An outlook on printed microsupercapacitors: Technology status, remaining challenges, and opportunities

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Abstract

The concept of the Internet of Things is dramatically changing the way society interacts with physical spaces and portable technologies. For the last couple of years, intensive research has been devoted on the design of several flexible and even wearable devices, such as displays and health-care sensors. Further developments on these new technologies are heavily conditioned by the lack of compatible energy storage/conversion units. Contrary to lithium-ion batteries, supercapacitors can be easily miniaturized and integrated on flexible/wearable technologies without losing their electrochemical performance. In this review, some of the most recent developments on the design and printing of light, flexible, and thin micro-supercapacitors along with promising and further practical applications are presented.

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Introduction

Modern technology and electronics are currently undergoing a transition from bulk and rigid configurations toward flexible/wearable designs [1–4]. Flexible displays, chemical sensors, and health-care devices are quickly becoming a part of every day's life [1,3]. These

devices demand the development of ultrathin, lightweight, and flexible energy storage devices [1,2,5,6]. Owing to their ubiquitous presence in modern society, lithium-ion batteries would likely be the ideal energy storage device for future flexible applications. However, state-of-the-art thin-film lithium-ion batteries (LIBs) still suffer from several technical disadvantages, as their energy per volume tends to rapidly decrease in the micrometer scale [7]. It is also quite challenging to integrate these devices within electronic circuits, severely conditioning the miniaturization of devices [5]. Moreover, LIBs are also plagued with short life cycles, safety concerns regarding the use of lithium, and flammable electrolytes [5]. Current energy storage technologies are still lagging other technical and circuitry components. Thus, the fast-paced development of emerging flexible/wearable technologies is driving a worldwide demand for new and improved energy storage devices [1,6,8]. In this context, microsupercapacitors (MSCs) are highly desired as power sources for flexible devices as they present an enhanced power density ($>10,000 \text{ W kg}^{-1}$), fast charge/discharge rates, optimal cyclability, long shelf life, and capability of direct on-chip integration [1,5,7,9–12]. MSCs are also considered suitable devices to complement (or even replace) microbatteries in applications requiring transient high peak power pulse [5,13,14]. Recent developments in materials synthesis and fabrication processes resulted in MSC exhibiting energy densities similar to those of thin-film batteries (10^{-3} and $10^{-2} \text{ Wh.cm}^{-3}$) [12]. However, to be fully integrated into wearable and flexible technologies, supercapacitors need to be flexible enough to undergo large mechanical deformations, without compromising the device performance [15]. Commercially available vertical sandwich supercapacitors do not present the most suitable configuration for devices meant to be bent or even rolled up, due to the presence of rigid components and the constant risk of harmful electrolyte leakage [8,14]. In this context, printed MSCs are being proposed as the best option for powering flexible/wearable electronics [1,6,8]. Thus, several printing methodologies are currently being considered for MSC fabrication, as briefly summarized in Figure 1. Printing methods allow an easy fabrication of devices, while being compatible

Example of the most promising materials for MSCs and some conventionally used printing methods such as direct ink writing (top left), ink jet printing (top right), stamping (bottom left) and screen printing (bottom right). Special focus is given to the interdigitated Q6 planar devices as this type of configuration provides a significant power density enhancement when compared with other more conventional structures [12]. MSCs, microsupercapacitors.

with emergent materials for energy storage/conversion applications (Figure 1) [10,12,16].

When deposited onto a flexible substrate, interdigitated in-plane MSCs usually exhibit optimal mechanical properties, while keeping their electrochemical performance and compatibility with the geometries of integrated microfabrication processes [5,8,14]. As expected, these technological shifts raise questions regarding suitable active materials, electrolyte formulations, substrate type, geometries, and, of course, fabrication methods [1,6,14]. Herein, an overview on the achievements and on-going shortcomings on the development of energy storage/conversion for flexible/wearable technologies will be provided. For the sake of simplicity, the term MSCs will refer (unless stated otherwise) to planar printed microsupercapacitors.

Printable MSC components: an overview

Carbon-based materials, such as activated carbon, have been usually selected as the ideal active material for supercapacitor applications. Besides presenting high specific surface area and good electrical conductivity, carbon is environmentally friendly, readily available, and

low cost. Thus, being very attractive for large-scale applications [12,17]. Moreover, carbon-based electrodes exhibit remarkable stability upon cycling [12,13,18]. Printed activated carbon supercapacitors (surface area of $700 \text{ m}^2 \text{ g}^{-1}$) exhibit a maximum specific capacitance of 220 F g^{-1} at 30 mV s^{-1} in $0-1 \text{ V}$ voltage window [18]. For the last couple of years, significant attention has been paid to graphene-based devices. As a one layer two-dimensional (2D) nanosheet, graphene exhibits the highest surface area of all carbon materials ($2600 \text{ m}^2 \text{ g}^{-1}$), with an areal capacitance of $21 \text{ } \mu\text{F cm}^{-2}$ and theoretical gravimetric capacitance of 550 F g^{-1} [5,6,19]. The ease on large-scale production [5,6,12,19,20] of this material has allowed the widespread printing of graphene-based supercapacitors [3,5,6,21]. As expected, these devices have an excellent cyclability performance ($>10,000$ cycles) and can be manufactured in different shapes and sizes, according to the desired application. For instance, it is common to find 2D and three-dimensional graphene printed supercapacitors of different dimensions, porosity, and shape [8,19]. However, despite all advantages, graphene-based supercapacitor applications are always limited by the typical low energy density of carbon

materials [4]. This problem can be easily addressed by printing metal oxides instead. Metal oxides have been largely used in supercapacitor applications because of their pseudocapacitive storage mechanism. These processes result in overall capacitances tens or hundreds of times larger than carbon materials. Fully functional MSCs based on MnO_2 [11,22], Co(OH)_2 [13], ZnO [23,24], SnO_2 [24], RuO_2 [25], and V_2O_5 [26], among others, have already been successfully printed. However, a poorer cycling stability and usually very low electrical conductivity renders metal oxides not suitable for large-scale supercapacitor applications. A similar comparison can be made for conducting polymers. Despite their optimal flexibility and electrical conductivity, the expansion/contraction of these pseudocapacitive materials upon cycling significantly reduces their life time [17]. At the moment, research efforts focus on metal–organic frameworks (MOFs) and novel 2D nanomaterials, such as MXene [27]. MOFs are attractive for supercapacitor applications, mostly because of their high porosity ($\sim 90\%$ free volume) and extremely high surface area ($>6000 \text{ m}^2 \text{ g}^{-1}$) [28,29]. Moreover, they exhibit a remarkable cyclability, way above 100,000 cycles. Unfortunately, with some exceptions, these materials tend to be very poor electrical conductors. Nevertheless, the combination of MOFs with conductive polymers or carbon conductive materials has led to the development of very promising supercapacitor frameworks [29,30]. However, more

research is still needed on the printing capabilities of MOFs. On the other hand, 2D nanomaterials have been exhaustively studied for printed technologies. Their multifunctionality, unique physicochemical, and mechanical and electrochemical properties have attracted attention for energy storage applications. Moreover, 2D nanomaterials can also be easily combined, thus allowing the construction of heterostructures [31]. In this context, printed MXenes have revealed a huge potential as electrode materials for supercapacitors. Firstly, titanium carbide — $\text{Ti}_3\text{C}_2\text{T}_x$ — by far the most thoroughly studied MXene, can exhibit areal capacitances up to 61 mF cm^{-2} at $25 \mu\text{A cm}^{-2}$ [16,32]. Secondly, because of its metallic conductivity (as high as $\sim 10,000 \text{ S cm}^{-1}$), titanium carbide can be used as both electrode material and current collector removing the need for binders and conductive additives [33]. In addition, a density of $\sim 3.8 \pm \text{g cm}^{-3}$ also contributes to superior energy charge storage. Finally, surface functional groups, T_x , ($-\text{O}$, $-\text{OH}$, and $-\text{F}$) increase MXene hydrophilicity, thus allowing sample processing in aqueous media [16,32,34,35]. Not surprisingly, microsupercapacitors based in MXene dispersions in water were already printed by stamping [32], inkjet [16,36], screen [4], and extrusion [4,16,37] printing, among others (Figure 2).

Plenty of research has as well been conducted regarding electrolytes, current collectors, and substrates. In general, MSC electrolytes are composed by an acid (H_2SO_4)

Figure 2

(a) MXene-based MSC fabricated on a paper substrate by extrusion and (b) correspondent scanning electron microscopy (SEM) micrographs. (c) 3D printed stamps used on the preparation of MXene MSC according to the study by Zhang et al [32]. MSC, microsupercapacitors.

[16], neutral salt (LiCl) [38], or a base (KOH) [39] dissolved in an aqueous polyvinyl alcohol matrices. This represents a simple, safe, and low-cost methodology for MSC fabrication. However, the voltage window for water-based systems is relatively low. Replacing the plasticizer by organic solvents, such as propylene carbonate and ethylene carbonate allows a 2.5–3 V window broadening. Nevertheless, the best electrolytes so far developed seem to rely on ionic liquids. Compared with other formulations, ionic liquid electrolytes are nonflammable, open the voltage window up to 3.5 V, and exhibit high ionic conductivity and mechanical stability. Choi et al., [21] used an ionic liquid electrolyte, based on 1-butyl-3-methylimidazolium tetrafluoroborate, [BMIM][BF₄]/ultraviolet-cured ethoxylated trimethylolpropane triacrylate, on activated carbon MSCs. The printed devices exhibited a good mechanical stability and electrochemical performance over 2000 cycles [21]. Besides, ionic liquid electrolytes can easily be printed allowing the fabrication of fully printed devices. However, their current high cost may represent a drawback when considering large-scale industrial applications [21]. In terms of current collectors, metal foams or nanometal particles are typically implemented in MSC construction [2]. More recently, conductive materials (graphene, carbon nanotubes, and MXene) are starting to be considered promising alternatives for current collectors because of their low cost and availability [34]. Moreover, as previously stated, they can also be used as both current collector and electrode, thus maximizing the energy density of the device [16,32,40].

Finally, a wide range of substrates can be considered for MSC manufacturing, if they present adequate mechanical properties, wettability, chemical resistance, and stability, among other properties. Most commonly reported MSC substrates include polyethylene terephthalate, paper [21,41,42], and textiles [1,12]. The former is receiving a lot of attention because of the fast development of wearable technologies [1,6]. For instance, Zhang et al., [1] printed MnO₂-coated hollow carbon microsphere-based MSC on silk fabric. These devices exhibited specific capacitances as high as 19.23 mF cm⁻² (at 1 mA cm⁻²) and capacitance retention of 84% after 2000 cycles. Moreover, the performance stability and performance devices were not compromised even after 100 bending and twisting cycles [1]. Bonaccorso et al., [12] have developed a cross-linked ethylene vinyl acetate-encapsulated graphene-based screen printed MSC, which retained its energy storage performance even after a washing cycle [12]. The appeal of wearable technologies relies on the possibility of incorporating devices (health monitoring sensors and even minicomputers) in textiles. Smart clothing will revolutionize the way a modern society interacts with technology. Moreover, it is possible to power up these devices by harvesting energy from external sources, such as solar radiation and even body

movement, thus promoting the use of greener and cleaner energy sources [43]. In this context, MSCs are of major importance as they can compensate for the low power output and irregular distribution of renewable energy sources [17,43]. MSCs are also capable of storing energy under favorable circumstances, thus assuring energetic self-sufficiency, even when surrounding conditions are less favorable for energy harvesting [43]. Guo et al., [44] integrated an MSC (MnO₂ and PPy) with a gas sensor, which in turn could be powered up by a solar cell. Other similar approaches can be found elsewhere [43,45,46].

Remaining challenges and opportunities

In Table 1 are shown the electrochemical performances of several MSCs along with their main components and fabrication methods. MSCs are very promising devices for future energy storage/conversion because of their high energy/power densities and cycle stability. Interestingly, these devices can as well be based on different types of components and fabricated via different routes. Thus, MSC manufacture can, in principle, be tailored toward specific applications needs.

Nevertheless, the realization of fully functional MSCs still faces many technical challenges [38,43]. First, printing techniques still need to secure high scalability and throughput, which are crucial requirements for industrial-level manufacture [43]. In fact, existing printing techniques should be optimized or new less restrictive approaches need to be developed [43]. Roll-to-roll and screen printing have poor overlay accuracies of ~10 μm and 50 μm at best, which can seriously compromise device uniformity, yield, and miniaturization [58]. Inkjet printing is a widely used process that may exhibit a maximum printing resolution of up to 1 μm. As a digital printing process, there is no need for a master template, as the image to be printed is stored in a computer. It easily allows multimaterials patterning, which are only deposited where they need to be, thus greatly reducing waste generation. However, in terms of large area and high-volume printing, the throughput for inkjet printing is still lower than that for more mature and conventional technologies [14,58]. Moreover, high-ratio fillers or materials can easily clog printing nozzles, thus undermining the fabrication efficiency. Significant efforts must be placed toward the development of suitable inks, as not only solid contents but also rheological properties such as viscosity, surface tension, and density are crucial to the jetability [59]. This limits the competitiveness of printing technologies and devices against other more established techniques [38,43]. Another widely used digital printing technique is extrusion printing. Although extrusion printing features only low resolution (typically within hundreds of μm), the simplicity of the process makes it highly feasible for laboratory-scale studies. Furthermore, extrusion printing

Table 1

Components and electrochemical performance of several MSCs reported in the literature.

Electrode material	Printing method	Electrolyte	Substrate	Electrochemical performance	Ref
Activated carbon	Inkjet printing	1 M Et ₄ NBF ₄	SiO ₂ /Si	2.1 mF cm ⁻² (1 mV s ⁻¹)	[47]
Porous carbon	Direct laser Writing	PVA/H ₃ PO ₄	Polymide	0.8 mF cm ⁻² (10 mV s ⁻¹)	[48]
Graphene	Inkjet printing	PVA/H ₃ PO ₄	Polymide	>3000 cycles (0.3 mA cm ⁻²) 9.3 F cm ⁻³ (0.25 A cm ⁻³)	[49]
Graphene/PEDOT	Spray coating	H ₂ SO ₄ /PVA	PET	>10,000 cycles (4.0 A cm ⁻³) 1.29 mWh cm ⁻³ (278 W cm ⁻³) 348 mF cm ⁻³ (1 V.s ⁻¹) 12 mWh.cm ⁻³ (4386 W.cm ⁻³)	[50]
Graphene	Inkjet Printing	PSS/H ₃ PO ₄ /Glycol	Glass/Kapton	>50,000 cycles 0.7 mF cm ⁻² (10 mV s ⁻¹) >11,000 (25 A cm ⁻²) 1.4 mWh.cm ⁻³ (0.05 W cm ⁻³)	[51]
Polyaniline (PANI)	3D printing	1.0 M H ₂ SO ₄	Carbon paper	420 F g ⁻¹ (0.2 A g ⁻¹)	[52]
MoS ₂	Direct laser writing	1 M NaOH	Si	8 mF cm ⁻² (0.22 A.m ⁻²) >1000 cycles (0.22 A.m ⁻²)	[53]
MnO ₂ /carbon	Screen printing and transfer	PVA/H ₃ PO ₄	Silk fabric	19.23 mF cm ⁻² (1 mA cm ⁻²)	[1]
FeOOH/MnO ₂	Screen printing	PVA/LiCl	PET, paper, and textile	>100 bending cycles 350.2 F g ⁻¹ (0.5 A g ⁻¹) 5 × 10 ⁻⁴ mWh.cm ⁻² (0.04 mW cm ⁻²) >10,000 cycles (15 A g ⁻¹)	[11]
CoO/CNT	Screen printing	PVA/KOH	PET	17.4 F cm ⁻³ 3.48 mWhcm ⁻³ (0.25 A cm ⁻³)	[54]
Phosphorene/graphene	Transfer printing	BMIMPF ₆	PET	9.8 mF cm ⁻² (5 mV s ⁻¹) 37.0 F cm ⁻³ (5 mV s ⁻¹) >1000 cycles (0.44 A cm ⁻²)	[55]
Ti ₃ C ₂ T _x MXene	Inkjet printing	H ₂ SO ₄ /PVA	AlO _x -coated PET	12 mF cm ⁻² (5 mA cm ⁻²)	[16]
Ti ₃ C ₂ T _x MXene	Extrusion printing	H ₂ SO ₄ /PVA	AlO _x -coated PET	562 mF cm ⁻² (5 mA cm ⁻²) 43 mF cm ⁻² (5 mA cm ⁻²) 0.32 μW h cm ⁻² (11.4 μWcm ⁻²) 0.11 μW h cm ⁻² (158 μW cm ⁻²)	[16]
Cobalt hexacyanoferrate (CoHCF)	Screen printing	PVA/LiCl/K ₃ [Fe(CN) ₆]	PET	12.5 mF.cm ⁻² (0.1 mA cm ⁻²) 0.0011 mWh.cm ⁻² (0.44 mW cm ⁻²) >8000 cycles (0.5 mA cm ⁻²)	[56]
Ni/MnO ₂	Stamp	CMC/Na ₂ SO ₄	PET/Kapton	4.15 mF.cm ⁻² (20 mVs ⁻¹) 0.18–0.47 uWh.cm ⁻² (0.42 mW cm ⁻²) 3000 cycles (400 mV s ⁻¹)	[57]

PET, polyethylene terephthalate; PVA, polyvinil alcohol; PEDOT, poly(3,4-ethylenedioxythiophene) ; CNT, carbon nanotubes.

of high-viscosity inks enables fabrication of 3D structures, overcoming the intrinsic limitations of planar devices made by other conventional printing techniques [34]. Finally, devices fully printed fabrication for integration in circuitry, and daily life applications is still a challenging process. Despite all these shortcomings, printed flexible/wearable technologies are still on the early stages of development. This research field has gained considerable momentum for the last couple of years, and significant breakthroughs are achieved at a considerable fast pace. Thus, MSCs may, in fact, be one of the most promising energy storage/conversion devices for future flexible wearable and portable technologies.

Conflict of interest statement

Nothing declared.

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