad (18)$$

x = mole fraction of a component of the mixture, η_1, η_2 = viscosities of each component of the binary mixture.

Using the values for the most common solvent for our electrolytes (EC and DMC), the theoretical value for the viscosity of the electrolyte solvent is 1.23 mPa·s, and from this, we calculate the Reynolds Number (using the remaining parameters from the system) to be $Re \cong 1 \times 10^{-4}$. This is orders of magnitude below the threshold of $Re=2600$ required for turbulence,^{32,36} but this calculation completely neglects entry effects as the fluid channel changes shape from a circular pipe to the quasi-rectangular duct of the window region, the sharp 90° directional change the fluid undergoes as it enters the window, and the multitude of impediments to flow in the cell (such as electrodes, material, and generated gas bubbles). These parameters may contribute to localised turbulence within the window region that cannot be trivially calculated. Such fluctuations may act as a possible mechanism for sudden membrane rupture during the experiment. It would be possible to model such turbulent flow dynamics using computational fluid dynamics methods based on the Navier-Stokes equations such as COMSOL.

The obvious solution to this is to avoid a continuous flow setup, and leave the

cell static; while implementation of this has improved window stability in these experiments considerably and has the added benefit of more accurately recreating a closed cell battery environment, it introduces other issues (discussed in Section 7.2.4). If no external fluid pressure is present, the solvent may dry out in the cell leaving no electrolytic connection between the electrodes.³⁷ The solution is to use a low flow rate ($<2\mu\text{l}/\text{min.}$) to maintain sufficient pressure in the cell to prevent dewetting, while maintaining window integrity. This is a compromise to the setup that has been deemed acceptable considering its observed benefits.

7.2.4 *Electron Beam Effects on Liquid Samples*

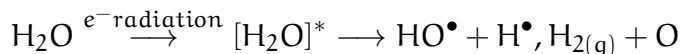
It has been verified by these experiments that the presence of the electron beam on our liquid environment system has the potential to alter the operating conditions of the cell beyond those of a traditional electrochemical cell,^{38,39} including, but limited to, beam charging inducing peak shifts in any electrochemical measurements.⁴⁰ A number of beam-induced reactions have the potential to occur during imaging,^{41,42} however by far the most prevalent in this setup are the effects that alter the local chemistry of the cell.

In general, electron-irradiation-induced damage is classified into three main categories: heating, knock-on damage, and radiolysis. A ubiquitous reaction in *in-situ* liquid cell TEM is the radiolysis of the liquid under electron beam illumination.⁴³⁻⁴⁸ Radiolysis is the breakdown of a molecule as a result of exposure to ionising radiation. Typically, this is in the form of α , β , or γ radiation, but high energy particles like protons or electrons (such as those generated by a TEM) can induce such effects also. Upon exposure to a high energy electron, radiolysis occurs in three main stages; the "physical", the "physio-chemical", and the "chemical".⁴⁹ In the so-called

"physical stage" a molecule may become ionised (by the ejection of an electron), or enter an excited state (by absorbing a portion of energy from the incoming electron). In Equation 19, the example of H₂O is used to illustrate this mechanism as it is a common liquid environment in the literature. From the excited or ionised states, the "physio-chemical" stage proceeds: The molecule may undergo dissociative relaxation into constituent molecules or radical species, as shown in Equation 19. Finally, during the "chemical" stage, the radiolytic products diffuse through the solution and react with other species present in the environment.⁴⁹

Of course, this specific reaction can only occur if the electrolyte is exposed to H₂O (such as from a humid atmosphere), which is definitely possible given the conditions of experimental assembly. If H₂O is present, the high energy (~300keV) electron beam can create an environment of solvated electrons (e_{sol}^-) by scattering events and a variety of hydrogen and oxygen radical species as outlined in Equation 19:

Excitation:



Ionisation:



The liquid environment created can contain any number of the following species in varying concentrations: e_{sol}^- , $HO^\bullet$, $H^\bullet$, H^+ , $HO_2^\bullet$, H_3O^+ , OH^- , H_2O_2 , $H_{2(g)}$, O .^{42-44,50-53} These reactive species can then go on to react further with the electrolyte or locally alter the pH of the liquid solution^{42,52,54} which may alter the working conditions of the cell or the materials under scrutiny.⁵⁴ Schneider *et al.* and Wang *et al.* recently reported an approximate theoretical dose rate threshold for H₂ gas production in pure water in such liquid cell setups, finding a threshold value of $\sim 7-15 \text{ e}^- \text{ \AA}^{-2} \text{ s}^{-1}$.^{55,56} For continuous irradiation at dose rates in excess

of this threshold, $\text{H}_{2(\text{sol})}$ production from radiolysis may cause the formation of $\text{H}_{2(\text{g})}$, either as bubbles or the vaporization and dewetting of large areas of the liquid-cell.^{56,57} Such phenomena have been observed in our own trials. By keeping the dose rate below such a threshold, (we attempt to keep the dose rate below $\sim 1 \text{ e}^- \text{ \AA}^{-2} \text{ s}^{-1}$ in future experiments⁵⁸) one can limit the radiolysis damage introduced to the system by the e^- beam.

It must be acknowledged that common organic battery electrolyte solvents (such as EC:DMC) are also prone to such e^- beam effects. Such excitation and ionisation reactions can also occur with organic solvents, such as those used in battery electrolytes used in this work, but the reactive products will differ, and are not fully understood. Due to the longer carbon chain lengths of such organic solvents, the permutations for radiolytic products are considerably larger than for water. It would be expected that various SEI formation products would be created away from the electrode surface under e^- beam exposure; a variety of combinations of organic radical species such as Li_2CO_3 , lithium ethylene dicarbonate $(-\text{CH}_2\text{OCO}_2\text{Li})_2$, and various lithium alkyl carbonates will be present,^{59–61} along with e_{sol}^- , $\text{H}^\bullet$, $\text{H}_{2(\text{g})}$, H^+ . In the case of more complex solvent-solute combinations, such as those present in Li^+ -ion battery electrolytes, the solvated electrons and other generated species would also interact through secondary chemical reactions with both the solvent and the lithium salt.

While such reactions are unavoidable, they may be limited by certain imaging practices. Reducing the e^- dose delivered to the sample can limit the production of radiolytic products. By using a crude dimensional analysis shown in Equation 20, it can be seen that there are two major ways of reducing the dose rate delivered to the sample.^{62,63} One can reduce the beam current through use of smaller condenser apertures, larger spot sizes, or increase the scanning area (reduce magnification for same beam current). Limiting the e^- beam current can also indirectly reduce the other source of electrons in the system, such as secondary electrons generated by

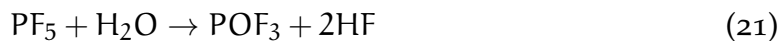
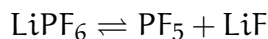
interaction with the sample. These secondary electrons are of a much lower energy than the primary incident beam, and as a result have a much higher interaction cross-section with the surrounding liquid sample.⁶⁴ The secondary electrons may be more damaging to the sample than the incident beam as a result of this increased interaction, and reducing the incident beam dose will have the ancillary effect of reducing the amount of secondary electrons generated. Another technique that stems from reducing this interaction cross-section is increasing the acceleration voltage of the system. While using a lower energy beam (such as 80keV) would reduce knock-on damage (dislocation of atoms into the sample by the beam), this would increase radiolytic damage. For this reason, a 300keV acceleration voltage is used in all liquid cell experiments performed, as knock-on damage is not the primary source of sample degradation in this case.

$$D_{e^-} = \frac{I_p}{eA} \quad (20)$$

(Where D_{e^-} = electron dose rate ($e^- \text{Å}^{-2} \text{s}^{-1}$), I_p = probe current (A, or C/s), e = electron charge (C/e), and A = scanned area (m^2). Multiply by frame/pixel dwell time (τ_d) to get total dose per frame/pixel.

As discussed previously, upon exposure to the atmosphere, H_2O may be absorbed by the electrolyte in small concentrations. The same can be said of oxygen, and other gasses in the atmosphere. Inhibiting the dissolution of excess atmospheric gasses into the electrolytes is preventable, to an extent; to combat the formation of undesired degradation products of the electrolytes, the electrolytes are kept in anhydrous and anoxic conditions. This necessitates the storage of the electrolytes used in an Ar-filled glove box. This storage solution mitigates the possibility of atmospheric-induced electrolyte degradation, and improves the effective lifetime of the home-made electrolytes used. However, in order to assemble the liquid cell holder, electrolyte must be introduced outside of this controlled environment. Maintaining these conditions during assembly is a challenge that has yet to be com-

pletely overcome; for now, the only approach is to limit exposure to the atmosphere as much as possible using an inert gas (such as Ar or N₂ filled glove bag,⁶⁵ or using gas-tight vials and syringes when transporting the electrolyte) during assembly. These solutions are more effective than using no such precautions, and has slowed the formation of degradation products compared to normal assembly procedures. Absorbed H₂O from the atmosphere can also cause other issues with common battery electrolytes, such as the ubiquitous LiPF₆. Upon exposure to the atmosphere, it is possible that any absorbed H₂O facilitates the degradation of LiPF₆, causing formation of Hydrogen Fluoride (HF) outside of an Ar-filled glove box (see Equation 21).⁶⁶ The PF₅ generated via such a mechanism has also been known to decompose carbonates such as those used in the electrolyte solvent,^{66,67} which is undesirable given the inherently high number of variables already present in *in-situ* TEM experimentation.



To eliminate this issue, a variety of other lithium-salts were substituted and tested to act as a viable replacement,^{18,67–70} and another common lithium salt, LiClO₄ was chosen as a substitute due to its lower reactivity and better electrochemical performance in this setup.⁷¹ (images from unsuitable salt trials can be seen in the Supplementary Information, Section 11.3 Figure 60.) While the "home-made" electrolyte does not perform as well as the commercial LP30 (due in part to the lower electrolytic conductivity as a result of reduced salt concentration and lack of performance enhancing additives^{4,59}), the system is still active and will be sufficient for a less optimised system (as can be seen in Figure 36).

Depending on the composition of the electrolyte, it was observed that the solvated electrons can react in different ways. Upon irradiation with the high-energy electrons from the beam, scattering within the solution generates these solvated

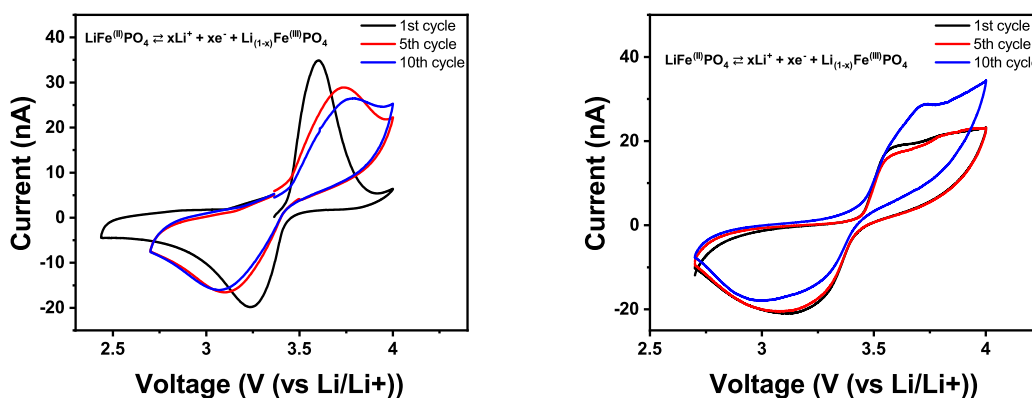
electrons. In the simplest case of a salt dissolved in a single solvent, hydrated electrons can be considered as a reactant in redox reactions that act, in theory, as a reducing agent.^{18,47,48,53,72-74} The generated e_{sol}^- induce the reduction of metallic ions in solution, and can be described generally in Equation 22:



In the case of Li^+ -ion battery electrolytes, this can be more specifically defined as the reduction of lithium as described in Equation 23, however any other similar trace metals ions that may be present in solution would be effected in a similar manner:



This reaction would result in the spontaneous deposition of insoluble metallic lithium under the illuminated area of the sample, and would likely grow as dendrites or nanocrystals, in a similar mechanism to metallic lithium dendrite formation in Li^+ -ion battery cells as a result of cycling.^{39,75,76} In Figure 37, an empty area of the electrolyte filled SiN_x window is exposed to a 300keV e^- beam in TEM mode.



(a) LiFePO_4 ink vs. Li/Li^+ ; 1M LP_{30} electrolyte (b) LiFePO_4 ink vs. Li/Li^+ ; 0.5M LiClO_4 EC:DMC electrolyte

Figure 36: Cyclic Voltammogram at 0.1mVs^{-1} of LiFePO_4/C water based ink vs. Lithium counter electrode using a) 1M LP_{30} , and b) 0.5M LiClO_4 EC:DMC. A pair of reversible peaks onset at $\sim 3.45\text{V}$ can be seen in each CV, indicating a lithiation-delithiation reaction.

Spontaneous reduction of the liquid is rapidly observed (<60s). This effect can be observed even before the application of an external voltage, which may also induce lithium dendrite formation at the electrodes.^{21,77}

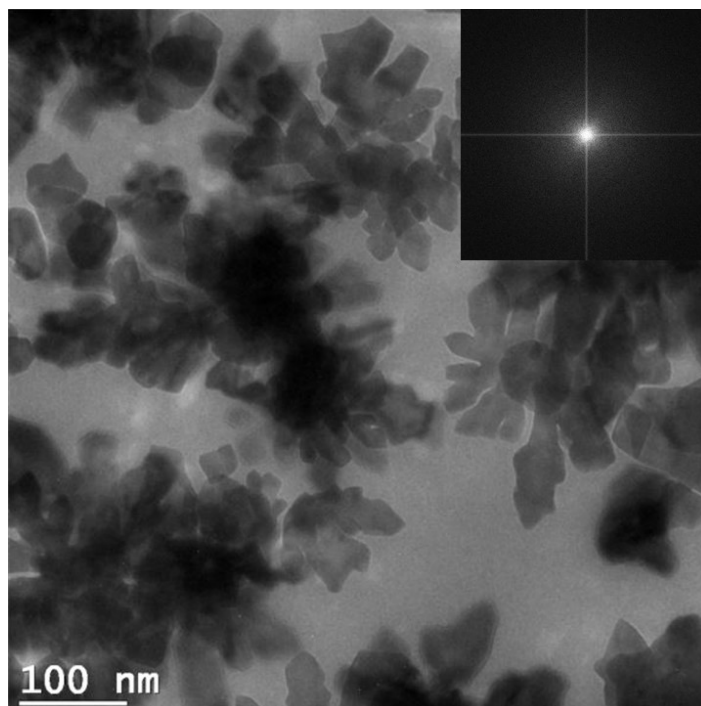


Figure 37: BF TEM image @300keV in FEI Titan of spontaneous Li-metal reduction in LiClO_4 EC:DMC electrolyte under e^- beam exposure after 60 second exposure with no external applied voltage. Dendritic grown completely obscures field of view in a matter of seconds, rendering further imaging impossible. Inset FFT signal dominated by amorphous liquid layer.

While in certain types of *in-situ* experiments, this may in fact be a desirable effect (such as if one wanted to induce a controlled reduction of a reactant using the electron beam),⁷⁸ such effects are considered extremely detrimental here as the last thing you want in a battery cell is formation of unexpected electrolyte reduction products. It is possible to limit these types electrolyte degradation by reducing the electron dose from the beam, while also reducing electrolyte concentration. By controlling the concentration of the reactant in the solution, controlled synthesis of nanoparticles can be achieved;⁷⁸ however this has already been studied in de-

tail and the desired effect of reducing concentration of dissolved lithium salt here is to prevent reduction entirely, thus a suitable concentration to achieve this goal was chosen and the experiment could proceed. It has been observed that dendritic growth depends primarily upon the ratio between current density and concentration of the solute in traditional macro-scale electrochemical setups.⁷⁹ Dendrites will not grow, for a given current density, if the concentration of metal ions is sufficiently low; and for a given concentration of metal ions, they will not grow if the current density is sufficiently low.⁷⁹ Further experiments were carried out to determine if this holds true when the source of current is from the e^- beam, rather than an external circuit; it appears to be equivalent, and so reducing the cumulative electron dose using smaller condenser apertures and reducing the concentration of the electrolyte eliminates this spontaneous dendrite formation.⁵⁰ In conventional microscopy, while this would have repercussions on image resolution and electrochemical performance, this is not a primary concern here. It may be necessary to do this for the sake of a fully functional setup, and for silicon, the high volumetric changes this work hopes to observe do not require a higher resolution. This may be a compromise that will not greatly effect any future results.

It has been suggested that flowing the electrolytes used would enable the continual removal of all these e^- beam generated reactive species,⁴⁴ however this would also introduce potential window stability issues as discussed in Section 7.2.3, as well as differ from the static environment of a battery cell which is trying to be reproduced in the experiment. Schneider *et al.* also demonstrated via computational methods that radiolysis products generated by the electron beam interactions reach a steady-state concentration over a very short time period (~ 2 s);⁵⁶ consequently, introducing a reasonable flow of electrolyte in the setup is unlikely to remove such products at a sufficiently fast rate, as in order for radiolysis products to not be considered the dominant species of the system, a flow rate in excess of 1m/s would be required.^{47,56} Once again, a compromise has been reached, where it has been de-

terminated that better control of e^- beam by-products is more useful to the end-goal of the project than efficient removal of those bi-products. An added benefit to not introducing a flow of electrolyte is the sample area of interest under observation in the TEM will not drift over time,⁸⁰ making localised changes much easier to track.

7.2.5 Image Resolution

Once the issue of e^- beam damage to the electrolytes was controlled, imaging of the Si nanoparticles is now possible over the necessary larger time-scale.

As described previously in Chapter 4, the samples in liquid cell setup are much thicker than the traditional setup, and due to the thickness limited resolution as a result of plural and multiple scattering of a TEM, the resolution of materials in a liquid environment is expected to be lower than solid-state TEM^{47,81,82} (as discussed in Chapter 3, shown in Figure 12, and can be seen in Figure 38). Fortunately this is not of particular concern in this work, as for now, this work is only observing physical volumetric changes in the Si nanoparticles, and individual particle contrast is more than sufficient for purpose here (see Figure 38).

Spatial resolution is often also limited by the low e^- beam doses needed to control radiation damage (discussed in Section 7.2.4) and low signal-to-noise ratios rather than by beam spreading in the cell.⁸³ For beam-sensitive specimens, the limited contrast is caused by a combination of the maximum dose allowed to maintain high-resolution structures, and the low scattering cross-section of low atomic number elements that constitute the sample.^{47,84–86} Little can be done to alleviate this particular issue, as a balance of resolution and beam damage must be determined on a sample-by-sample basis; however this works to the advantage of this particular experiment, as observation of silicon's large volumetric expansion upon lithium

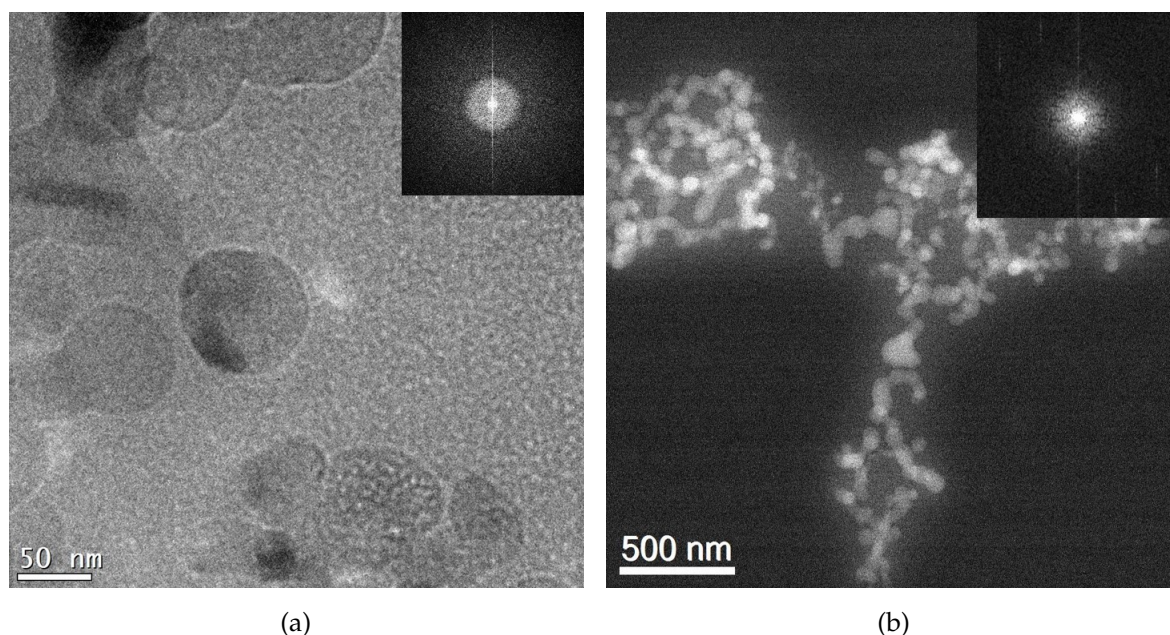


Figure 38: a) BF-TEM image of Silicon nanoparticles in the liquid cell, immersed in a LiClO_4 electrolyte imaged @300keV in FEI Titan. Fine detail (such as lattice planes) is difficult to distinguish in the presence of a liquid layer for low Z elements. Inset FFT of each image shows no crystallinity, as the amorphous liquid layer dominates the signal. b) HAADF-STEM image (FEI Titan @300keV) of Si nanoparticles immersed in a LiClO_4 electrolyte. Image blurring a result of beam broadening due to thick sample interactions. HAADF demonstrated to provide greater contrast on the SiNP than BF TEM. (Image processed using DigitalMicrograph (Gatan Inc.), and ImageJ.)

insertion⁸⁷ may not be affected too much by this loss of resolution, as individual particles can be distinguished before electrochemical lithium insertion as can be seen in Figure 38; this is exactly why it was chosen as a material of scrutiny.

7.2.6 Operando Cycling

Once all of this is put together, we can begin *operando* imaging and cycling of the material. The SiNP are printed in contact with the chip electrode, and a ramped electrical bias is applied.

As can be seen in the acquired images and corresponding *in-situ* CV, the problem is one of an electrochemical nature. No structural change is observed in the material, and no corresponding reaction peak is visible in the CV (See Figure 39). The current remains positive throughout the experiment (even becoming more resistive with cycle number), indicating some kind of irreversible pseudocapacitive energy storage. The reason for this is believed to come down to the geometry of the setup. With the current configuration, the LFP counter electrode is located off the window. This is necessary as the LFP particle size is too large to be placed over the window without causing window ruptures, and allows for more material to be deposited. Unfortunately, this adds a lot of internal ionic resistance to the cell. The electrolyte is not flowing directly across the counter electrode material like it is over the working electrode. This introduces an element of luck to even immerse the counter in electrolyte, and even then the resistance of the cell becomes too great to allow for electrochemical cycling. With lower electrolyte conductivity between the (relatively) distant electrodes, the cell experiences severe ionic transport issues, resulting in an inability to function properly.

7.2.7 Conclusions

Recent revisions to the design of the holder itself, new chip layouts, and competition in the market have made this type of complex experiment much easier. In the newest versions of this type of liquid biasing holder the counter electrode is much larger, and located directly in the path of the flowing electrolyte away from the window.⁸⁸ This type of holder design can allow for near-bulk type electrochemical responses from the material *in-situ*. Repeating the experiments with such a holder may be the final piece of the puzzle in allowing such a relatively complex, real-world facsimile of a battery cell to function in the microscope cell. Furthermore,

the benefits of improved *in-situ* chip geometry and holder design are evidenced by the results obtained in the next chapter. By using the knowledge gained from the developmental experiments described in this chapter and using a more efficient chip layout, a full battery cell is successfully assembled and cycled in Chapter 8 using the same techniques.

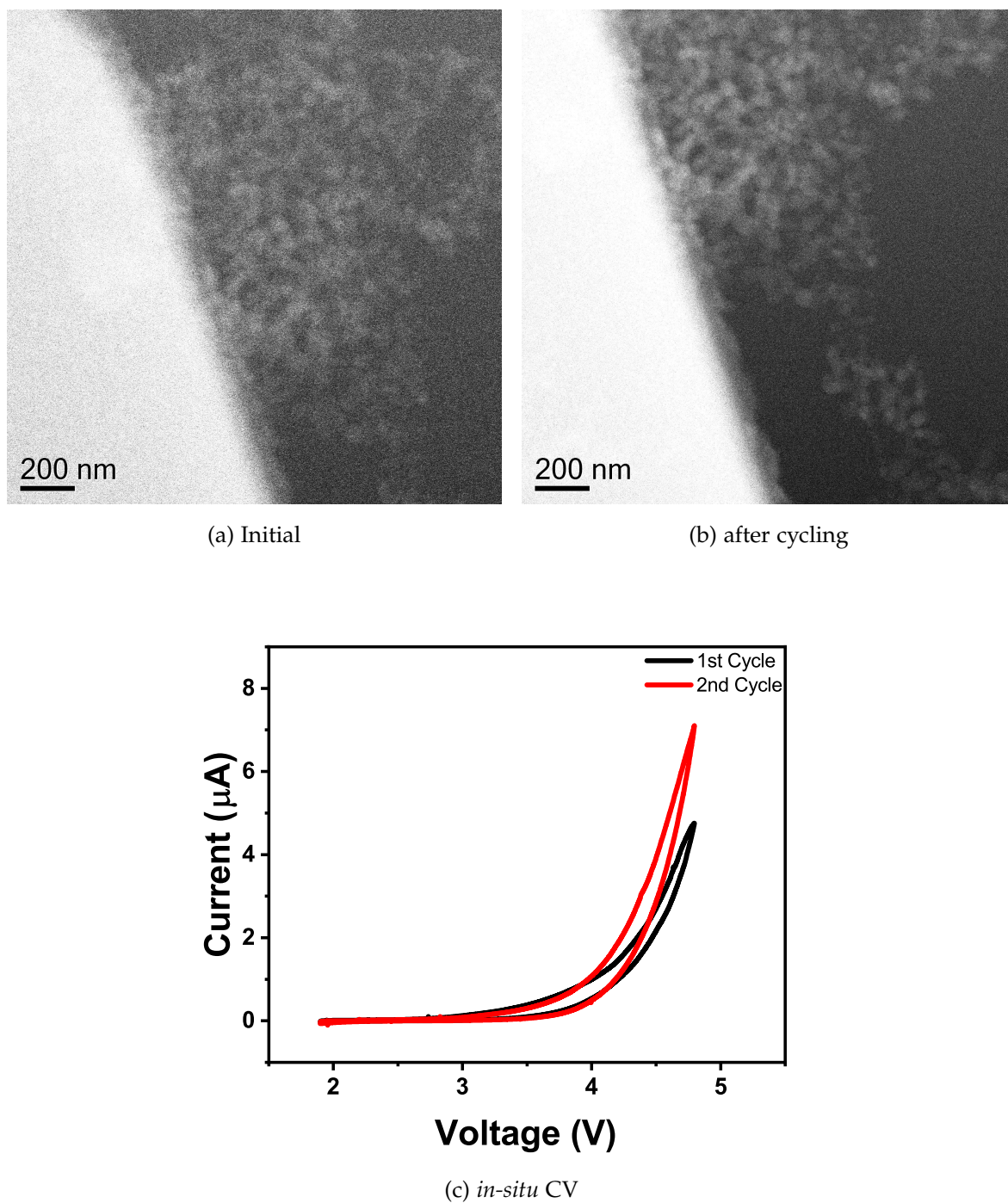


Figure 39: Operando cycling HAADF STEM images of the electrode at (a) an early point in the cycling and (b) after the first cycle (approximately 1 hour at 2 mV/s). Neither structural change nor electrochemical activity is detected. Images acquired on FEI Titan @300 keV.

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In the past decade, MXenes (layered, 2-dimensional metal carbides/nitrides) have emerged as a promising new candidate for anode materials in Li^+ -ion batteries by virtue of its unique and tailorable 2-D transition metal carbide structure.¹⁻⁵ The current most significant challenge of MXene anodes is a rapid degradation in energy storage capacity after a couple of initial battery operation cycles.⁴ However, the series of events during these cycles have not been comprehensively understood yet. In this work, the *in-situ* liquid cell STEM analysis of Ti_3C_2 -type MXene is utilised for investigating initial operation cycles in a Li^+ -ion battery cell. This approach enabled real-time visualisation of complex phenomena such as electrolyte decomposition, and lithiation/delithiation. Regarding these phenomena, four distinctive potential regimes were identified in virtue of our integrated analysis with particle growth kinetics, Z-contrast, and electrochemistry. In particular, evidence of re-stacking of MXene flakes (which is considered to be an additional factor for performance degradation process) is observed.

8.1 ELECTRODE DEPOSITION AND CHARACTERISATION

To deposit the Ti_3C_2 to the working electrode, Aerosol Jet Printing was employed. The use of this technique has been well documented in previous works by the Nicolosi group.⁶ This allows direct coating of Ti_3C_2 on the window of any *in-situ* microchips, in a similar fashion to the inkjet printing described in Chapter 6 and

Chapter 7. Based on the TEM analysis, these Ti_3C_2 flakes show a few-layered 2-dimensional structure with a size of around 0.5-1.5 μm (as shown in Figure 40). This layered feature can also be seen in the atomic resolution medium angle annular dark-field (MAADF) images with a hexagonal lattice, which is a characteristic structure of layered Ti_3C_2 MXene aligned along the $[001]$ axis (Figure 40). MAADF was chosen for imaging as it provided a higher contrast for the lower Z Ti_3C_2 flakes than HAADF.

To deposit the counter electrode, the same inkjet printing method described in Chapter 6 was used. The counter electrode in this setup was LFP, as in Chapter 7, and was used as a source of Li^+ -ions for the system, and charge/capacity balancing for the whole cell.⁸ The materials were deposited on *in-situ* TEM microchips from Protochips, and utilised in a Protochips Poseidon TEM holder (see Supplemental Information, Section 11.4, Figure 61). This system functions in a similar fashion to the Hummingbird Scientific holder described in Chapter 4 and Chapter 6, but differs in its geometry and electrochemical chip layout (shown in Figure 41). The glassy carbon working electrode is positioned over the SiN_x window. The counter electrode is positioned as a large outer ring, allowing for capacity matching. A platinum pseudo-reference electrode is positioned around the SiN_x window, close to the glassy carbon working electrode.

8.2 *operando* CHARACTERISATION

Before the electrochemical measurements are taken, the platinum reference electrode must be calibrated for the system to allow for accurate voltage measurements at the working and counter electrodes. As platinum is a pseudo-reference electrode (pseudo-RE), it does not possess a well defined potential.^{9,10} In this case

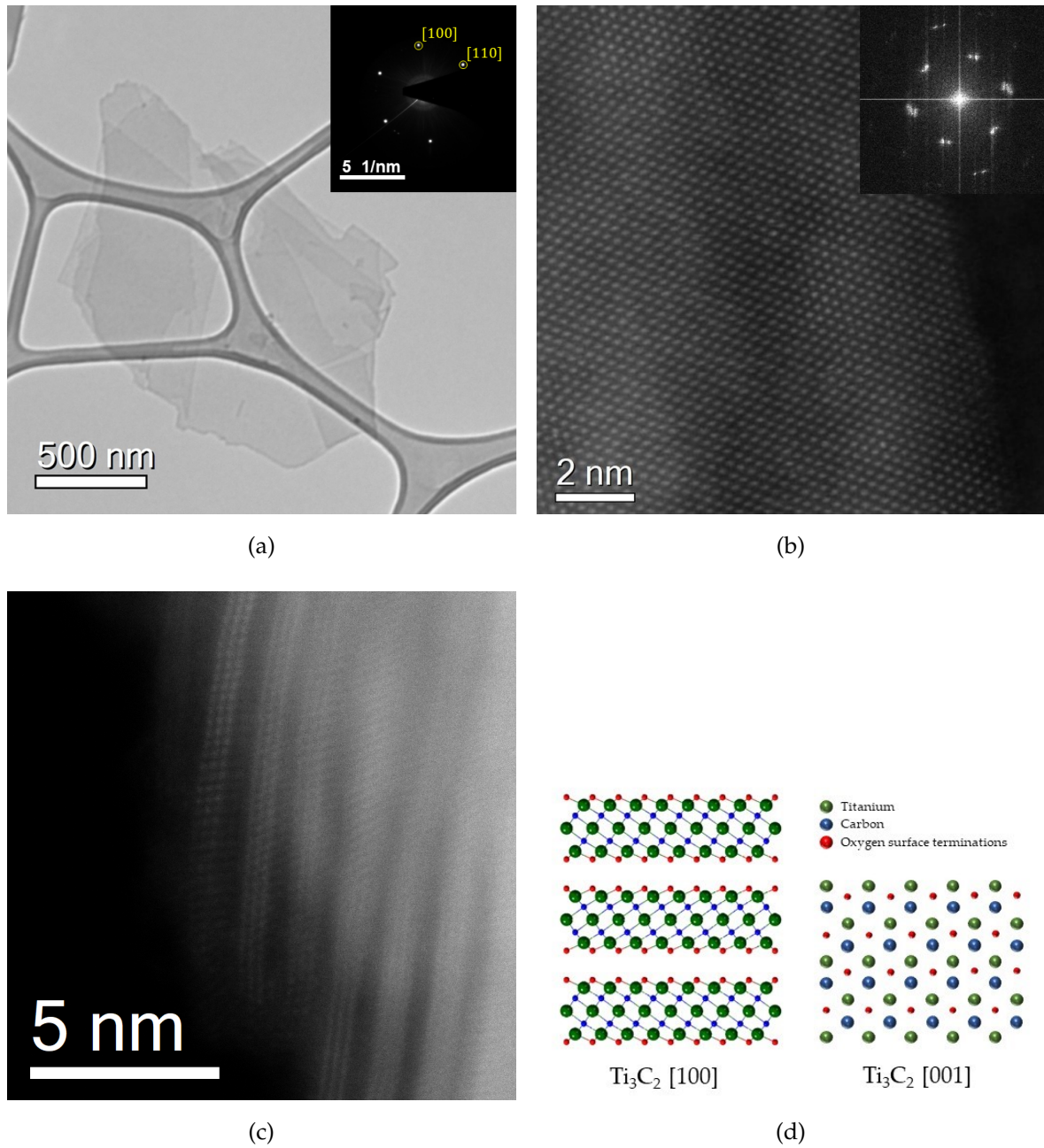


Figure 40: TEM Characterisation of layered Ti_3C_2 MXene. a) BF TEM of multi-layered Ti_3C_2 . SAED inset showing hexagonal structure of the material along the $[001]$ zone axis of the 2-dimensional flake. b) Atomic resolution Average Background Subtraction Filtered (ABSF) MAADF STEM of Ti_3C_2 flake edge along $[001]$ zone axis. Hexagonal pattern visible in both STEM image and inset FFT, concurrent with SAED from TEM. c) HAADF STEM of folded edge of Ti_3C_2 approximately along its $[100]$ zone axis, showing layered structure.⁷ d) Schematic of Ti_3C_2 along $[100]$ and $[001]$ zone axes, consistent with observations in TEM and STEM images in a), b), and c). Atomic resolution STEM acquired on Nion UltraSTEM operated at 60keV.

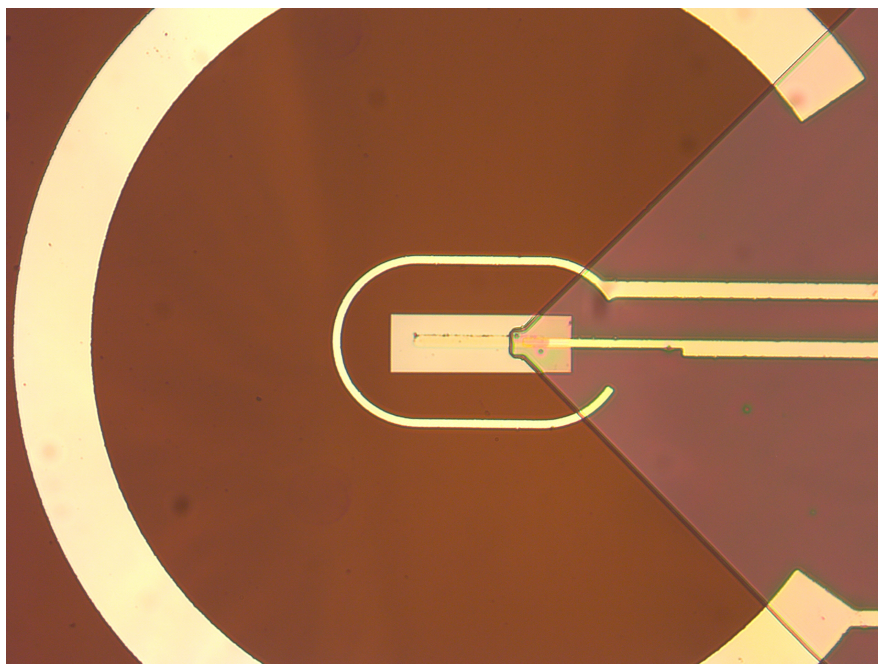


Figure 41: Optical microscope image of Protochips Poseidon electrochemical chip. The electrode geometry differ from the Hummingbird Chips used shown previously in Figure 35. Electrodes are arranged concentrically. A single glassy carbon working electrode is located centrally over the SiN_x window. A Pt pseudo-reference electrode is surrounding the SiN_x window. A large Pt counter electrode is positioned surrounding the other two electrodes. All electrodes are located in the fluid path of the holder.

the Pt electrode was calibrated using a standard ferrocene/ferrocenium (Fc/Fc^+) redox couple. A 20mM ferrocene solution in the 1M LiPF_6 electrolyte was used to calibrate the pseudo-reference electrode as shown in Figure 42.

Using this data and known values of standard potentials of the (Fc/Fc^+) redox couple vs the Standard Hydrogen Electrode (SHE) ($E_0 + 0.4\text{V}$ vs SHE)^{11,12} and Li/Li^+ vs SHE ($E_0 - 3.045\text{V}$ vs SHE)¹³⁻¹⁶ a conversion can be made from potentials vs Pt to potentials vs Li/Li^+ ; from this, it can be calculated that the potential of the Pt electrode is approximately +3.249V vs Li/Li^+ and all measured potentials are offset by this value vs Li/Li^+ . This is consistent with literature values of similar Fc/Fc^+ couples with Pt electrodes in lithium salt solutions.¹⁷

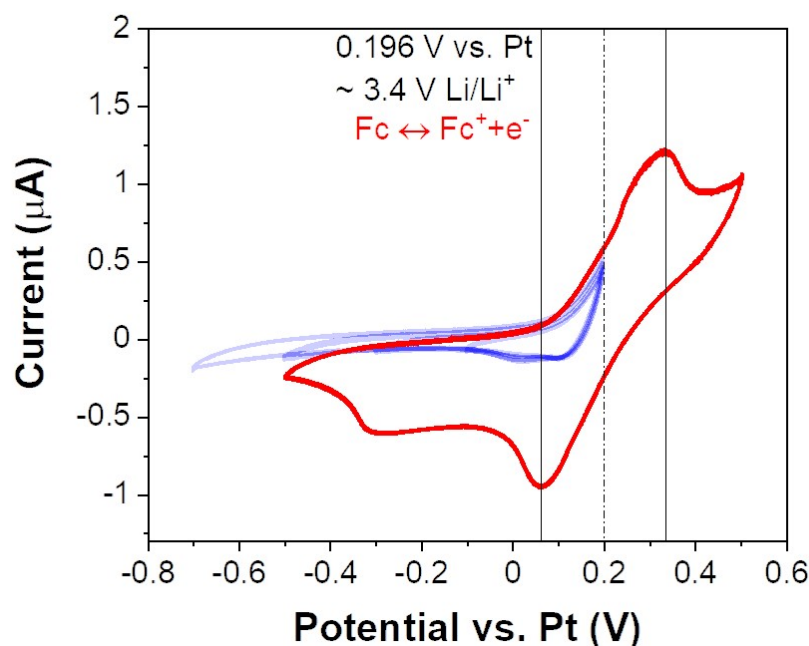


Figure 42: Calibration of Pt pseudo-reference electrode using 20mM ferrocene/ferrocenium (Fc/Fc^+) redox couple in 1M LiPF_6 electrolyte. Offset from 0V is used to convert measured voltage values at the Pt pseudo-reference electrode to more conventional voltages vs. Li/Li^+ in subsequent electrochemical graphs.

During initial electrochemical cycling, the working electrode was cycled from 3V to -3V vs Pt pseudo-RE, with subsequent cycles between -3V and -1V vs Pt pseudo-RE. During the first cycle, the cell undergoes a number of irreversible reactions on the reduction side of the CV (see Figure 45). This would indicate electrolyte decomposition at the counter electrode, which is outside the field of view of the electron beam. Electrolyte decomposition is to be expected at the counter electrode, due to the large measured potential. At 6.2V vs Li/Li^+ , such voltages are well beyond the threshold for the breakdown of standard battery electrolytes.^{18,19} Such a breakdown would release gaseous and solid decomposition products into the cell, resulting in the electrolyte depletion seen in the first cycle CV and Chronopotentiogram shown in Figure 43.

After the first cycle, the *in-situ* cell was purged with argon gas from a gastight syringe and the working electrode was studied. Compared to the initial state, more

visible particles can be observed after the first cycle; most probably due to the solid-electrolyte interface (SEI) formation on the glassy carbon electrode. The majority of these components are expected to provide brighter contrast compared to the electrolyte based on their densities.²⁰ The newly formed particles are also distinct from the Ti_3C_2 MXene flakes as their morphology is much smaller. For the second cycle, the cell was refilled with the fresh electrolyte.

As the reduction scan starts at 1 mV/s for the second cycle (Figure 45), the bulk volume initially expands until the potential reached 1.83 V vs Li/Li^+ . At the same time, fragmentation of some particles was observed, which can be possibly understood by delamination of MXene particles or a break of loosely bound MXene layers. In general, the delamination procedure is the most crucial step for the synthesis as it greatly enhances the performance of MXene-based materials, and various strategies have been applied to prevent the re-stacking of delaminated MXene sheets.²¹ Ion insertion is a well documented method for delamination of layered materials to create dispersions of 2D materials.²² During electrochemical operation, delamination and re-stacking may occur. While the comprehensive understanding of the

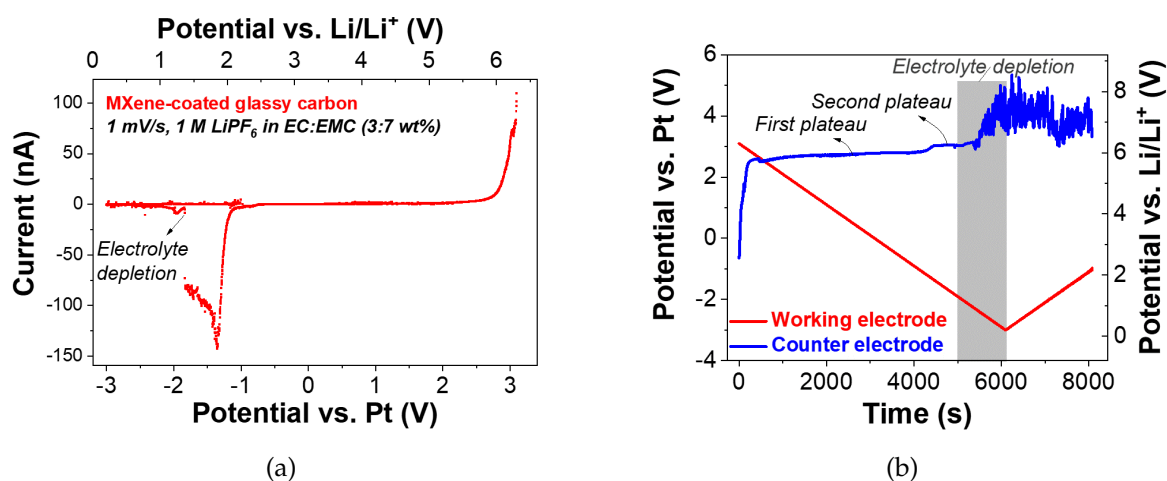


Figure 43: Cyclic Voltammogram and Chronopotentiogram of the first cycle of operation in the *in-situ* cell. Strong reduction peaks and electrolyte depletion (as evidenced by dramatic change to SNR later in cycling process) can be observed.

relationship between the charge storage performance of MXene and the delamination process is still a missing gap in research communities, the re-stacking during the electrochemical operation is considered to bring negative effects such as electrode pulverisation, and breaking of conductive pathways to the active materials.²³ According to the real-time STEM imaging analysis, not only is the fragmentation of the particles observed but also the stacking of the particles (Figure 44). This observation indicates that MXene particles can undergo both delamination and stacking during the electrochemical reduction process. The origin of these processes can be due to the formation of SEI, adsorption/desorption on the surface, Li^+ -ion intercalation between the MXene sheets, change in surface charge, etc. However, the detailed mechanisms and governing factors for these processes are unclear at the moment.

As the potential is further scanned, the particles start growing (Figure 44) until the direction of the scan was reversed, and shrinking during the oxidation scan (see Figure 45, and Figure 44). The latter phenomenon is an indication of deintercalation process of Li^+ -ions in the MXene sheets, and this process is further supported by the decrease in the total area while the particle number was relatively constant during this period. For this particular cycle, the scan direction was reversed as soon as the CV showed indications of partial electrolyte depletion. This approach enabled observation of the oxidation half cycle of the electrolyte covered area of the MXene coated glassy carbon electrode.

Along with the initial volume expansion and fragmentation and stacking of particles, new visible particles arise on the image after a notable reduction reaction was initiated at the onset potential around 2.06V vs Li/Li^+ . According to the analysis, the number of particles increases while the total area of the field of view stays constant. Also, it is worthy to note that there are flexible particles loosely bound to the electrode.

During the reduction scan for the first cycle, a couple of peaks can be identified in

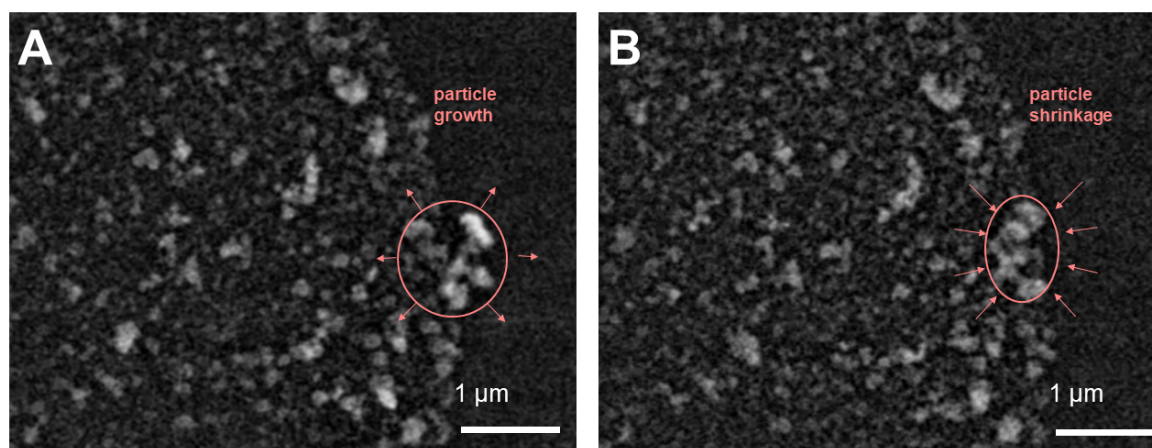


Figure 44: Operando HAADF STEM images of individual MXene cluster growth and shrinkage at specific redox peak positions during electrochemical cycling. Corresponding redox peaks in the CV indicate that the MXene flakes are delaminating and re-stacking as Li^+ -ions intercalate and deintercalate during the charge and discharge cycles. A) Particle growth is observed on the working electrode at -2.07V vs. Pt (time: 1078s) during the reduction (charge) phase. B) Shrinking is observed at -1.02V vs. Pt (time: 2254s) during the oxidation (discharge) phase. Dynamic change of particle size is due to intercalation and deintercalation of Li^+ -ions between the layers of the MXene sheets. Images acquired on Jeol 2100 STEM operated at 200keV.

Figure 45 at 1.0V, 1.3V, 1.6V, and 2.4 V vs Li/Li^+ as well as a considerable reduction current at 0.2 V vs Li/Li^+ . As reported in many cases,^{24,25} the reduction reaction around this potential is most probably related to the lithiation process at the glassy carbon electrode. During the oxidation scan for the first cycle, peaks can be seen at 1.2V, 1.6V, 1.9V, and 2.1V vs Li/Li^+ , which indicate the delithiation process of the MXene material.

As the cycle number increases the intensity of the oxidation peaks gradually decreases. One of the reasons for this dramatic change could be the rapid capacity fading of MXene after initial cycles. This is typically due to loss of material contact from electrode destruction from repeated Li^+ -ion insertion and removal. For the first cycle, the reduction current is high overall in the applied potential range when

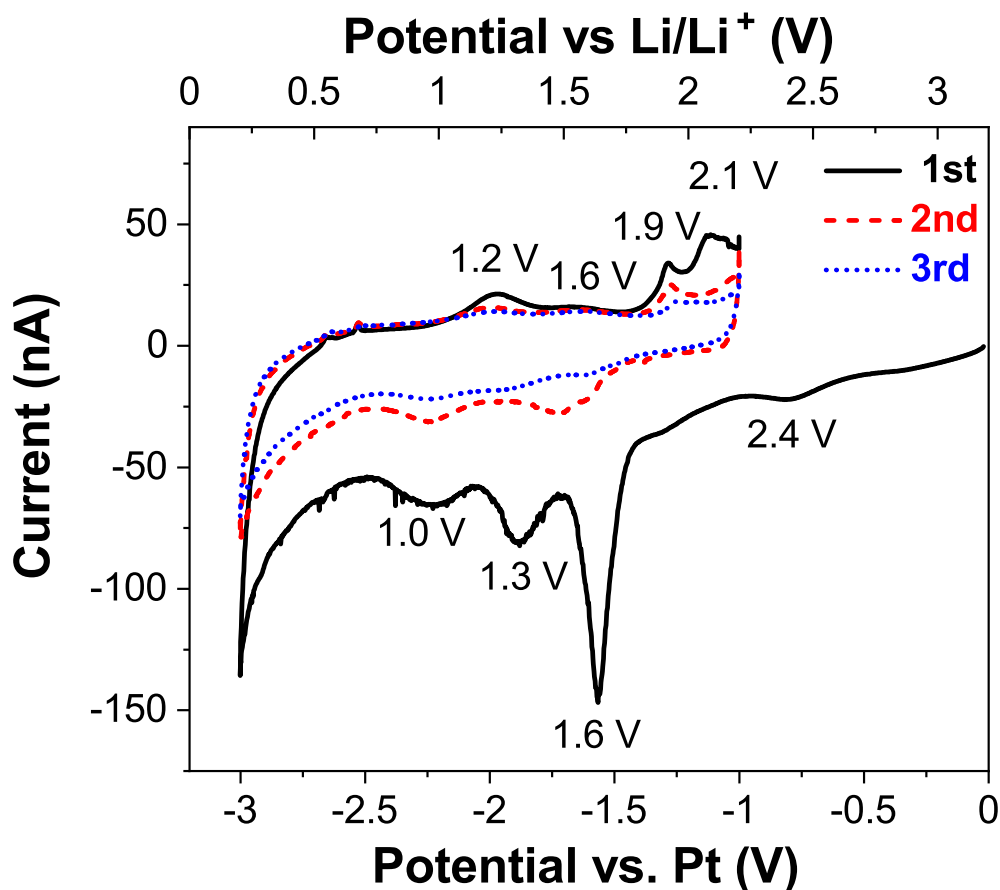


Figure 45: Cyclic Voltammogram of Ti_3C_2 MXene flakes vs LiFePO_4 at 1mVs^{-1} . 1M LiPF_6 EC:DMC electrolyte used. A number of oxidation and reduction peaks related to SEI formation and Li^+ -ion intercalation can be observed. Marked peak voltages are quoted vs Li/Li^+ .

compared to the oxidation current leading to a Coulombic efficiency value of 20%. This low value implies that the most of the reduction current was consumed for the formation of solid electrolyte interface (SEI), irreversible reactions with the active surface groups of the MXene material, and inefficiencies in Li^+ -ion extraction from the material.^{21,26,27} Particularly high irreversible currents arise at the onset of 1.8V and 1.5V vs Li/Li^+ . Despite the strong irreversible reaction around 1.6V vs Li/Li^+ for the first cycle, relatively reversible reactions can be seen as evidenced by reduction and oxidation peaks for the second and third cycles in the potential range from 1.5V to 2V vs Li/Li^+ . Considering the typical redox potential of TiO_2 intercalation/deintercalation process for $\text{Ti}_3\text{C}_2/\text{TiO}_2$ type materials in this range, TiO_2

seems to exist in the MXene electrode.^{28–30} It is to be expected that some amount of TiO_2 will be present on the Ti_3C_2 MXene flakes due to oxidation after synthesis or during the aerosol jet printing process.³¹ The rest of the reversible peaks and capacitive-like current contribution are most probably the consequences of Li^+ -ion intercalation/deintercalation process for Ti_3C_2 .²⁷

After the third cycle, the cell was once again purged with Argon gas. Upon observation of this dried cell, the SEI is clearly visible. As can be seen in Figure 46, a considerable amount of material has been deposited on the working electrode. Details on the formation of the SEI can be found in Chapter 2, but essentially as the electrolyte surrounding the electrode is exposed to potentials that expedite its degradation during the course of normal electrochemical activity. The SEI would be composed of LiF , LiOH , Li_2CO_3 , polyethylene oxides, lithium-oxide-polycarbonates, and a variety of other lithium-based organic molecules..^{32–38} These reaction products have been reported to form well within the voltage parameters of the cell tested here, and it is believed that this is what the deposited material is. EDX analysis was also carried out on the Ar-purged cell and is shown in Figure 63 in the Supplementary Information Section 11.4. The spectrum confirms the presence of MXene as evidenced by the Ti signal. The Si signal originates from the silicon nitride window. No O or C peaks are present, as one would expect from the many oxygen and carbon containing compounds that form the SEI as well as the glassy carbon electrode itself. This is likely because these peaks are of a lower energy than the absorption energy of Si from the SiN_x window, and x-rays are thus absorbed by the window before reaching the detector.³⁹

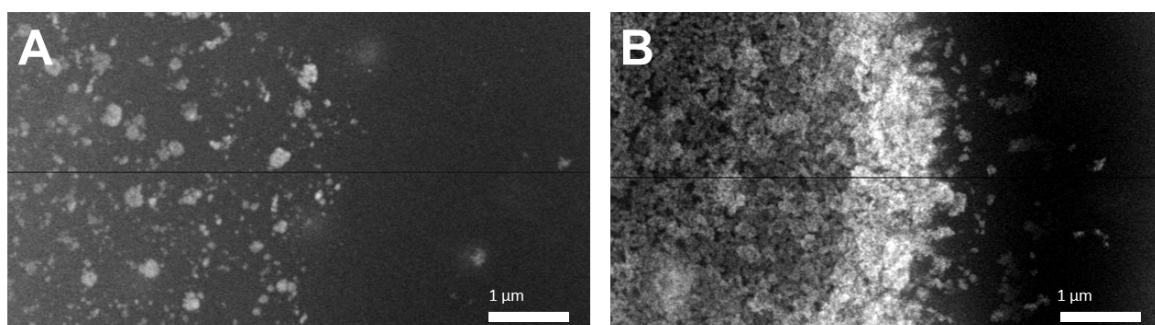


Figure 46: HAADF STEM images of SEI formation at the glassy carbon electrode after electrolyte flushing with argon. Electrolyte decomposition products have been deposited on the electrode during the course of 3 cycles. A) Showing the MXene coated glassy carbon electrode after the first cycle. B) Showing the MXene coated glassy carbon electrode after the third cycle. Images acquired on Jeol 2100 STEM operated at 200keV.

8.3 CONCLUSIONS

In conclusion, an advanced in-situ STEM analysis of a Ti_3C_2 -type MXene anode in a Li^+ -ion battery with the aid of additive manufacturing methods based on inkjet and aerosol jet printing (described previously in Chapter 6) has been presented. The approach enabled visualising a formation of new phases in gas and solid states and the change in bulk volume as well as growth, shrinkage, fragmentation, and re-stacking of MXene flakes during initial battery operation cycles. The STEM imaging data was linked with the electrochemical data from the cell, which allowed the connections to complex battery phenomena such as chemomechanical degradation of the electrodes, electrolyte decomposition, SEI formation, and Li^+ -ion intercalation/deintercalation processes. These results shed new light on these phenomena and bring new insights to research communities in terms of developing a comprehensive understanding of lithiation mechanisms for MXene anodes and new strategies for enhancing performance. Additionally, the approach with back-and-forth filling with Ar gas and electrolyte is expected to mitigate the issue with the radiolysis damage described in Chapter 7 which are caused by the high electron beam doses required for techniques such as EELS and EDX, as well as higher resolution imaging.^{40–44}

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NOVEL METHOD FOR IMAGING SULPHUR SAMPLES WITHOUT SUBLIMATION ARTEFACTS

As one of the many potential candidate materials for high capacity lithium ion batteries, sulphur poses a few interesting challenges before it can gain widespread utilisation. The most pertinent issue is known as the polysulphide shuttling effect (described previously in Chapter 2, specifically Figure 4), which contributes to rapid capacity loss after cycling. As a quick recap, the S_8 allotrope is broken down and re-formed during reversible cycling, intermediate reactions can leech S from the process, depositing insoluble Li-S compounds on the lithium electrode in the system. As Figure 47 shows, the relatively large decrease in current response of the sulphur anode after just 10 cycles ($\approx 50\%$ by comparing peak currents), along with peaks indicating irreversible shuttling/SEI formation reactions contribute to this rapid capacity loss.¹⁻³

9.1 SULPHUR SUBLIMATION

Of concern here is another property of sulphur. One of the challenges to Li-S battery development is the difficulties in TEM characterisation of sulphur. Accurate characterisation of novel sulphur materials designed for battery applications is critical to our understanding of techniques to mitigate the polysulphide shuttling effect by electrode design. It is well documented that sulphur undergoes sublimation at a point above the typical pressures found in the column of a TEM at

room temperature.^{4,5} This makes the imaging and characterisation of any sort of nanostructured sulphur samples challenging, as the material will be modified or even disappear rapidly as soon as it is inserted into the TEM vacuum.^{5,6} As a result, materials characterised by such methods are prone to deviation from normal conditions to a great extent. In order to prevent this, the sample must be forced back into the solid region of the phase diagram (shown in Figure 48). This can be achieved in two ways; by cryogenically cooling the sample to a temperature past the sublimation line, or by increasing the pressure surrounding the sample to a level greater than sulfur's equilibrium vapor pressure of $\approx 10^{-7}$ Torr (at 20°C).⁴ Both methods have been previously demonstrated by Levin *et. al.*,⁵ showing stable imaging of sulphur using a Cryo-holder for the TEM, and using an ambient pressure SEM. Building on this work, a novel method for imaging sulphur in the TEM using a SiN_x window gas cell holder is proposed. With the introduction of commercially available gas cell holders, a sample can be held at a set pressure with

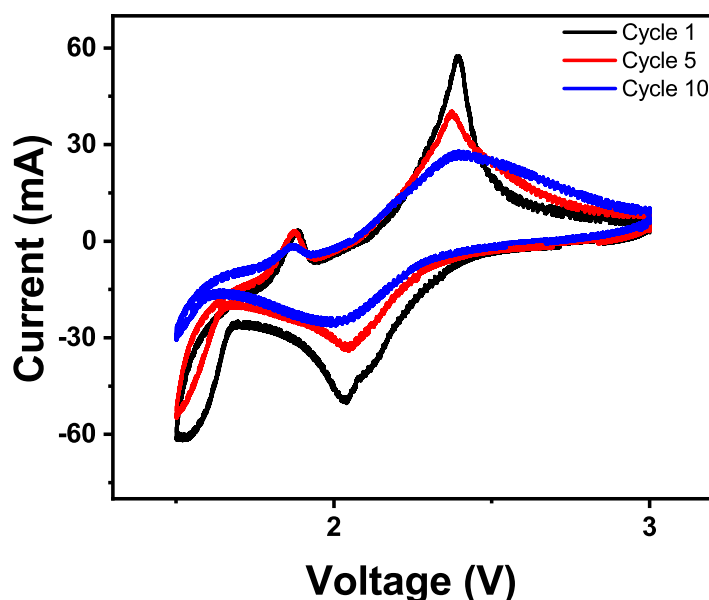


Figure 47: CV of Sulphur electrode vs Li/Li⁺. Single pair of reversible peaks indicating reversible lithium transfer reaction, and single irreversible peak indicating sulphur leeching ancillary reaction. Rapid capacity fade over small number of cycles also visible.

any compatible gas connected to the sample holder. In this case, the sample was left open to air. Given that the only necessary modification to the system would be the pressure, a set pressure of any non-reactive gas (such as N_2 or Ar) would also work. The concept of protectively encapsulating a sample to inhibit degradation in the microscope environment has been used in previous work by Kwon *et. al.* to limit oxidation of copper nanowires, and a conceptually similar solution is demonstrated in this work.⁷

A sample of elemental sulphur was prepared by dispersing the as purchased sulphur powder (325 mesh, 99.5% purity, Alpha Aesar) in isopropanol *via* ultrasonication. The dispersion was dropcast onto a lacey carbon film covered copper TEM grid for the control experiment. The same sample was also dropcast onto a DENS

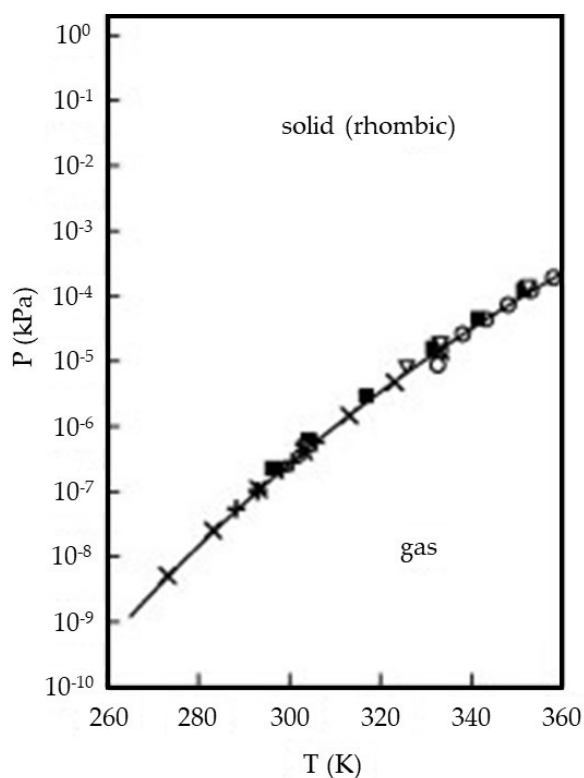


Figure 48: Temperature-Pressure phase diagram of sulphur. At typical TEM vacuum pressures ($\approx 10^{-7}$ kPa at room temperature), sulphur exists in the gas phase. cryogenic cooling to sub 250K, or increasing pressure around sample is required to keep sulphur in the solid orthorhombic phase. (Adapted with permission from Reference [4]. Copyright 2011 Elsevier.)

Climate MEMS chip (see Chapter 5, Figure 21).

The standard copper grid sample was loaded into the microscope, and a sulphur particle was chosen as the region of interest. The particle was imaged in TEM mode at 300keV, and the column valves were closed between each consecutive image to reduce any beam-induced artefacts. As can be seen in Figure 49, the sulphur particle sublimates in the column vacuum over a period of 10 minutes. The residual material is vacuum-stable, and is believed to be super-sublimated polymeric sulfur,⁸ which is known to have a much lower vapour pressure than elemental sulphur,⁸ and is comparable to the experiments conducted by Levin *et. al.*⁵ Examination of the residue by EDX STEM mapping at 300keV confirms the residue as sulphur (Figure 50).

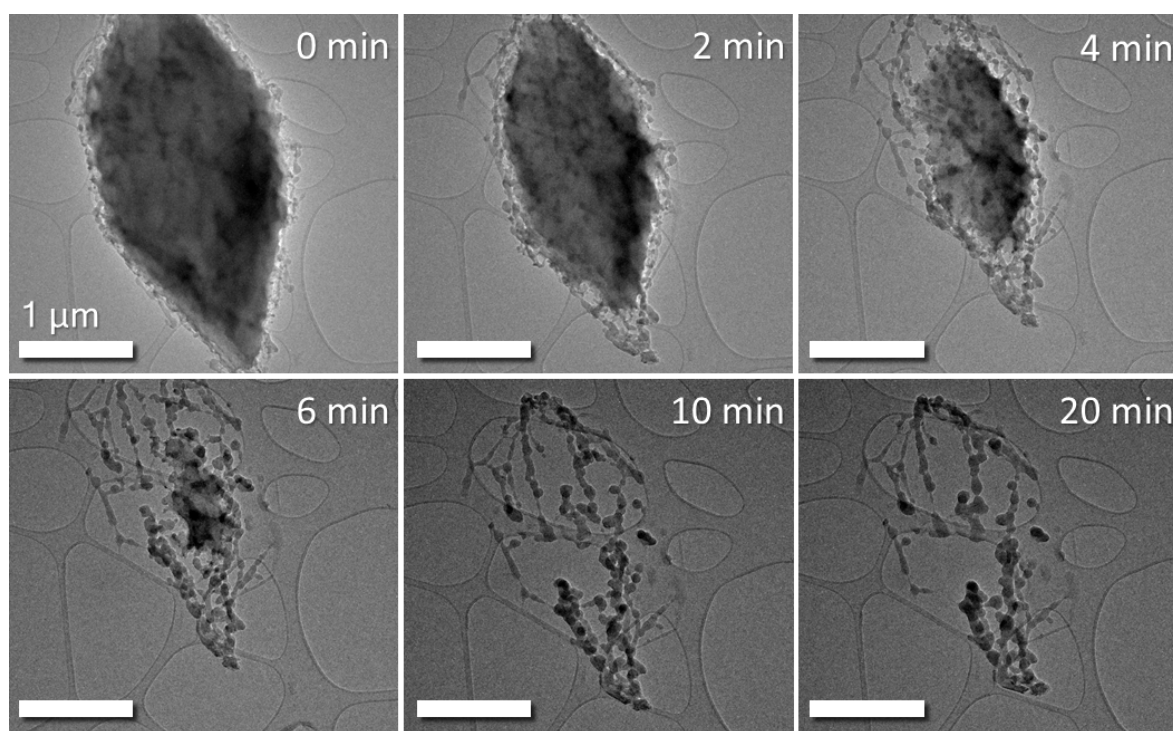
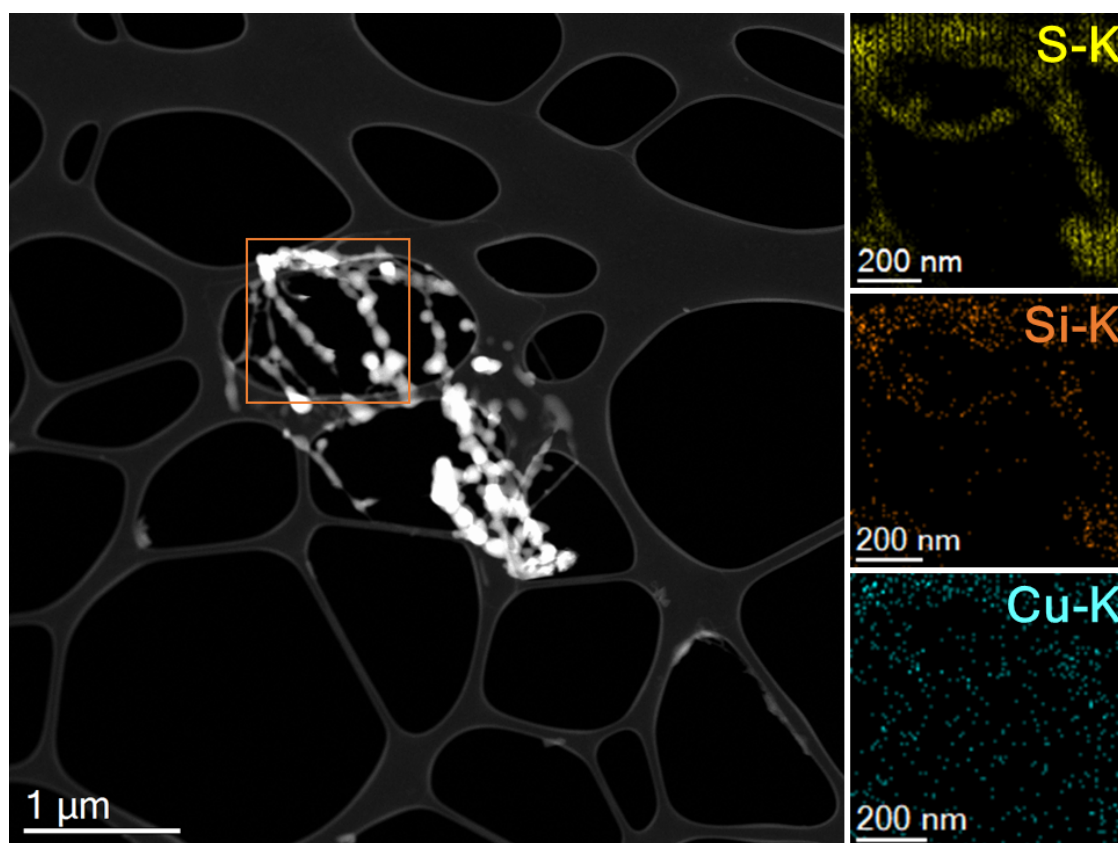


Figure 49: BF TEM time series images of sulphur particle subliming in TEM column vacuum of 7×10^{-8} Torr. The large particle in the region of interest is seen to dramatically shrink over time under vacuum exposure. Column valves were closed between images to prevent beam-induced effects altering the sublimation process. Images acquired on FEI Titan operated at 300keV. Scale bar is $1 \mu\text{m}$ in all above images.

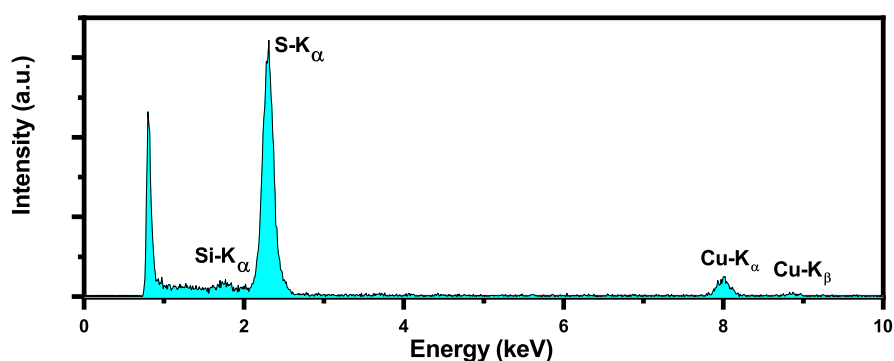
9.2 SUBLIMATION INHIBITION *via* ENCAPSULATION

In order to investigate the potential of the commercial gas cell sample holder as a method to image the sulphur without sublimation, the sample was inserted into the column, and imaged over a period of 2 hours using the same experimental conditions as the previous experiment (300keV TEM and STEM for EDX analysis). No change in particle morphology was observed over the observation period of 2 hours (as seen in Figure 51, as the particle was kept at ambient pressure, and the column valves were closed between image acquisitions to reduce any beam-induced artefacts. The EDX spectrum acquired after the 2 hours showing S-K $_{\alpha}$ and Si-K $_{\alpha}$ peaks in Figure 52 confirms that the particle is indeed sulphur supported on a SiN $_x$ window. The suppression of the sublimation clearly demonstrates the viability of the use of windowed *in-situ* sample holders for imaging and characterisation of high vapour pressure materials in the TEM.

Obviously being an electrical insulating material, sulphur is still very susceptible to radiation damage from the electron beam, and careful consideration must be made to the beam current passing through the sample for quantitative and qualitative spectroscopy.⁹⁻¹¹ For example, in order to acquire data for an EDX map of the sulphur particle, higher beam dosages must be used in order to generate enough counts for the detector. Unfortunately this damages the sample heavily due to sulphur's susceptibility to knock-on damage, and alternate methods must be employed to characterise the elemental composition of the sample with this method. It is still possible to collect enough counts to confirm elemental composition of the sample via EDX spectra using a lower dose with a 12° holder tilt, as can be seen in Figure 52. In this regard, the cryo-EM method utilised by Levin *et. al*⁵ has its



(a)



(b)

Figure 50: a) HAADF STEM of residual S post-sublimation acquired on FEI Titan @300keV. Inset shows EDX maps of S, Si, and Cu corresponding to the EDX spectrum. b) Integrated spectrum of region of interest, confirming elements listed in a) are present. Maps confirm that the residue is indeed composed of sulphur. (Si peak due to an EDX spectral artefact; an internal fluorescence peak from the silicon window on the silicon drift detector likely. Cu peak background signal from grid.)

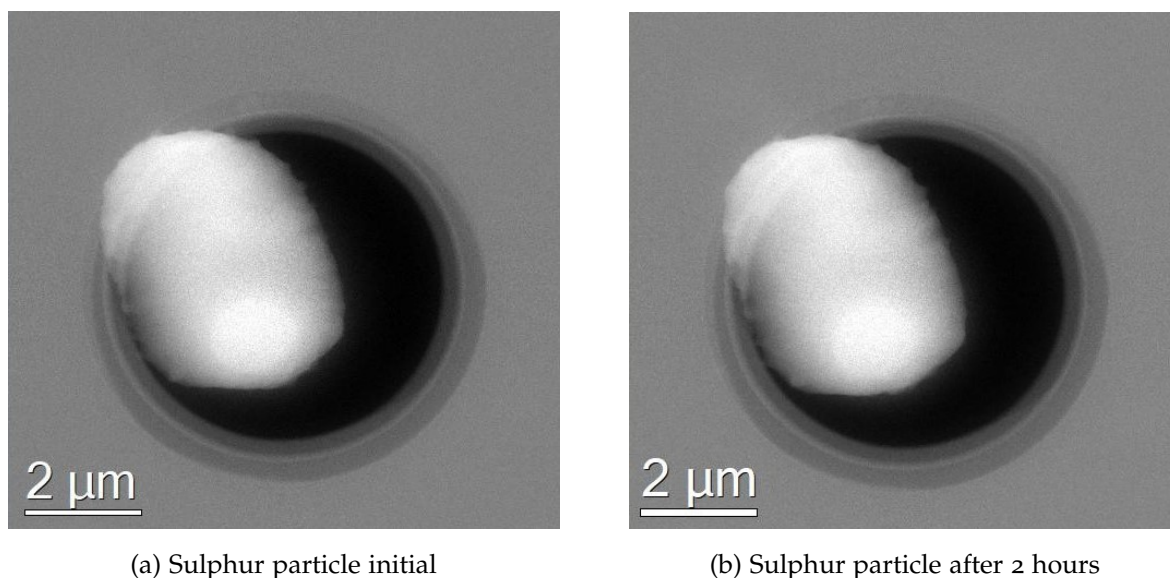


Figure 51: HAADF STEM images of a sulphur particle before and after a 2 hour exposure inside the TEM column vacuum in DENS Solutions Climate chips. The particle is isolated from the column vacuum by the SiN_x window of the gas cell chips, thus preventing sublimation of the sample. Images acquired on FEI Titan operated at 300keV.

benefits over the SiN_x window approach that can be found in many *in-situ* holders. Cryogenic electron microscopy has the secondary benefit of slowing or even inhibiting beam induced artefacts and sublimation artefacts simultaneously, allowing for easier collection of mapping data.

9.3 CONCLUSIONS

The ability to image potentially vacuum sensitive materials for energy storage applications such as sulphur composites without sublimation artefacts creates new possibilities for their characterisation. To control sublimation in TEM analysis, an encapsulation method utilizing a commercial gas cell TEM sample holder is demonstrated. Where before, samples would sublime before imaging could take place, this novel encapsulation method allows for sample stability over the time frames

necessary for both imaging, and spectroscopic analysis by EDX, or even EELS with ultra-thin SiN_x windows. The proposed method is suitable for the TEM analysis of other specimens that may undergo sublimation at TEM vacuum pressures, such as zinc or magnesium to name a few. Such techniques would have been impossible for such materials in the past, and presents new opportunities for battery material researchers.

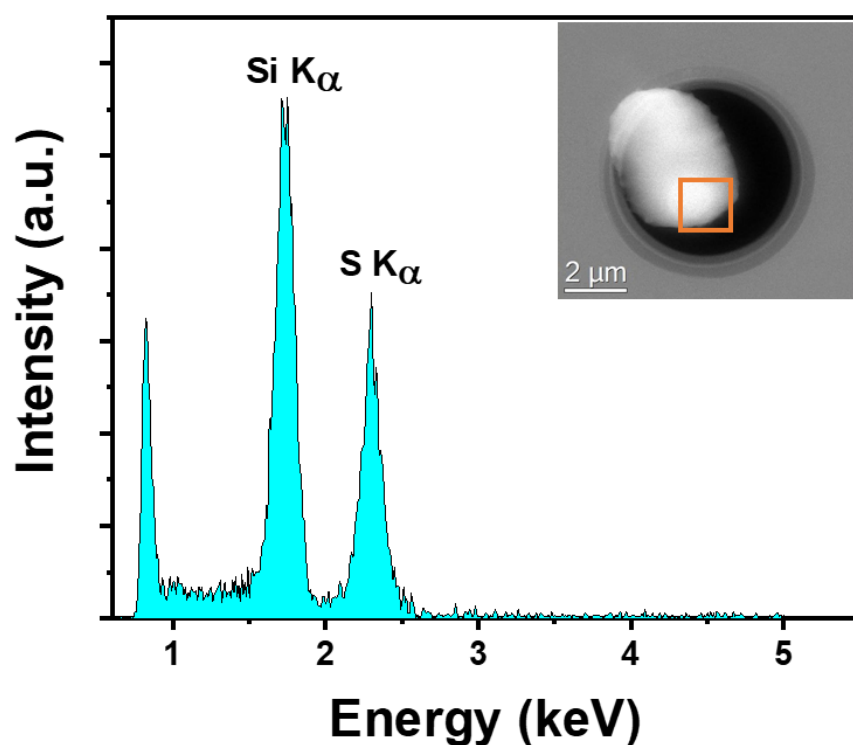


Figure 52: Integrated EDX Spectra of highlighted area of sulphur particle on SiN_x window of the gas cell chips after two-hour exposure acquired @300keV in FEI Titan equipped with an Ametek 30mm² EDX detector. Low dose acquisition parameters of the spectrum, along with inefficiencies of the Ametek EDX detector give rise to low SNR. Confirmation of elemental composition is still possible, with S and Si peaks from the S particle and SiN_x window respectively clearly detected with a 12° holder tilt.

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IV

CONCLUSIONS AND FUTURE WORK

"Two gin-scented tears trickled down the sides of his nose. But it was all right, everything was all right, the struggle was finished. He had won the victory over himself. He loved *In-Situ* Transmission Electron Microscopy."

— George Orwell (...mostly)

CONCLUSIONS

In this work, a large number of technical considerations for proper experiment design and interpretation of electrochemical measurements inside a TEM have been considered.

A working micro-scale electrochemical cell consisting of LiFePO_4 vs Si has been developed using facile inkjet printing methods.

While initial observations of the Si-nanoparticles immersed in electrolyte in the TEM proved problematic, with a number of issues preventing effective imaging arising; namely rapid e^- beam induced damage to the electrolyte solution necessary for battery operation, and difficulties maintaining cell integrity during imaging. The e^- beam was determined to be inducing radiolysis of solvent components of the electrolyte, and reducing lithium salt components and their degradation products. The efforts of this work have located the underlying causes of these issues, and sought to remove them from the experiments, and these issues have been overcome by careful consideration of the experimental parameters. The major limiting factor to complex full-cell battery fabrication for analysis in the TEM was determined to be the design of the electrochemical chips. With an insufficient counter electrode to working electrode ratio, charge balancing and capacity matching proved impossible, resulting in little electrochemical activity during *operando* experiments.

Using the techniques developed during these experiments, a MXene- LiFePO_4 Li^+ -ion battery cell was successfully inkjet printed, and subsequently analysed *via operando* liquid cell STEM. Using a more modern revision of liquid cell TEM holder

design, charge and capacity matching proved a much easier task; as a result, a complete battery cell was fabricated and electrochemically cycled during STEM analysis. The STEM imaging data was linked with the electrochemical data from the cell, which allowed the connections to complex battery phenomena such as chemomechanical degradation of the electrodes, electrolyte decomposition, SEI formation, and Li^+ -ion intercalation/deintercalation processes. These results shed new light on these phenomena and bring new insights to research communities in terms of understanding lithiation mechanisms for MXene anodes.

Finally, a novel method for imaging of vacuum incompatible materials was explored. The ability to image potentially vacuum sensitive materials for energy storage applications such as sulphur composites without sublimation artefacts creates new possibilities for their characterisation. To control sublimation in TEM analysis, an encapsulation method utilizing a commercial gas cell TEM sample holder is demonstrated. Where before, samples would sublime before imaging could take place, this novel encapsulation method allows for sample stability over the time frames necessary for both imaging, and spectroscopic analysis by EDX, or even EELS with ultra-thin SiN_x windows. The proposed method is suitable for the TEM analysis of other specimens that may undergo sublimation at TEM vacuum pressures, such as zinc, magnesium, or some polymers to name a few. Such techniques would have been impossible for such materials in the past and presents exciting new opportunities for battery materials researchers.

While further efforts must be made to fully realise *in-situ* TEM analysis of an operating Li^+ -ion battery, the first steps toward this goal have been made, and the design of future experiments can take the limiting factors of the setup into account to avoid the pitfalls discussed. As the technology is still in the early stages of development, this is work that must be done to advance the technique to the point it

needs to be for future energy storage material characterisation.

10.1 FUTURE WORK

While a number of issues have arisen during the course of this project, considerations can now be made regarding future experiments. New techniques for imaging to limit potential e^- beam specimen damage learned during the course of this work will continue to be used for future liquid cell experiments. This technique (ubiquitously used in nearly all cryogenic-Electron Microscopy (cryo-EM) applications)¹⁻³ involves performing all microscope focusing and alignment procedures on an empty part of the cell, before moving to an area of interest; more frequent blocking of the beam will also be introduced to this effect and keep cumulative e^- dose as low as possible. While this may seem to compromise the aim of the work, the lithiation that future work hopes to observe occurs over a time-scale of several hours (at the slow scan-rate used in the experimental technique), so this should not cause issues.

The possibility of performing EFTEM or EELS in the *in-situ* electrochemical setup is an exciting possibility for this technique. It has been shown that such analysis can be done to observe meaningful data in the low-loss signal for thicker liquid layers; Dai *et al.* were able to demonstrate shifts in the plasmon peaks of gold nanoparticles between 1-8eV.⁴ Some core-loss data (above losses of 600eV)⁵ can be extracted from thin liquid layers also.⁶⁻¹¹ Plural scattering becomes negligible after the oxygen K-edge¹⁰ due to high inelastic scattering cross section at low-losses, and small cross-section at higher losses.¹² Obtaining counts at higher losses will be limited by dose restrictions and low SNR, due to the direct relationship between irradiation dose and attainable resolution.^{12,13} Using a direct electron detector might allviate this issue if the Titan was equipped with one.¹⁴ For example, the possi-

bility of detecting oxidation state changes as Li^+ -ions are inserted and removed from a material or the depletion of lithium from a region of material immersed in a lithium-based liquid electrolyte would be a leap forward in energy storage materials characterisation,^{6,15} so this is something I hope to use in my own future work. Using EFTEM as a technique to improve image resolution may also prove useful. Using zero-loss filtering, it may be possible to offset the resolution limiting effects of the thicker specimen by filtering out irrelevant signal generated by electron-plasmon scattering. Such techniques have been known to improve resolution in cryo-TEM, where similarly low doses are required to prevent radiolysis damage to the sample.^{16–18} Similarly, the possibility of using an EFTEM filter to selectively form an image from signals from a particular material in the cell may also prove beneficial. This method, known as contrast tuning, could be used to highlight specific materials using an energy slit where an element's EELS peak has been observed.¹⁹ Such methods would require larger electron doses to be delivered to the sample, so such techniques may turn out to not be viable for certain liquid samples.

The SEI layer in Li^+ -ion batteries is also of interest to this work, as its exact mechanism of formation, as well as its true chemical composition is relatively unexplored,^{20–22} and the concept of studying its formation *in-situ* with the assistance of EELS and EFTEM would shed light on a much debated topic of interest in the energy storage community.^{8,23,24}

One such solution to the electron dose - resolution problem may be to use a low-dose (S)TEM technique known as "sparse-sampling" or "compressive sensing" for image acquisition to distribute the dose over many identical copies of the imaging region.^{25–34} Using such a method, (common among studies of biological samples in (S)TEM^{26,27,35}) low-dose, low-resolution images with a low signal-to-noise ratio can be reconstructed via *a posteriori* image processing into an interpolated higher

resolution image for more detailed analysis.^{25,28–31,33,36,37} Such algorithmic random image sub-sampling has been shown to enable a reduction in sampled pixels (and subsequently e^- beam dose) by up to 95% while still being able to reconstruct images similar to fully sampled images.²⁸ This may prove to be a useful method for reducing e^- beam dose to the radiation-sensitive electrolytes, while maintaining a useful resolution and minimising scanning and drift distortions by decreasing pixel dwell-time.³⁴ Such an imaging technique would require an upgrade to current TEM infrastructure available in TCD, and a Gatan Digiscan would need to be equipped on the Titan in order to use the scan coil control software necessary to carry out sparse sampling.

From these observations, I believe a breakthrough in successful *in-situ* imaging is close, with all of these issues discussed taken into consideration. Work is progressing on a full setup with precautions taken to reduce or eliminate the issues discussed here.

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V

SUPPLEMENTAL INFORMATION

SUPPLEMENTAL INFORMATION

11.1 SUPPLEMENTAL INFORMATION FOR CHAPTER 3

11.1.1 *Equation Derivations*

deBroglie Electron Wave relation:

$$\lambda = \frac{h}{p}$$

$$E = eV$$

$$E = \frac{1}{2}m_0v^2$$

$$\mathbf{p} = m\mathbf{v}$$

$$E = \frac{p^2}{2m}$$

$$p = \sqrt{2mE} = \sqrt{2meV}$$

Substituting the above relations into the de Broglie relation, the formula relating the energy of the electron beam to the wavelength of the electron becomes:

$$\lambda = \frac{h}{\sqrt{2m_0eV}}$$

or, with relativistic momentum corrections with the Lorentz factor:¹

$$\lambda = \frac{h}{\sqrt{2m_0eV \left(1 + \frac{eV}{2m_0c^2}\right)}} \approx 1.97\text{pm}$$

11.2 SUPPLEMENTAL INFORMATION FOR CHAPTER 6

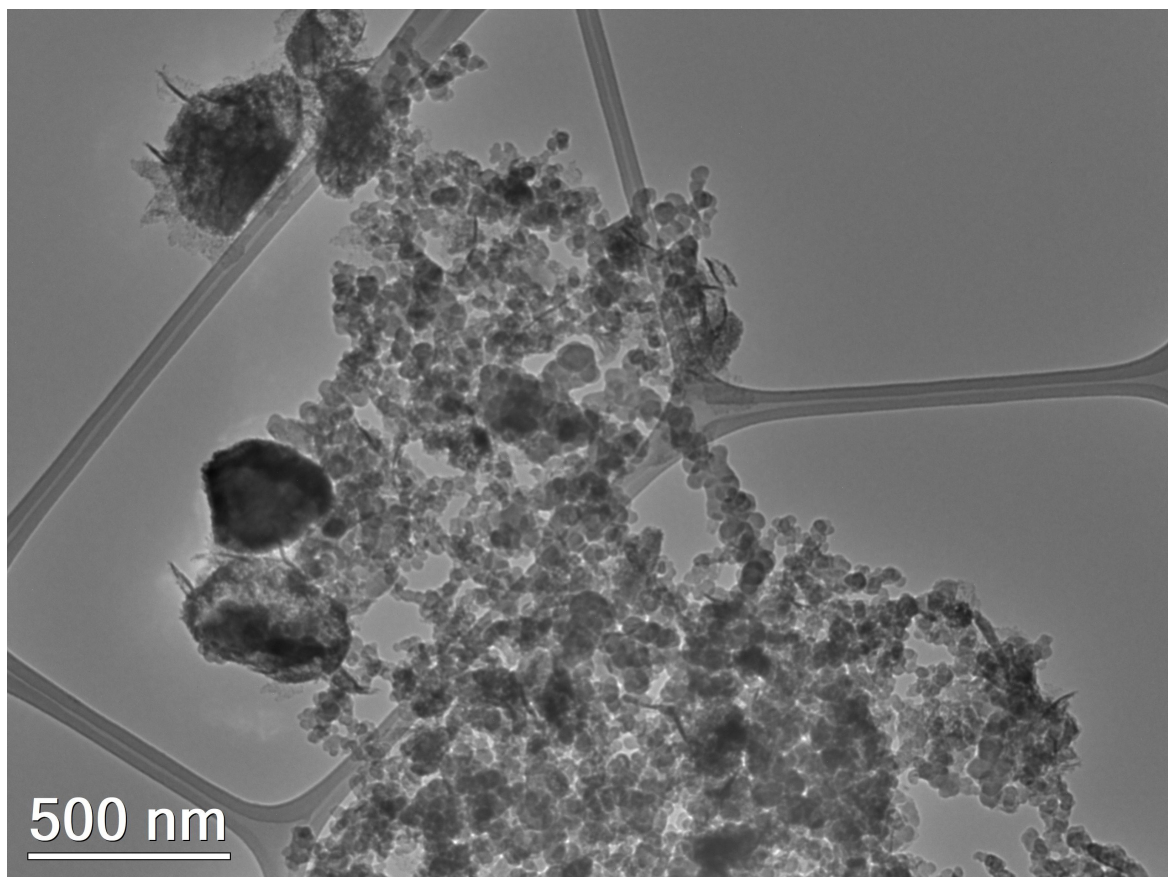


Figure 53: BF TEM image of region from which spectrum of LFP/C ink shown in Figure 24 was acquired. Larger, darker contrast particles are LFP. Smaller, lower contrast particles are carbon black. Image acquired on Jeol 2100 @200keV.

11.3 SUPPLEMENTAL INFORMATION FOR CHAPTER 7

11.3.1 Statistical Analysis of SiNP Size Distribution

Raw statistical data on SiNP size distribution:

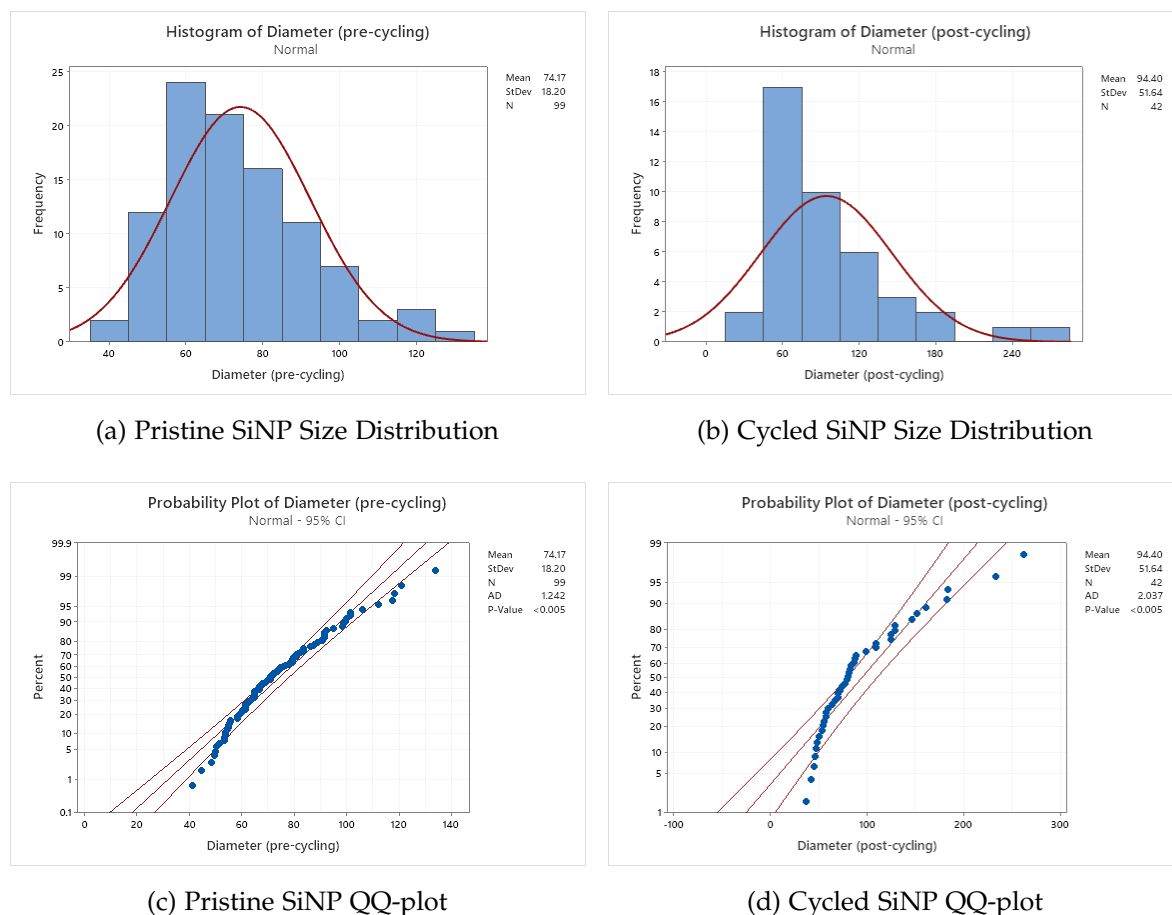


Figure 54: Statistical analysis of SiNP pre- and post-cycling. a) and b) Histograms of size distribution of particle diameters. c) and d) quantile-quantile plots of diameters demonstrating severe deviation from normality.

As Figure 54 demonstrates, the size distribution data deviates from normal. Thus conclusions cannot be made through comparative test statistics. A transformation must be applied to the data to force normality in order to formally test a null hypothesis. As the data approximately follow a log-normal distribution, a log trans-

formation is applied. Log-normal distributions are common in the size distribution of laser-synthesised nanoparticles,^{2,3} and so using a log-transform is appropriate in this case.⁴⁻⁶

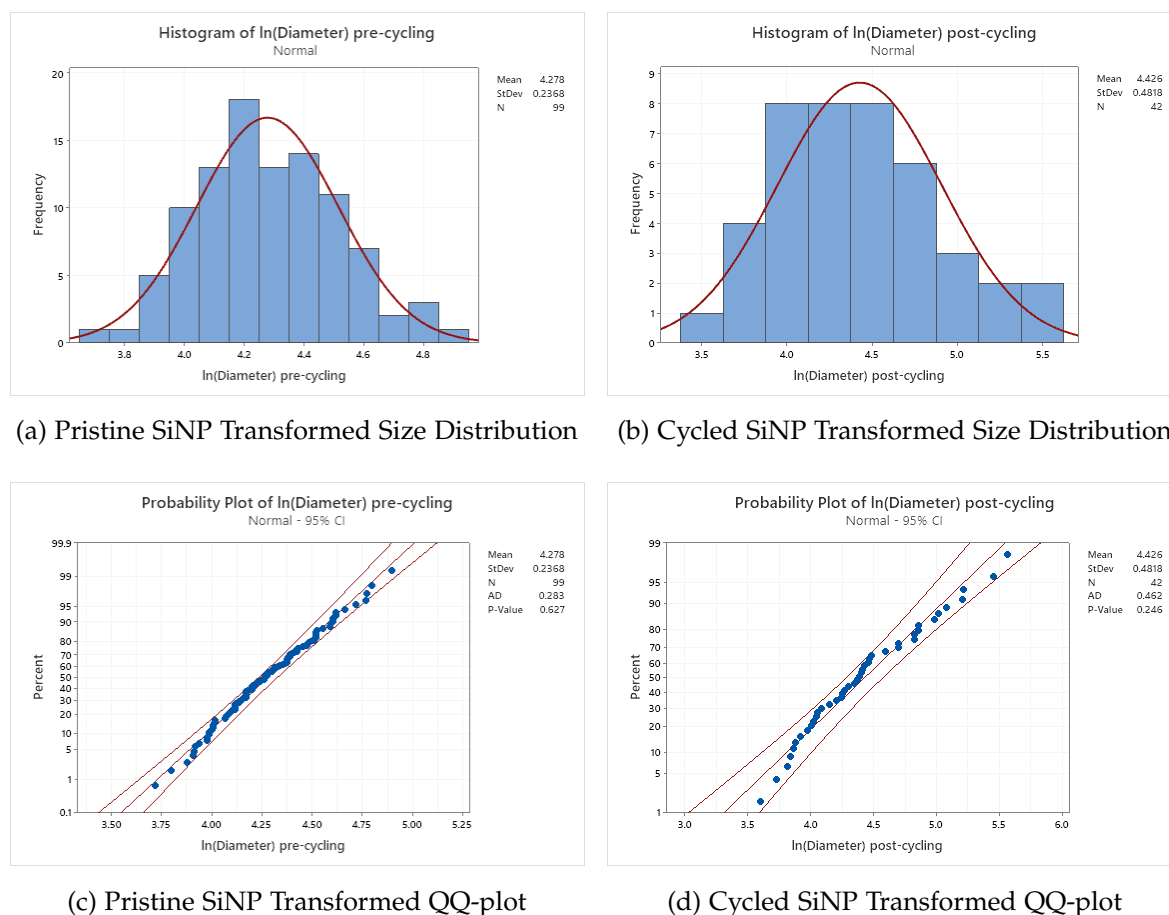


Figure 55: Statistical analysis of SiNP pre- and post-cycling. a) and b) Histograms of size distribution of natural logarithm of particle diameters. c) and d) quantile-quantile plots of diameters demonstrating normality within a 95% confidence interval.

The log-transformed data are approximately normal, and pass the Anderson-Darling test. Skewness has been reduced for pre- and post-cycling data from 0.843 and 1.539 respectively to 0.239 and 0.527 respectively. As a rule of thumb, skewness (calculated using Equation 24) between -0.5 and 0.5 is considered "normal", whereas skewness >0.5 or <-0.5 deviates from "normal", as backed-up by the QQ-plots in Figure 54 and Figure 55.

Skewness calculation:

$$\frac{\frac{1}{n} \sum_{i=1}^n (x_i - \bar{x})^3}{\left(\frac{1}{n} \sum_{i=1}^n (x_i - \bar{x})^2 \right)^{3/2}} \quad (24)$$

Where n = number of data points, x_i = each value of x , and $\bar{x}$ = mean of x .

The following null hypothesis is tested for the log-transformed SiNP data:

$$H_0 : \mu_1 = \mu_2, H_a : \mu_1 \neq \mu_2 \quad (25)$$

Where H_0 is the null hypothesis, H_a is the alternative hypothesis, μ_1 is the mean SiNP diameter pre-cycling, and μ_2 is the mean SiNP diameter post-cycling.

A two-tailed t-test is performed on the log-transformed data sets to compare the means, and determine if the null hypothesis (H_0) is correct:

$$t = \frac{\bar{X}_1 - \bar{X}_2}{\sqrt{\left(\frac{(n_1 - 1)\sigma_1^2 + (n_2 - 1)\sigma_2^2}{n_1 + n_2 - 2} \right) \left(\frac{1}{n_1} + \frac{1}{n_2} \right)}} \quad (26)$$

$$t = \frac{4.28 - 4.43}{\sqrt{\left(\frac{(99 - 1)0.24^2 + (42 - 1)0.48^2}{99 + 42 - 2} \right) \left(\frac{1}{99} + \frac{1}{42} \right)}}$$

$$|t| = 2.472$$

Where $\bar{X}$ = mean, n = degrees of freedom (number of data points in each set), σ = standard deviation for each of the two datasets being compared.

As this $|t| \geq 2.021$ (for $\alpha/2 = 0.025, \nu = 41$); the null hypothesis (H_0) is rejected. It can then be stated that there is a statistically significant difference in the means, and that $\mu_1 > \mu_2$.⁷

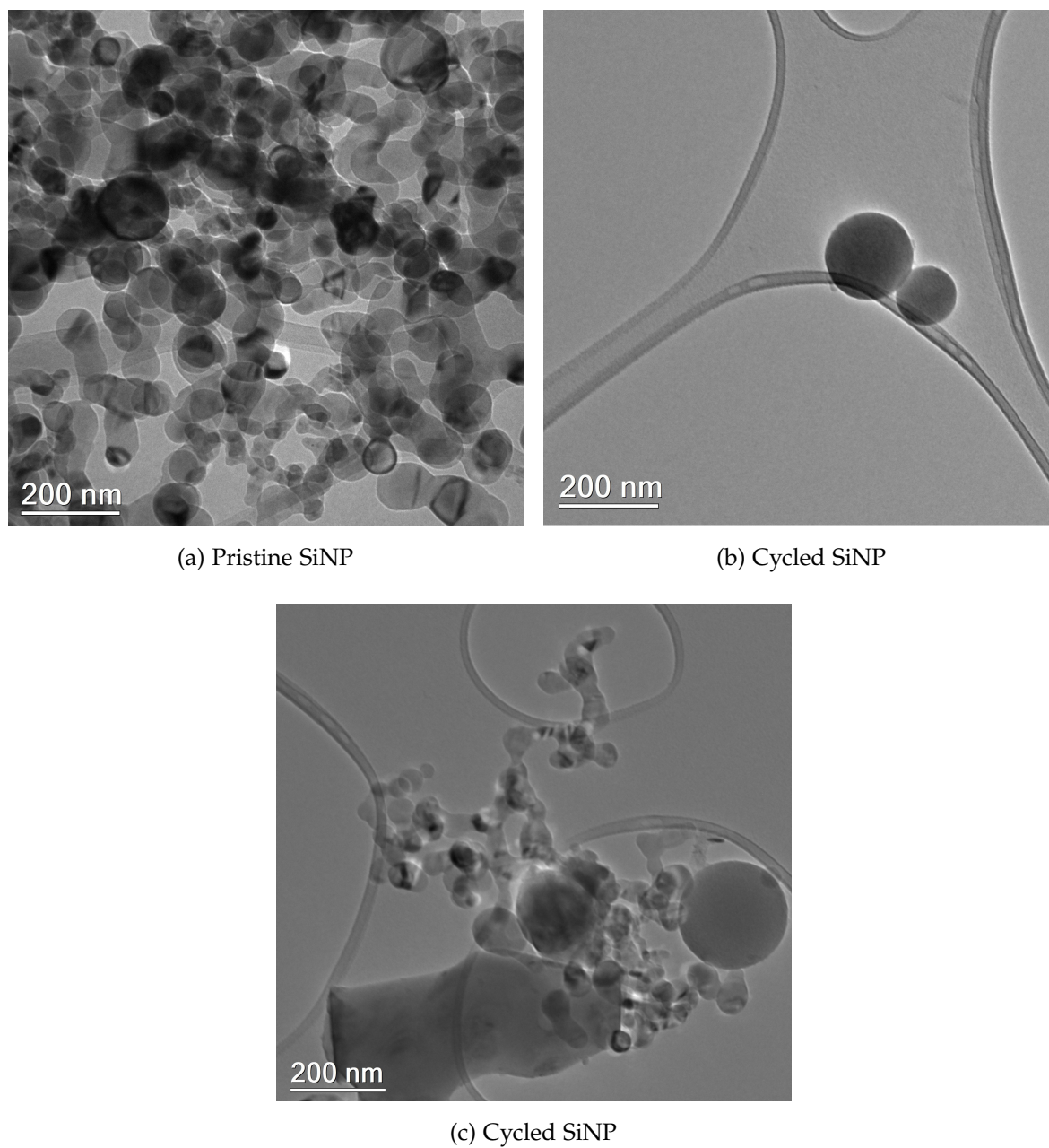


Figure 56: Additional BF TEM images (supplemental to Figure 33) used in statistical analysis of SiNP (Figure 54) processed using ImageJ. Images acquired on Jeol 2100 @200keV.

11.3.2 EELS analysis of SiNP

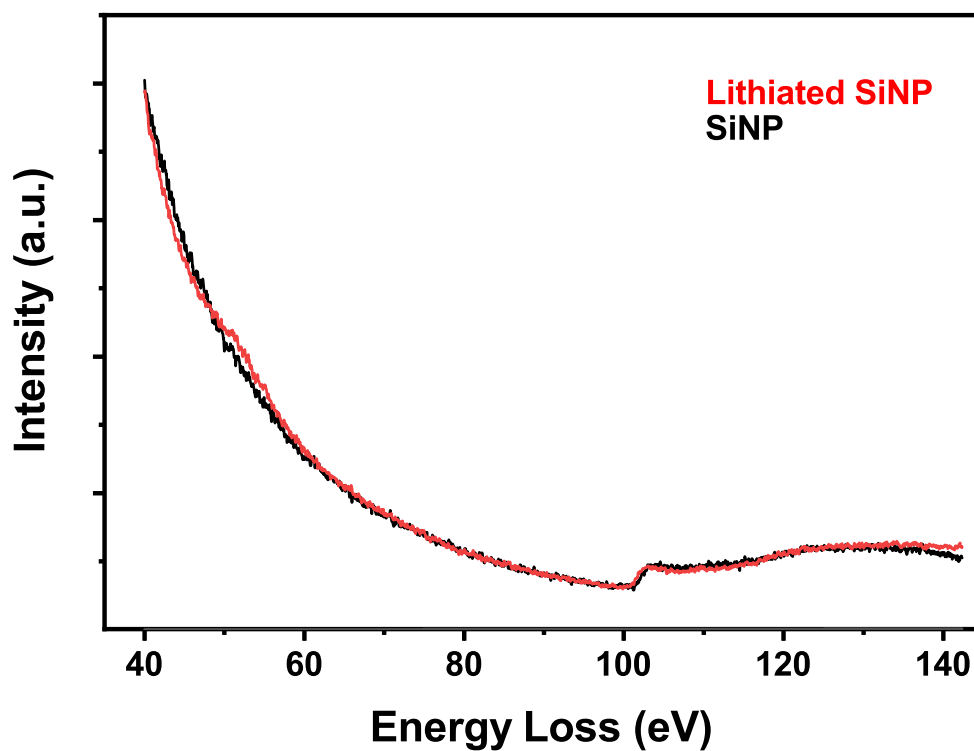


Figure 57: Raw, uncorrected for background signal EELS spectra shown in Figure 34 showing presence of lithium within a SiNP after electrochemical cycling shown in Figure 31. (Spectra were collected from single points on the SiNPs to reduce knock-on beam damage. Spectra acquired @300keV in FEI Titan with an energy dispersion of 0.05eV/Ch, drift tube bias of 40V, and a collection semiangle of 7.8mrad.

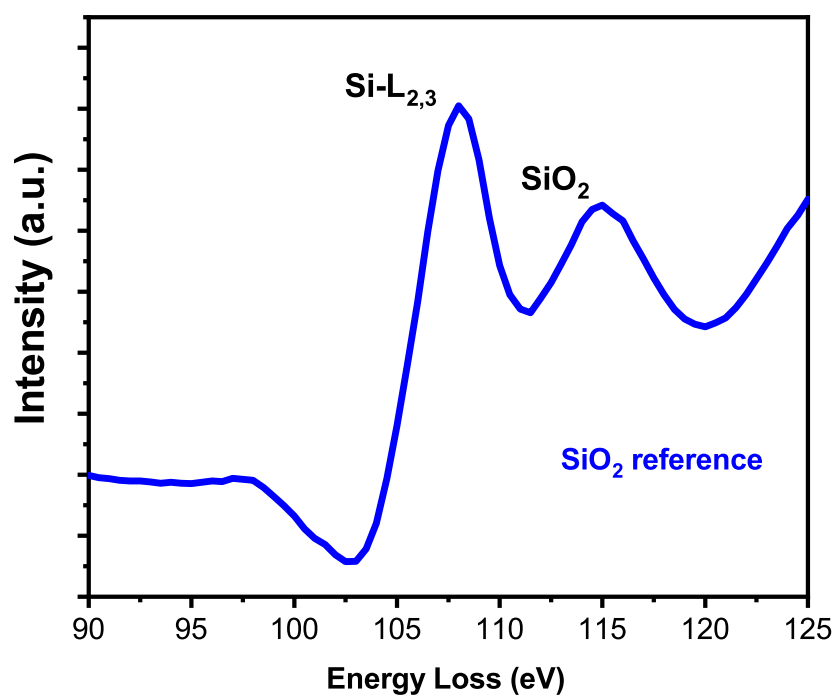


Figure 58: Reference background subtracted EELS spectra of SiO₂ showing Si-L_{2,3} post-edge fine structure.⁸ Secondary ELNES peak at ≈ 110 eV also present in Figure 34. Graph created from data acquired from Reference [8].

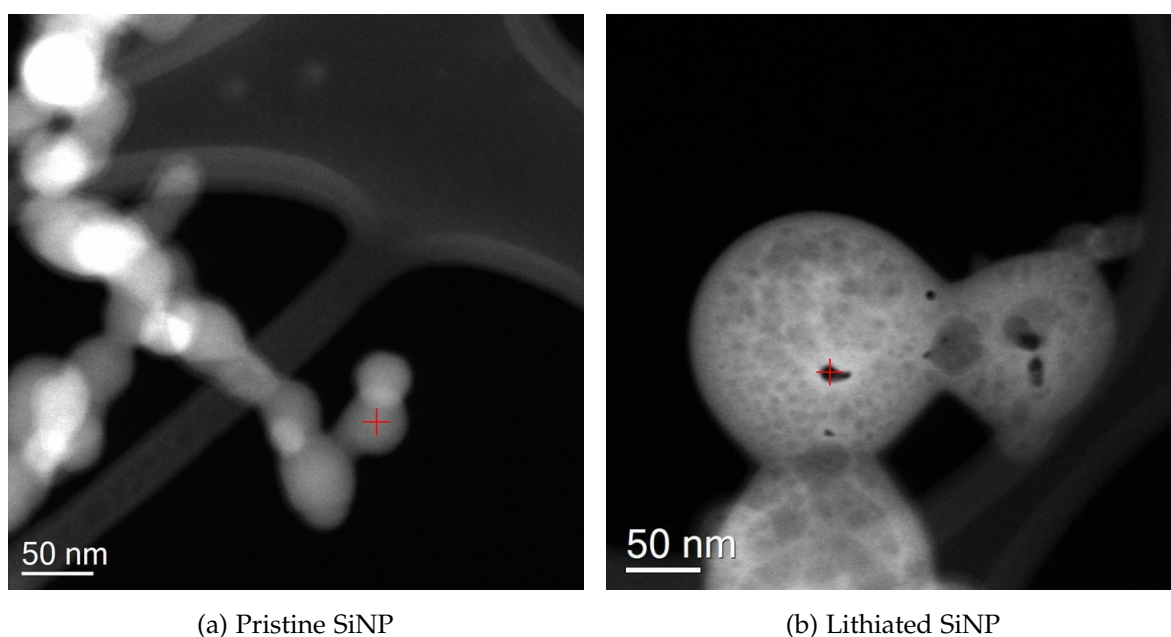


Figure 59: HAADF STEM images of points from which (a) unlithiated and (b) lithiated SiNP EELS spectrum shown in Figure 34 was acquired. STEM image acquired @300keV on FEI Titan.

11.3.3 Electrolyte Substitute Experiments

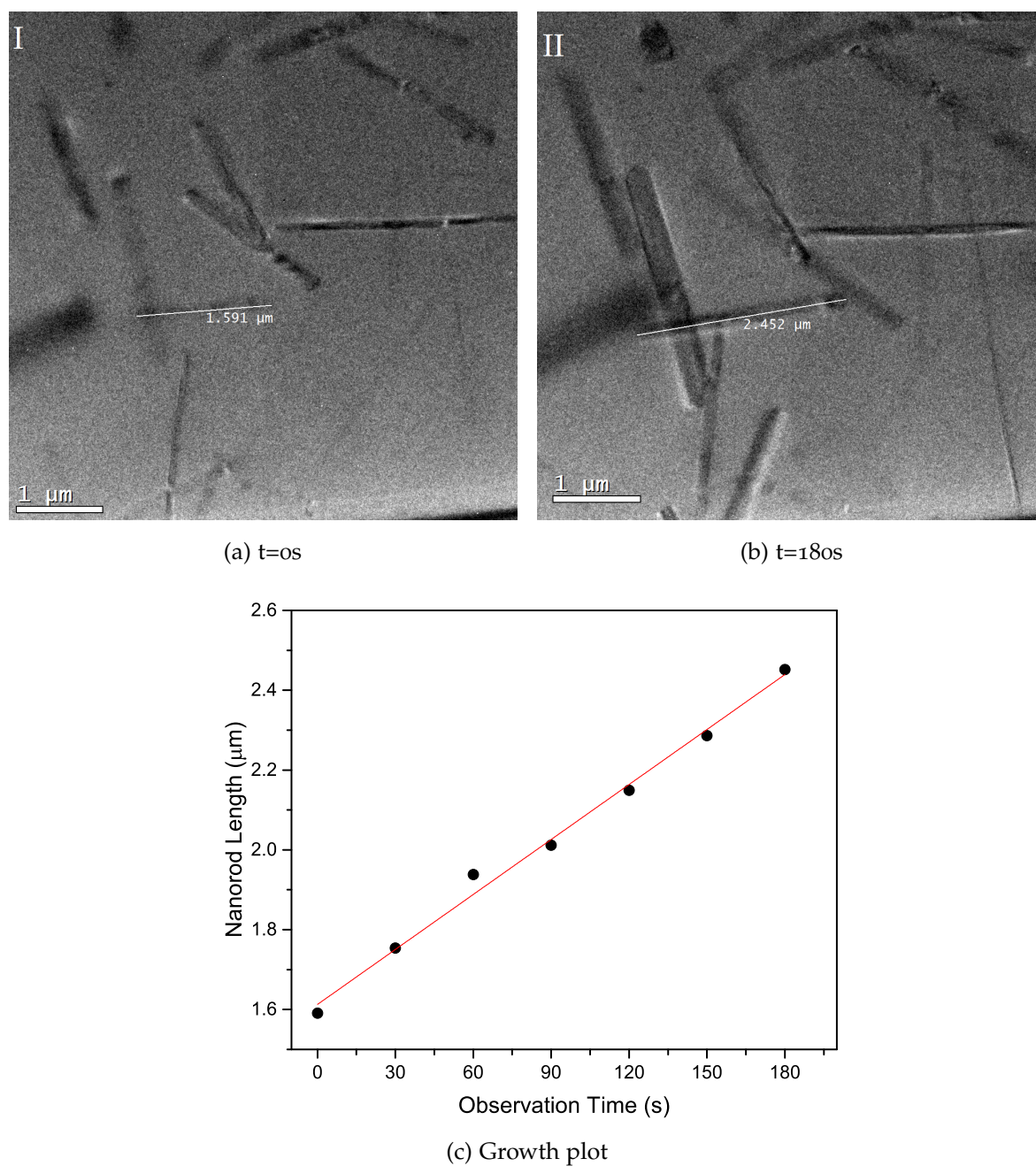


Figure 60: BF TEM of nanorod formation in lithium trifluoromethanesulfonate in propylene carbonate ($\text{LiCF}_3\text{SO}_3\text{:PC}$) solution under the effects of a constant dose e^- beam exposure over 180 seconds from I to II. Electrolyte was tested as a substitute to LiPF_6 EC:DMC, and rejected due to instability under e^- beam exposure. Nanorod under scrutiny linearly increases in size (see graph) from 1.59 μm to 2.45 μm during observation.

11.4 SUPPLEMENTAL INFORMATION FOR CHAPTER 8

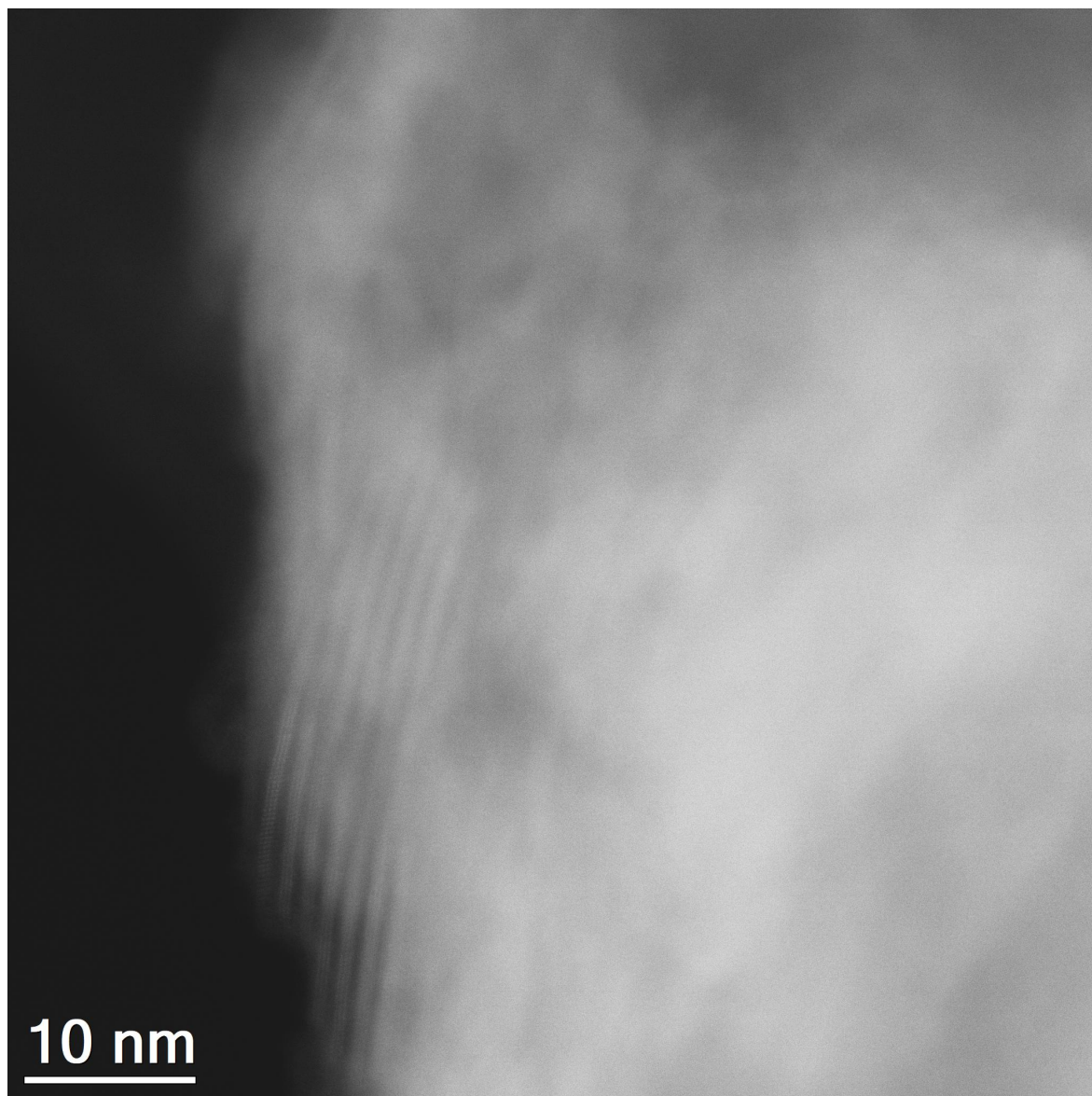


Figure 61: HAADF STEM image of MXene edge shown in Figure 40(c). Edge folding visible only near edge of the flake, indicating partial alignment of $[100]$ zone axis by flake folding at the edge. STEM acquired on Nion UltraSTEM @60keV.

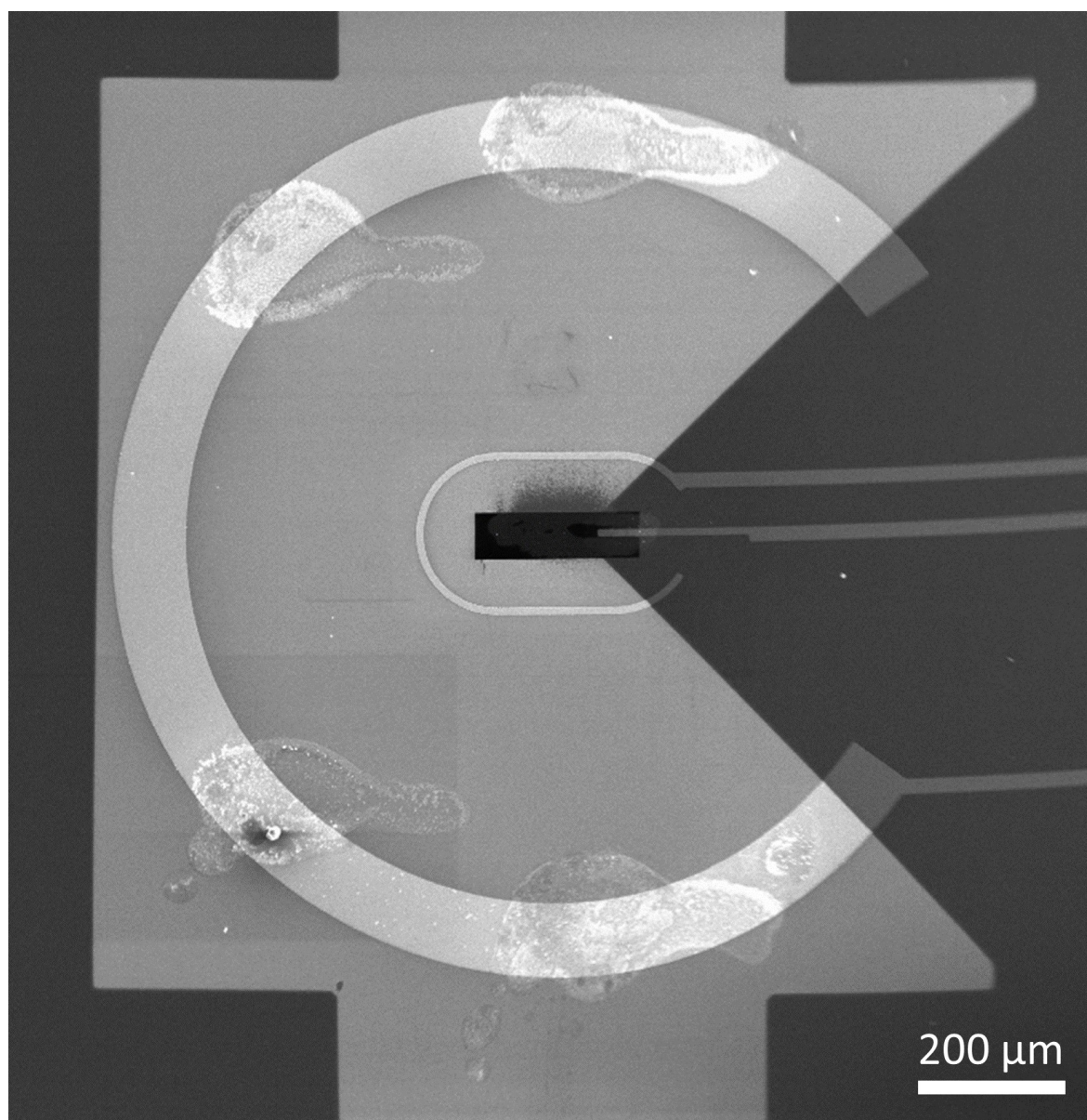


Figure 62: SEM image of Protochips Poseidon chip with inkjet printed LFP on the outer counter electrode, and Ti_3C_2 MXene coated on the central glassy carbon electrode. Image acquired at 15keV using Secondary Electron detector.

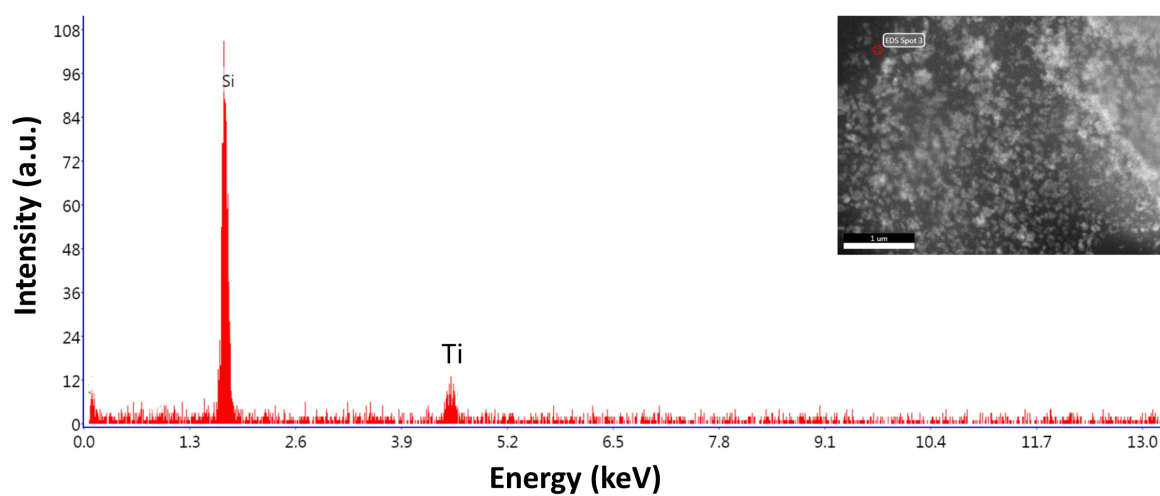


Figure 63: EDX spectrum of MXene coated glassy carbon electrode post-electrochemical cycling. Ti peak confirms presence of Ti_3C_2 MXene, and Si peak arises from the SiN_x window. Expected O and C peaks are absorbed by the SiN_x window. Spectrum captured with Octane T Optima 60mm^2 windowless silicon drift detector using a Jeol JEM 2100 STEM @200keV. Inset HAADF STEM image shows spot from which EDX spectrum was captured.

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