

Direct Ink Writing of Aqueous Electrochemical Energy Storage Devices

by
Stefano Tagliaferri

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Supervisor: Dr Cecilia Mattevi

Imperial College London
Faculty of Engineering, Department of Materials
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Declaration of Originality

I confirm that this Thesis, submitted in partial fulfilment of the requirements for the award of the degree of Doctor of Philosophy in the Department of Materials, Imperial College London, is a result of my own work unless referenced or acknowledged otherwise. This Thesis has not been submitted for qualifications at any other academic institution.

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August 2023

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Abstract

Electrochemical energy storage devices (EESDs) will play a key role in the future development of portable and wearable electronics. The current manufacturing methods for EESDs rely on toxic and flammable solvents, raising concerns about user safety and environmental sustainability. Energy storage devices containing aqueous electrolytes are intrinsically safer; however, their low energy density and cycle life hinder commercialization.

Direct Ink Writing (DIW) is a 3D printing technique emerging as a promising manufacturing method for customizable EESDs with tailored size and enhanced performance. Inks for DIW can be formulated using water and environmentally sustainable solvents. Additionally, 3D printed EESDs present superior surface-to-volume ratios and high loading of active material, overcoming the energy density limitations of aqueous EESDs and the low rate capability of thick electrodes.

DIW has the capability to print a broad range of materials, enabling the fabrication of electrodes, electrolyte and passive components in the same manufacturing process. Nonetheless, the composition of the inks for DIW must be carefully designed to achieve structures with the desired geometry and functional properties. Therefore, in this work we investigated new ink formulations for the manufacturing of aqueous EESDs using DIW, with specific focus on aqueous graphene supercapacitors, zinc hybrid capacitors and zinc ion batteries. The printability of the inks was optimized to fabricate electrochemically-active structures with the desired degree of geometric complexity. We demonstrated that 3D printed graphene and zinc electrodes achieve superior energy density, rate capability and stability in aqueous supercapacitors and zinc hybrid capacitors. Additionally, we shed light into the charge storage and ageing mechanisms of 3D printed electrodes for aqueous supercapacitors and zinc ion batteries, using a combination of physical and electrochemical characterization tools. Finally, we successfully demonstrated an all-printed zinc-ion battery, combining interdigitated zinc anodes and manganese oxide cathodes with printable gel electrolytes.

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The material presented in Section 2 of Chapter 4 is under consideration for intellectual property protection.

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List of Symbols and Abbreviations

$\dot{\gamma}$	shear rate
τ_Y	yield stress
ϕ	volume fraction
ϕ_c	critical volume fraction for gelation
BET	Brunauer–Emmett–Teller
CA	chronoamperometry
CB	carbon black
CE	coulombic efficiency
CFD	computational fluid dynamics
CMC	carboxymethylcellulose
CNF	cellulose nanofiber
CNT	carbon nanotube
CP	chronopotentiometry
CV	cyclic voltammetry
DIW	direct ink writing
DMSO	dimethyl sulfoxide
EDL	electrical double layer
EDS	energy dispersive X-ray spectroscopy
EESD	electrochemical energy storage device
FDM	fused deposition modelling
G'	storage modulus
G''	loss modulus
GCD	galvanostatic charge discharge
GNP	graphene nanoplatelet
HC	hybrid capacitor
HR-TEM	high resolution transmission electron microscopy
IJP	inkjet printing
LAOS	large amplitude oscillatory shear
LIB	lithium-ion battery
LiTFSI	lithium bis(trifluoromethanesulfonyl)imide
LSV	linear sweep voltammetry
LVE	linear viscoelastic

NMP	N-Methyl-2-pyrrolidone
PANI	Polyaniline
PEDOT:PSS	poly(3,4-ethylenedioxythiophene) polystyrene sulfonate
PTFE	polytetrafluoroethylene
PVA	poly(vinyl alcohol)
PVDF	polyvinylidene difluoride
SAED	selected area electron diffraction
SAOS	small amplitude oscillatory shear
SEM	scanning electron microscopy
TAA	thioacetamide
TEM	transmission electron microscopy
TGA	thermogravimetric analysis
WISE	water-in-salt electrolyte
XCT	X-ray computed tomography
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
ZHC	zinc hybrid capacitor
ZHS	zinc hydroxysulfate
ZIB	zinc-ion battery

Motivation and Thesis Outline

The development of printable inks is paramount for manufacturing electrochemical energy storage devices using Direct Ink Writing. In the last 20 years, great progress has been made in the fabrication of functional ceramics and biomedical devices. In contrast, the field of energy storage has only recently started to investigate DIW as a viable manufacturing process for batteries and supercapacitors. The driving force behind the growing interest in 3D printed EESDs has been the demand for customizable, safe and high-performing devices to power portable and wearable electronics, beyond commercial lithium-ion batteries which present fixed geometries and contain flammable electrolytes. Three-dimensional electrodes with a tailored design enable higher surface-to-volume ratios and enhance the areal loading of active materials, boosting energy density and rate capability. In the formulation of inks for DIW two essential objectives must be achieved: firstly, optimizing printability, in order to obtain structures with the desired geometry and resolution; and, secondly, optimizing the electrochemical and functional properties of the printed structures, *e.g.*, electrical conductivity, energy density and mechanical stability.

The aim of this study was to demonstrate the capability of DIW in manufacturing aqueous EESDs with customized design and suitable electrochemical performance. In particular, our first objective was to develop new ink formulations specifically designed for the requirements of carbon supercapacitors, zinc hybrid capacitors (ZHCs) and zinc ion batteries (ZIBs), and optimize their printability for the DIW process. Our second objective was to demonstrate that 3D printed electrodes can achieve superior energy density, rate capability and stability than the corresponding tape-casted devices, and investigate the origin of the improvement in performance through physical and electrochemical characterization. Finally, our third objective was to demonstrate the integration of different ink formulations to fabricate all-printed aqueous ZIBs with interdigitated geometry.

In Chapter 1 we provide a general overview of the different types of electrochemical energy storage systems available today, their charge storage mechanism and industrial manufacturing process. In particular, we critically analyse the limitations of commercial EESDs in terms of sustainability, safety and design flexibility. In this context, the advantages of aqueous batteries and supercapacitors are presented, alongside the main factors that have prevented their wider commercialization so far. The second part of the chapter provides a critical overview of the 3D printing processes that have been investigated to manufacture EESDs, with a detailed discussion on DIW. The printability of inks for DIW and the general principles to design an ink formulation will also be examined.

In Chapter 2, we describe the experimental methodologies employed throughout this work for the synthesis of electroactive materials, for ink preparation and for the characterization of inks and printed electrodes.

In Chapter 3 we propose the use of capillary suspensions of graphene nanoplatelets to print aqueous supercapacitors that do not require energy-intensive post-processing. We assess the printability of these inks, and we correlate the microscopic and macroscopic structure of the printed filaments with the rheological properties and flow history of the inks. The electrochemical properties of the printed electrodes are demonstrated in a three- and two-electrode configuration and benchmarked against state-of-the-art devices. A laser debinding treatment is also examined to enhance the performance of electrodes printed on cellulose paper. In the second part of the chapter, we demonstrate a graphene/CNTs ink to print highly conductive electrodes for zinc hybrid capacitors. Additionally, we assess the use of a chronoamperometric method as a viable alternative to galvanostatic charge-discharge tests to evaluate the rate capability of the 3D printed electrodes.

In Chapter 4 we propose two different approaches to formulate aqueous inks for zinc electrodes. The former relies on the destabilization of PEDOT:PSS suspensions to obtain a printable and electrically conductive binder. The latter is based on the use of polyvinyl alcohol as a highly hydrophilic polymeric binder, made electrically conductive by the addition of carbon black particles. We demonstrate that the PEDOT:PSS binder is highly thixotropic and therefore unsuitable for the fabrication of self-standing 3D electrodes. On the other hand, the electrodes obtained from polyvinyl alcohol inks have excellent shape fidelity, resulting in high cycling stability and low plating-stripping overpotential. The origin of the improved electrochemical performance of the 3D printed electrodes is analysed with *ex-situ* characterization tools.

Chapter 5 delves into the fabrication of all-printed EESDs. The initial focus of the chapter is the development of cathodes for zinc-ion batteries, using hydrothermal vanadium disulfide and manganese oxide. We provide insight into the synthesis and physical properties of the active materials and on the electrochemical properties of the printed electrodes. We then investigate the formulation of a printable gel electrolyte for ZIBs, drawing inspiration from the colloidal processing of ceramic suspensions. In the last part of the chapter, we successfully demonstrate the assembly of fully-printed interdigitated ZIBs and we characterize their electrochemical properties.

Finally, Chapter 6 concludes this work offering some final remarks and indicating promising directions for future research.

Chapter 1

3D Printing for Electrochemical Energy Storage Devices

Electrochemical energy storage devices (EESDs) are going to play a crucial role in the transition to green energy, as a growing fraction of the energy demand is supplied by renewable sources, such as solar and wind power.¹ Although renewable energy sources are sustainable and present a low CO₂ footprint, they are intermittent, thus requiring large-scale EESDs to supply power in the periods of high demand and stabilize the electric grid.² In parallel with grid-scale energy storage applications, batteries and supercapacitors will also ensure the penetration of sustainably sourced energy into the rapidly expanding market of electric vehicles and electronic systems. In particular, small-size EESDs are increasingly needed as lightweight and portable power sources for wearable devices and consumer electronics. The market of consumer electronics is expected to reach a 950-billion-dollar revenue worldwide by 2027, driving the development of safer and better performing EESDs in the near future.^{3–5} Today, the leading energy storage systems used in portable electronics is represented by rechargeable batteries, which store electrical energy as chemical energy *via* redox reactions inside the electrodes. Although modern batteries can achieve large energy densities ($> 200 \text{ Wh kg}^{-1}$), they are typically inefficient for applications which require fast charge or discharge rates.^{6,7} Batteries in electronic systems are often complemented by electrochemical capacitors, or supercapacitors, characterized by large power densities and able to quickly release the energy stored *via* electrochemical processes. However, commercial batteries and supercapacitors are typically produced in fixed sizes and geometries, which hinder the integration into wearable electronics, and they contain flammable and hazardous electrolytes, posing health hazards to users. Water-based chemistries and alternative manufacturing processes, such as 3D printing, can meet the demand for customizable and safer EESDs.

This chapter will provide an introduction to the field of 3D printed aqueous EESDs, serving as a background for the discussion presented in the following chapters. In detail, Section 1 will introduce the differences in the energy storage mechanism of batteries and supercapacitors, and describe the materials and conventional manufacturing methods for commercial EESDs, highlighting the limitations of conventional energy storage devices as power sources for portable and wearable electronics. Section 2 will then discuss the use of a novel family of manufacturing techniques, namely

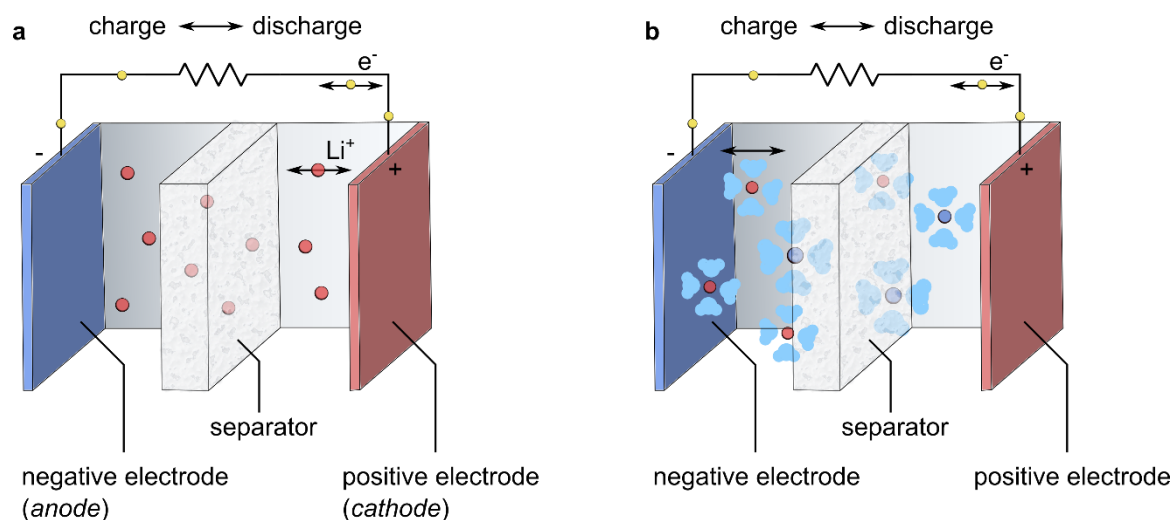


Figure 1.1: Schematic showing the structure of EESDs and the charge transport during charge/discharge for (a) a rechargeable lithium-ion battery and (b) an aqueous supercapacitor.

3D printing, to fabricate EESDs and the advantages of printed EESDs for wearable electronics. The recent progress in the field will be critically reviewed, with particular focus on Direct Ink Writing, *i.e.* the extrusion-based 3D printing technique employed throughout this work. Finally, the general principles to formulate printable inks for Direct Ink Writing will be discussed, alongside a description of the main components and requirements of the ink system.

1. Batteries and supercapacitors

EESDs typically consist of two electrodes, containing the active materials responsible for the charge storage processes, and separated by an ionically conductive electrolyte (Figure 1.1). In rechargeable batteries the negative electrode and the positive electrode are conventionally named *anode* (the electrode with the lower potential) and *cathode* (the electrode with the higher potential), even though during the charge process the positive electrode undergoes electrochemical reduction and the negative electrode oxidation.^{8,9} A permeable membrane (*separator*) is usually placed between the electrodes to prevent mechanical contact and short circuits. During the discharge process, the electrons generated inside the active material, or near its surface, are transferred from the negative electrode to the positive electrode, *via* an external circuit connected to the electrodes through a conductive current collector. Simultaneously, inside the electrolyte, anions flow to the negative electrode and cations to the positive electrode to complete the electric circuit and preserve the charge neutrality of the system (Figure 1.1).⁹

In rechargeable batteries, electrical energy is reversibly stored *via* faradaic processes involving the transfer of charges through the interface between the active material and the electrolyte. The main figure of merit describing the charge storage capability of a battery is thus its specific capacity,

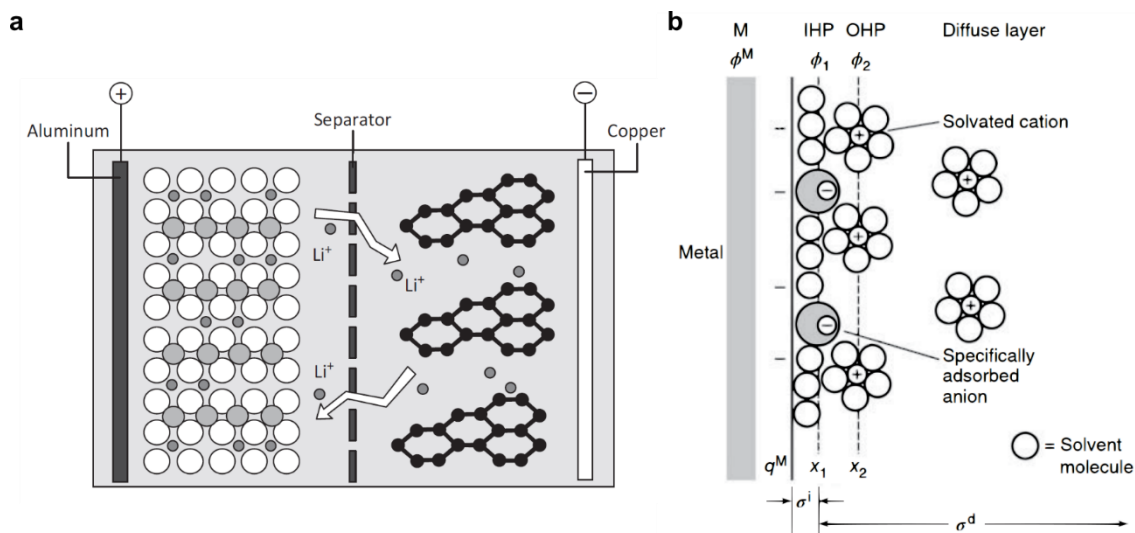


Figure 1.2: (a) Schematic showing the setup of a commercial lithium-ion battery (adapted with permission from ref.²⁶); (b) structure of the electrical double layer, showing the inner Helmholtz plane (IHP) *i.e.* the limit of the region with specifically adsorbed ions, and the outer Helmholtz plane (OHP), *i.e.* the limit of the region with non-specifically adsorbed solvated ions (adapted with permission from ref.¹³, Copyright 2022, John Wiley and Sons)

i.e. the maximum charge that the battery can store, normalized by the battery mass, volume or footprint area. Typical redox reactions occurring during charge and discharge involve the chemical conversion of the active material, intercalation processes inside its crystal structure or the formation of alloy compounds. When metallic negative electrodes are considered, *e.g.* in zinc- or lithium-metal batteries, the redox reactions at the metal electrode surface typically encompass the reduction of metal ions from the electrolyte during charge and the oxidation of the metal electrode to generate soluble ions during discharge. These redox processes occur at characteristic potentials; therefore, batteries ideally operate as voltage sources, providing a constant potential independent of the external load. However, real batteries often present chemical changes in the active materials during operation, alongside an increase in internal resistance caused by the formation of discharge products and concentration and activation polarization of the electrodes, which result in a decrease of the battery voltage at increasing state-of-discharge.⁹

The worldwide market of rechargeable batteries for consumer electronics is today dominated by lithium-ion batteries (LIBs), owing to their high energy density and long cycle life.¹⁰ The charge storage mechanism in LIBs is based on the shuttling of lithium ions between a negative graphite electrode and a positive transition metal oxide or phosphate electrode. During charge, the transition metal centres in the positive electrode are oxidized, donating electrons to the π -system of the graphite electrode (Figure 1.2-a).¹¹ At the same time, lithium ions are deintercalated from the crystal structure of the positive electrode, migrating towards the negative electrode where they form a

graphite intercalation compound. The process is reversed during discharge, with the migration of lithium ions towards the positive electrode and the reduction of the transition metal centres.

Even though rechargeable batteries can store large specific energy through faradaic processes, their rate capability and power density are typically unsuitable for applications requiring extremely fast charge and discharge rates. As a consequence, rechargeable batteries can be complemented in high power electronics by capacitors and electrochemical capacitors, also known as supercapacitors.⁶ Supercapacitors store charges at the interface between the electrodes and the electrolyte, either through the formation of an electrical double layer (EDL) or through near-surface faradaic reactions (pseudocapacitance).⁸ The former mechanism is purely electrostatic (*i.e.* non-faradaic), and it is based on the formation of a charged layer at the electrode interface, which produces a high local electric field (as high as 10^7 V cm^{-1}), with no charge transfer across the interface.¹² In particular, the electrical double layer consists of an inner region made of ions and molecules specifically adsorbed on the electrode surface, and of an outer region made of non-specifically adsorbed ions, which interact through long-range electrostatic forces independent of the chemical nature of the species involved (Figure 1.2-b).¹³ As a consequence of Brownian motion, the non-specifically adsorbed ions occupy a diffuse region of space typically $< 10 \text{ nm}$ in thickness, extending from the inner region of the EDL to the bulk of the electrolyte.¹³ The EDL forms almost instantly ($\sim 10^{-8} \text{ s}$) at the interface with the electrodes, resulting in a much faster charge storage response than faradaic processes.¹⁴ All EESDs, including batteries, store a fraction of the charge through the formation of an electrical double layer during charge and discharge, which is directly proportional to the accessible surface area of the electrodes.¹²

Unlike EDL supercapacitors, pseudocapacitors predominantly store energy through faradaic reactions involving the transfer of charges across the double layer, similarly to what happens in battery electrodes. Nonetheless, the redox processes in pseudocapacitors do not interest the entire bulk of the electroactive material, but only a layer near the particle surface, presenting a thickness much smaller than the typical diffusion layer in battery materials.⁸ As a consequence, redox reactions in pseudocapacitive materials occur at a much faster rate than conventional battery materials, presenting timescales closer to the electrochemical response of EDL supercapacitors. Both EDL and pseudocapacitive charge storage can result in a capacitive response, *i.e.* a direct proportionality between the charge stored and the electrode potential, leading to rectangular cyclic voltammograms (Figure 1.3-a). In these circumstances, the electrochemical response of supercapacitors is described in terms of capacitance, defined as the proportionality coefficient between the charge stored in the electrode and the electrode potential. Depending on the specific faradaic mechanism underlying the charge storage process, *e.g.* adsorption, intercalation or other surface redox processes, pseudocapacitive

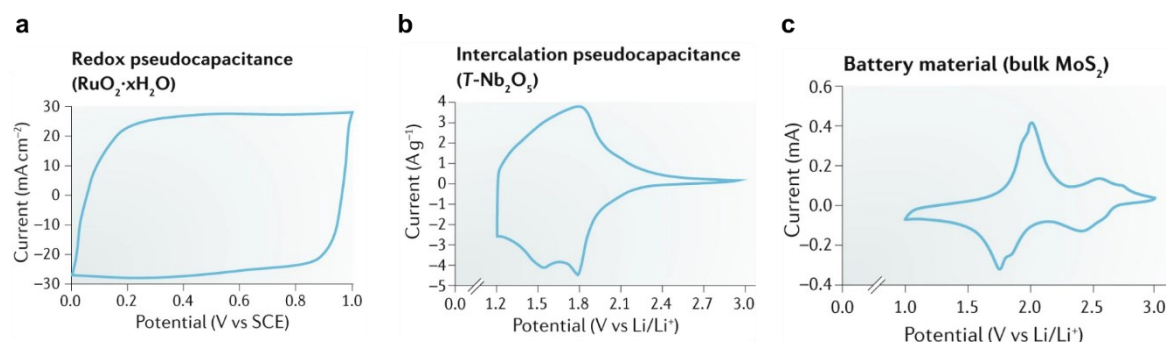


Figure 1.3: Typical cyclic voltammograms for (a) pseudocapacitive RuO_2 characterized by surface redox reactions; (b) pseudocapacitive Nb_2O_5 characterized by intercalation processes; and (c) a battery material (adapted with permission from ref.¹⁵, Copyright 2019, Springer Nature Limited)

materials might also present faradaic charge-transfer peaks in their cyclic voltammograms, which are usually broader than the ones observed in battery materials (Figure 1.3-b,c).^{15,16}

Carbonaceous electrodes such as activated carbon, graphene and carbon nanotubes typically exhibit a predominantly EDL charge storage response, promoted by the high conductivity and large specific surface areas of these materials.¹⁷ A pseudocapacitive response might also occur if reactive surface functionalities or heteroatoms are introduced onto the surface of the carbon particles. However, the presence of reactive sites typically reduces the cycling stability and rate capability of the devices, and it can limit the electrochemical stability window of the electrolyte.¹⁸ More conventional pseudocapacitive materials include transition metal oxides, such as bulk ruthenium oxide (RuO_2) and manganese oxide (MnO_2). In acidic electrolytes protons can be electrosorbed on the surface of hydrated ruthenium oxide, whereas migration in the bulk of the material is energetically unfavourable.^{15,17} Transition metal dichalcogenides such as MoS_2 and VS_2 have recently been studied as active materials for pseudocapacitors, owing to their high surface area and multiple accessible oxidation states on the transition metal centres.¹⁹

The typical values of energy and power densities for supercapacitors and rechargeable batteries are compared in Figure 1.4-a. Lithium-ion batteries can provide high energy ($\sim 50\text{-}300 \text{ Wh kg}^{-1}$) for prolonged operation times, but their cycling stability and power density are limited by the faradaic reactions involving diffusion and transformations in the bulk of the active materials.⁷ In contrast, supercapacitors can supply energy at very fast rates, presenting power densities $> 10^4 \text{ W kg}^{-1}$ and typical operation times $\sim 10\text{-}100 \text{ s}$, as a result of the surface or near-surface energy storage reactions.⁷ Hybrid capacitors (HCs) are hybrid energy storage devices that combine the features of both batteries and supercapacitors, providing improved power densities compared to batteries and higher energy densities compared to supercapacitors. HCs consist of two electrodes with different

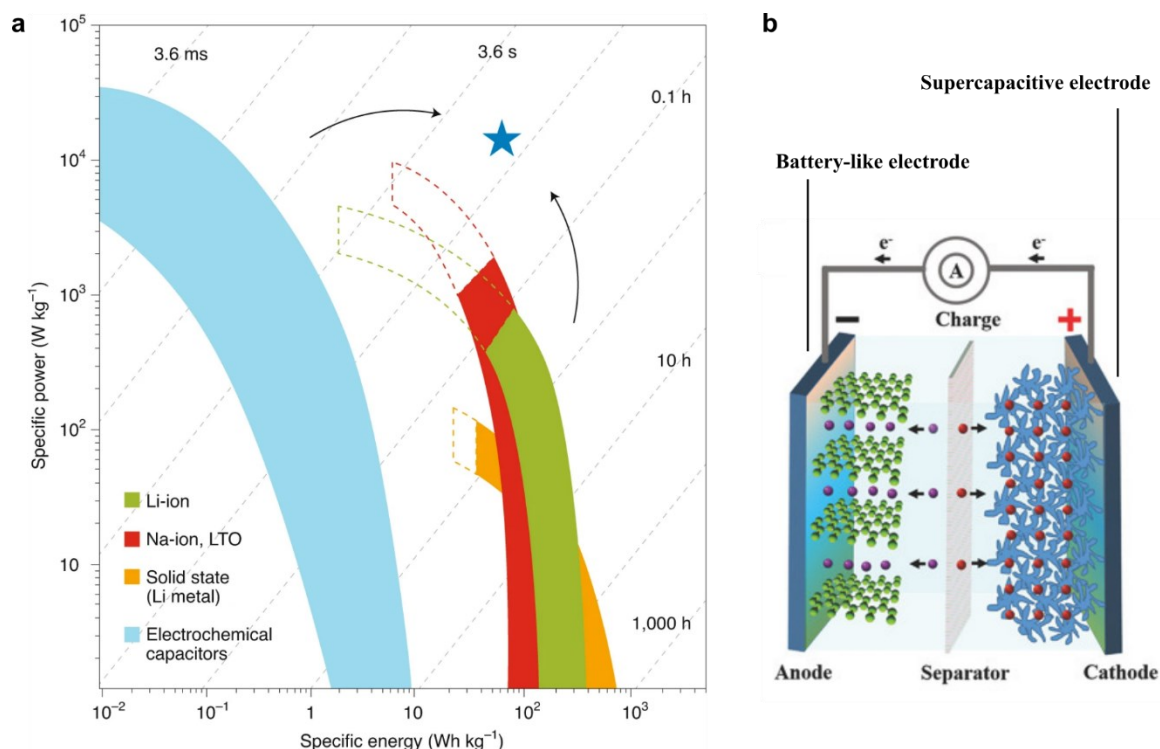


Figure 1.4: (a) Ragone plot comparing the specific energy and power for rechargeable EESDs (adapted with permission from ref.⁷); (b) cell structure and charge storage mechanism for a lithium-ion hybrid capacitor (adapted with permission from ref.³⁷⁹, Copyright 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim).

charge storage mechanism, usually a capacitive electrode, such as a porous carbon or graphene electrode, and a faradaic battery-like electrode, such as a graphite or a metal electrode (Figure 1.4-b). The former provides a fast electrochemical response and high power density, while the latter ensures large energy storage capabilities. Pre-lithiated graphite or mixed graphite-lithium electrodes have been widely used in combination with activated carbon anodes to fabricate lithium HCs.²⁰ The intercalation of lithium into the graphite anode during charge provides higher energy densities than symmetric supercapacitors based on activated carbon electrodes.

1.1. Manufacturing methods and materials for commercial EESDs

The conventional approach to manufacture EESDs involves depositing the electrodes onto conductive current collectors using coating or extrusion processes (Figure 1.5).²¹ A highly porous separator is inserted between the electrodes and the cell is then filled with the electrolyte. Finally, the device is sealed to prevent leakage and uptake of moisture from air. The primary active material employed for the electrodes of commercial supercapacitors is activated carbon, usually obtained from coconut shell biomass and activated with water vapour to obtain high surface areas $> 1000 \text{ m}^2 \text{ g}^{-1}$.²² Activated carbon typically presents an EDL charge storage mechanism, which ensures long cycle life and stable performance. On the contrary, pseudocapacitive materials are not extensively used in

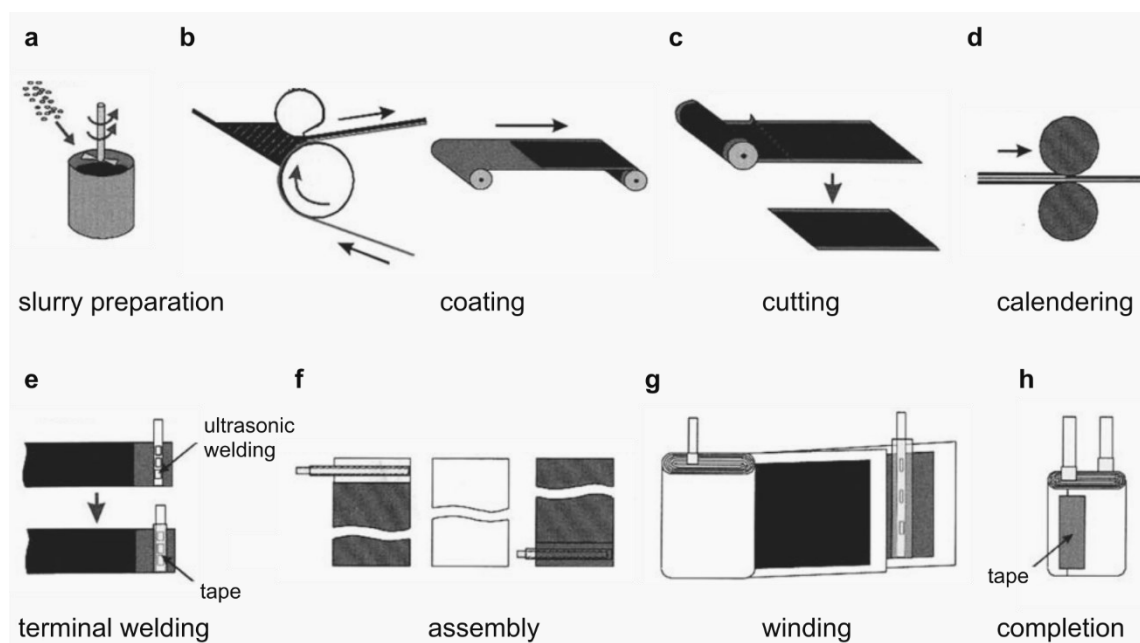


Figure 1.5: Overview of the conventional manufacturing steps for commercial EESDs: (a) preparation of a slurry containing the active materials, binders and additives; (b) coating of the slurry on the current collector; (c,d) cutting and calendering of the electrodes; (e) ultrasonic welding of the terminals to the electrodes; (f) assembly of the cell; (g, h) winding and completion. Adapted with permission from ref.²⁴, Copyright 2009, Springer Science Business Media, LLC.

commercial applications, owing to the need for aqueous electrolytes with small stability windows and to the low stability and the high cost of the active materials (*e.g.* RuO_2).⁷ The carbon electrodes are fabricated by mixing activated carbon with a polymeric binder, which promotes adhesion between the solid particles and the current collector, and conductive additives (such as carbon black or acetylene black). The most common binder for commercial supercapacitor is polytetrafluoroethylene (PTFE), which is widely employed for its chemical stability and dispersibility in water, alongside polyvinyl alcohol and cellulose.²¹ An aqueous paste is obtained by mixing the active materials, binder and additives, and then coated on the current collector using a doctor blade or slot die equipment. The metallic current collectors are typically made of aluminium or copper, presenting high conductivity and ensuring a low equivalent series resistance during operation.²¹ Commercial carbon supercapacitors mainly rely on organic electrolytes, which are characterized by large stability windows, maximizing the energy density that can be stored through EDL processes (which is proportional to the square of the applied voltage). In particular, tetraalkylammonium ions (such as tetraethylammonium tetrafluoroborate) dissolved in acetonitrile provide high conductivity ($\sim 5.5 \text{ S m}^{-1}$) and wide electrochemical stability windows ($> 3.8 \text{ V}$), and they have become the standard for commercial supercapacitors based on activated carbon.²¹

The industrial manufacturing of rechargeable batteries follows similar steps as activated carbon supercapacitors, with differences related to the specific cell chemistry and composition. In the

manufacturing of lithium-ion batteries, the active materials for the negative and positive electrode (e.g. graphite and LiCoO_2 or $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$) are respectively mixed with acetylene black and a polyvinylidene fluoride (PVDF) binder, and then ball-milled in the presence of a solvent to obtain a processable slurry. N-Methyl-2-pyrrolidone (NMP) is the conventional solvent used to disperse and cast the active materials, producing slurries with low viscosity $\sim 100 \text{ Pa}\cdot\text{s}$.^{9,23,24} During the drying process, the NMP vapours must be recovered with costly processes to prevent release into the environment, which might pose risks to the ecosystem and human health.²⁵ After coating, the electrodes are calendered to increase their density and conductivity and accurately control the thickness of the coated layer.²⁴ An aluminium tab is welded to the aluminium current collector of the positive electrode and a nickel tab to the negative electrode, providing connection to the external circuit, and the electrodes are then inserted in the cell case, typically an aluminium polymer-laminated film for pouch cells. All the steps of the cell assembly process must be carried out in a dry atmosphere, to prevent moisture contamination that would affect the operation and safety of the lithium-ion battery. In particular, LIBs must be rigorously assembled in an environment with humidity concentrations $< 20 \text{ ppm}$, since the presence of moisture in the electrolyte can result in the formation of toxic and corrosive HF during operation.²⁶ The electrolyte for LIBs usually contains LiPF_6 dissolved in organic carbonates, and it is poured into the cell by vacuum injection before sealing the case.²⁴ Safety systems must also be incorporated in LIBs during assembly, owing to the risk of thermal runaway, explosion and fire if the cell is abused. However, this increases the costs of the assembly process and complicate the design of the cell. Common safety systems include positive temperature coefficient resistors, which minimize the current flow when the temperature of the cell exceeds a threshold limit, and current interrupt devices, which stop the current flow if the internal pressure of the cell increases.²⁴

Although commercial supercapacitors and LIBs are able to provide excellent electrochemical performance (energy densities $\sim 10 \text{ Wh kg}^{-1}$ and power densities $> 2 \text{ kW kg}^{-1}$ for supercapacitors and $> 200 \text{ Wh kg}^{-1}$ and $\sim 1 \text{ kW kg}^{-1}$ for batteries),^{7,9,21} the assembly of commercial EESDs relies on large amounts of hazardous solvents (such as NMP) to disperse and cast the active materials.^{9,23} Additionally, electrolytes based on organic solvents (such as acetonitrile and organic carbonates) must be employed in commercial lithium-ion batteries and carbon supercapacitors, posing safety and flammability issues in wearable systems.^{27,28} The EESDs that are used to power wearable electronics should be safe and environmentally sustainable, *i.e.* durable, made of environmentally-friendly materials and manufactured through material-efficient processes with low carbon footprint. In particular, the sustainability aspect of EESDs must be crucially accounted for, considering the scale of the battery market today and the growing volume of electronic waste associated with the diffusion of portable consumer electronics. Additionally, energy storage devices used to power wearable systems are in direct contact with the user's body for extended period of time, and should therefore be intrinsically safe to eliminate the risk of harm or injury in case of malfunctioning.

The safety and sustainability issues currently presented by commercial EESDs can be addressed investigating alternative cell chemistries compatible with aqueous electrolytes, and alternative manufacturing methods based on the aqueous processing of the active materials. Advanced manufacturing methods for EESDs should overcome the limitations of tape casting processes, which are not able to meet the customization and miniaturization requirements of wearable systems, and are not suitable for the direct integration of multi-material EESDs into portable electronics.²⁹

1.2. Aqueous EESDs

Electrochemical energy storage devices based on aqueous electrolytes showcase several advantages in terms of safety, cost and environmental sustainability over the conventional systems outlined in the previous section. Aqueous electrolytes are characterized by higher ionic conductivities than organic electrolytes based on carbonates or acetonitrile ($\sim 100 \text{ S m}^{-1}$ vs. $\sim 0.1\text{-}1 \text{ S m}^{-1}$).³⁰ Additionally, aqueous EESDs are intrinsically safer, since they are non-flammable and can better tolerate overcharging and mishandling; therefore, the integration of battery management systems and safety systems during manufacturing is not as crucial as for organic electrolytes.³¹ The active materials for aqueous EESDs can be typically processed in air, with no need for the strict control over the manufacturing environment required by LIBs, resulting in lower capital costs.³²

The main obstacle to the commercialization of aqueous EESDs today is represented by the lower energy density and cycle life of these devices, associated with the small potential window of aqueous electrolytes.²¹ Water has a thermodynamic stability window of 1.23 V, outside of which it undergoes electrochemical oxidation with the production of oxygen (oxygen evolution reaction, OER) or electrochemical reduction with the production of hydrogen (hydrogen evolution reaction, HER), Figure 1.6-a.³² The gaseous species generated by the decomposition of aqueous electrolytes can damage the structure of the electrodes and reduce the contact area between the electrode and electrolyte, causing large polarization during operation and progressively consuming the electrolyte. More importantly, HER and OER do not contribute to energy storage in the electrochemical cell, resulting in lower energy efficiencies. Several strategies have been proposed in order to limit the decomposition of water electrolytes and achieve satisfactory energy densities, involving the modification of the electrolyte composition or the design of three-dimensional electrodes for batteries and supercapacitors (Figure 1.6-a).

Historically, aqueous batteries were the first rechargeable EESDs commercialized, and today they still constitute a significant fraction of the battery market for automotive applications.³² However, LIBs are expected to take over more than 80% of the rechargeable battery market in the next years, replacing traditional aqueous EESDs which often contain toxic and critical elements, such as cadmium and nickel.³² As a consequence, new aqueous chemistries for rechargeable batteries are receiving attention today, in particular zinc-ion batteries (ZIBs). ZIBs combine low costs and safe and available active materials with competitive energy and power densities compared to other

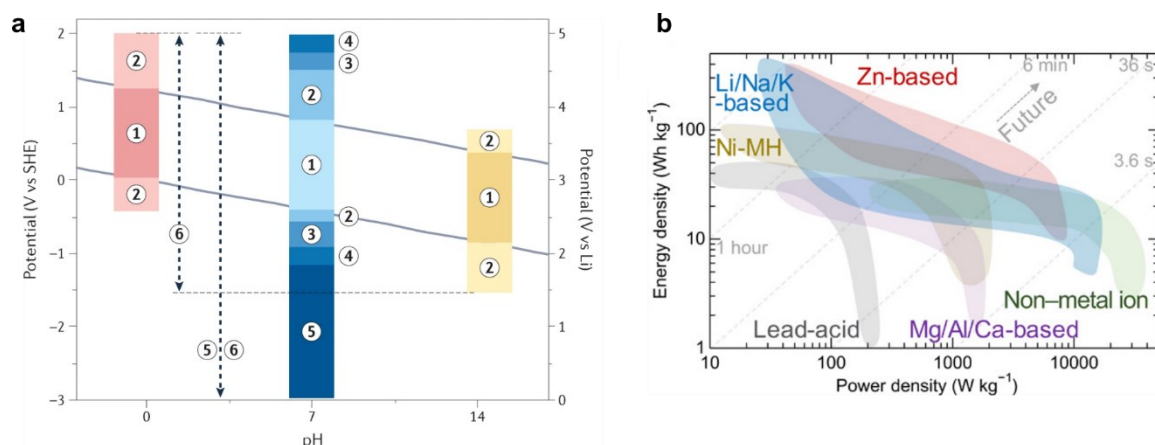


Figure 1.6: (a) Plot showing the thermodynamic stability window of conventional aqueous electrolytes (1) and how it can be expanded by controlling the overpotential for HER and OER (2), by using lean-water electrolytes (3), solid electrolytes (4) and electrode protection layers and ion-selective membranes (5, 6), adapted with permission from ref.³², Copyright 2022, Springer Nature Limited; (b) Ragone plot comparing the energy and power density of aqueous batteries (adapted with permission from ref.³¹).

aqueous batteries (Figure 1.6-b). The energy storage mechanism in ZIBs is based on the reversible shuttling of cations between a zinc negative electrode and a positive electrode. In particular, zinc metal electrodes are the prominent anodes for ZIBs owing to the low reversible potential of zinc (-0.76 V vs, SHE), high theoretical capacity (~ 820 mAh g⁻¹) and low specific cost.³³ Despite these advantages, the widespread application of zinc anodes in rechargeable batteries is still impeded by the continuous corrosion of zinc in aqueous electrolytes and by the growth of dendrites and insulating species during electrochemical cycling.³⁴ While zinc metal is a well-established anode for ZIBs, the development of cathode materials is still at an early stage.³¹ Manganese oxides have been widely investigated as promising cathodes presenting tunnels or layered crystal structures able to host divalent cations. Although an intercalation charge storage mechanism was initially proposed for manganese oxide in acidic zinc electrolytes (*e.g.* ZnSO₄),³⁵ further studies have shown that the intercalation of Zn²⁺ can also be accompanied by the insertion of H⁺ ions and, in some instances, by the chemical conversion of the active material.^{36–38} The intercalation of H⁺ is more favourable than Zn²⁺ for the energetic cost of zinc desolvation and for the strong electrostatic interactions of divalent Zn²⁺ with the crystal lattice of manganese oxide.³⁹ A progressive capacity fading during cycling has often been observed for manganese oxide cathodes in zinc sulfate electrolytes, owing to the disproportionation of Mn³⁺, which is produced during discharge, to soluble Mn²⁺. The addition of MnSO₄ into the electrolyte can hinder the irreversible loss of manganese from the electrode, stabilizing the cycling response.³⁶ Layered transition metal sulfides, such as VS₂ and MoS₂, have also been explored as alternative cathodes for zinc-ion batteries. VS₂ has a high electronic conductivity and a large interlayer spacing (~ 5.76 Å), able to accommodate Zn²⁺ cations.⁴⁰ Unlike manganese oxide, current studies indicate that the energy storage mechanism in layered sulfides is dominated by the direct intercalation of Zn²⁺ into the layered structure of VS₂.^{40,41} However, VS₂

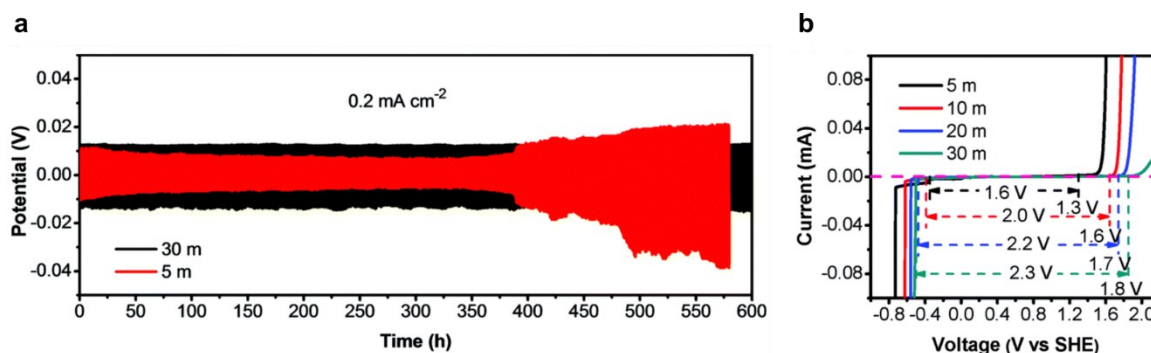


Figure 1.7: (a) Plating and stripping tests on a symmetric zinc cell in 20 m ZnCl_2 ; (b) electrochemical stability window of a ZnCl_2 aqueous electrolyte at different concentrations (adapted with permission from ref.⁴⁵, Copyright 2018, Royal Society of Chemistry).

electrodes suffer from gradual dissolution in aqueous ZnSO_4 and $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ electrolytes, negatively affecting the cycling stability of the zinc-ion battery.^{42,43} Several strategies have been proposed in order to enhance the stability of ZIB electrode materials, and to overcome the energy density limitations posed by aqueous electrolytes. In particular, the utilization of water-lean electrolytes (with concentrations higher than 5 mol L⁻¹) and the optimization of the electrode design have yielded promising results in terms of battery performance and lifespan.

A water-in-salt electrolyte (WISE) based on 1 m $\text{Zn}(\text{TFSI})_2$ mixed with 20 m LiTFSI was first proposed for ZIBs by Wang *et al.*⁴⁴ The highly-concentrated LiTFSI salt was added to the aqueous electrolyte to limit the presence of free water molecules, preventing hydrogen evolution and suppressing the hydrolysis reaction caused by the interaction between Zn^{2+} and H_2O molecules. As a consequence, the WISE hampered the growth of zinc oxide on the zinc electrodes, stabilizing the cell for more than 500 charge-discharge cycles.⁴⁴ Despite the high solubility of LiTFSI in water (~ 21 m at room temperature), fluorinated salts are deemed impractical for adoption in industrial applications, owing to their prohibitively high cost, particularly in the context of highly-concentrated water-ion-salt electrolytes. Therefore, Zhang *et al.*⁴⁵ proposed an inexpensive WISE solely based on ZnCl_2 (30 m), presenting a structure similar to an ionic liquid with no free water molecules. Similarly to the LiTFSI electrolyte, the 30 m ZnCl_2 electrolyte was able to suppress the formation of inert $\text{Zn}(\text{OH})_2$ and ZnO , by preventing water molecules from reacting with the metal anode, ensuring stable cycling for 600 h at 0.2 mA cm⁻² (Figure 1.7-a).⁴⁵ Additionally, the electrochemical stability window of the cell could be widened from 1.6 to 2.3 V using the ZnCl_2 water-in-salt electrolyte, improving the energy density of the device (Figure 1.7-b).

Another viable option to increase the specific energy of aqueous devices is to redesign the electrode architecture, so to minimize the local surface current density and enhance the number of electrochemically active sites.³¹ In particular, electrodes with three-dimensional architectures can improve the specific capacity and energy of EESDs, by minimizing the mass fraction of passive and

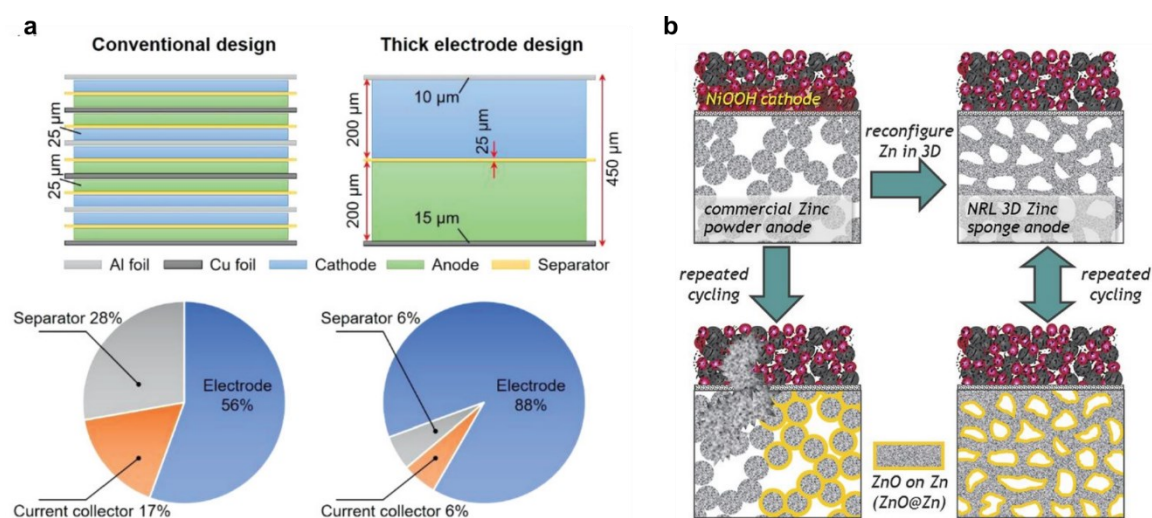


Figure 1.8: (a) Relative mass ratio of battery components considering a conventional design and a thick-electrode design (adapted with permission from ref.⁴⁶, Copyright 2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim); (b) schematic showing the structure of a 3D zinc anode with sponge-like structure and the effect of recharging the 3D ZIB (adapted with permission from ref.⁴⁹, Copyright 2017, American Association for the Advancement of Science.).

inactive components in the cell and reducing the material and manufacturing costs (Figure 1.8-a).^{25,46} This is particularly beneficial to wearable and portable electronics, which often possess restricted footprint areas. Nonetheless, electron and ion transport is a critical issue to address in thick electrodes, since the resistance to charge transfer increases proportionally with the thickness of the electrodes, restricting the accessible material and causing inhomogeneities in the electrochemical potential.⁴⁷ The architecture of the electrodes must thus be tailored to efficiently deliver charges and to ensure high material utilization even at high charge-discharge rates, so to retain high energy density and rate capability at increasing areal mass loading of active materials.⁴⁸ To this end, a three-dimensional zinc anode with a sponge-like porous and aperiodic structure was proposed by Parker *et alii*.⁴⁹ The three-dimensional zinc sponge was obtained preparing an emulsion of decane in water, to which zinc particles were added. After drying, the emulsion was annealed in argon to initiate the formation of bridges between the zinc particles, followed by further annealing in oxidising atmosphere to form a zinc oxide shell, which preserved the sponge shape while the zinc in the core melted, forming a monolithic structure (Figure 1.8-b). The three-dimensional anode ensured a material utilization $> 90\%$ during discharge and suppressed dendrite formation, owing to the presence of continuous metallic pathways for electron transport and to the large electrode-electrolyte interface area which promoted a homogeneous current distribution.⁵⁰ A freeze-drying templating process was instead employed by Wang *et al.*⁵¹ to fabricate a porous and interconnected structure made of VO_2 sheets coated with carbon. The porous structure offered a large accessible area when used as ZIB cathode, providing an 80% capacity retention after 1000 cycles (5 A g^{-1}) and a high energy density of 349 Wh kg^{-1} (at 0.1 A g^{-1}).⁵¹

Three-dimensional electrode designs have also been used for aqueous supercapacitors based on carbonaceous materials, in order to overcome the intrinsic energy density limit of water-based electrolytes and approach the electrochemical performance of commercial devices. Graphene electrodes with open porosity and high electrical conductivity were obtained by Shao *et al.*⁵² using a freeze-casting process. Reduced graphene oxide dispersions were initially immersed in liquid nitrogen, causing the formation of a continuous ice crystal framework inside the structure, which acted as a template. The ice template was then removed by sublimation at low pressure and the graphene structures were used to assemble symmetric supercapacitors, which achieved an energy density of 9.9 Wh kg⁻¹⁵² at a power density of 282 kW kg⁻¹.⁵² These electrochemical properties can rival the performance of commercial devices, containing flammable and toxic electrolytes. A similar 3D templated carbon structure was proposed by Wang *et al.*⁵³, who prepared a carbon aerogel made of graphitic walls ~ 20 nm in thickness by the carbonization of a glucose foam. The resulting supercapacitor presented a better capacitance (250 F g⁻¹) and capacitance retention compared to commercial activated carbon electrodes, owing to the high accessibility of the graphitic structure and high connectivity of the conductive walls in the structure.⁵³

These examples show the wide popularity of templating strategies to obtain 3D-structured electrodes for batteries and supercapacitors. However, templating strategies do not offer rational control over the design of the electrodes, since they are typically limited to porous aperiodic structures. The random tortuosity and unoptimized pore size of the template can hinder charge transport inside the electrodes.⁴⁷ In contrast to templating strategies, 3D printing techniques can offer deterministic control over the electrode architecture, expanding the possibility of structural optimization.⁵⁴ The use of 3D printing to fabricate three-dimensional electrodes and its advantages will be presented in Section 2 of this chapter.

1.3. EESD performance parameters and normalization

The performance of supercapacitors and batteries can be benchmarked through the evaluation of key electrochemical parameters, typically obtained with galvanostatic charge-discharge tests, as discussed in the next chapter. A common metric to characterize capacitive charge storage processes, *i.e.* processes in which the charge stored in an electrode q is directly proportional to its potential V , is capacitance ($C = q/V$). In contrast, batteries are typically described in terms of charge capacity, namely the maximum amount of charge that the cell provides during discharge.⁹ Capacitance and capacity alone do not provide a complete characterization of the EESD performance, since they do not account for the average potential at which the electrical charge is transferred, which is also an important parameter for application. For example, biomedical heart rate sensors usually require a voltage of 1.8-3.3 V to operate.⁵⁵ A better performance parameter to compare different EESDs, irrespective of their charge storage process, is the specific energy that the cell can deliver, accounting for the voltage at which a certain quantity of charge can be provided (as discussed in Chapter

2).⁹ The specific energy, together with the rate at which the stored energy can be provided (specific power), are important metric to determine the suitability of an EESD (or a family of EESDs, such as lithium-ion batteries) for a specific application. Biomedical sensors usually have a power consumption of ~ 1 -100 mW,⁵⁵ and would therefore require batteries able to provide such power for a sufficiently long period of time (hours, days or even years, depending on the sensor).

Other two important parameters for EESDs are rate capability, corresponding to the ability of a cell to retain its capacity (or capacitance) at high discharge currents; and cycling stability, indicating the capacity retention over repeated charge and discharge cycles. These properties account for the stability of the cell against degradation, providing a metric to determine the lifespan of EESDs and their response under intense utilization conditions. However, the testing methods reported in literature for these properties are not standardized, therefore a direct comparison of the rate capability and capacity retention measured at different discharge currents is not easy.

The capacity (or capacitance), energy and power density of a cell can be normalized either by the mass, the volume or the footprint area of the device. Throughout this work, areal properties are mainly considered, since they are the most significant metrics for integration into portable systems having limited available footprint area.^{56,57} Areal performance can also provide insight into surface charge storage processes, when the total electrochemically-active area of the active material in contact with the electrolyte is used for the normalization.⁵⁸

Gravimetric properties, normalized by the mass of the active material inside the electrode (*e.g.* milligrams of VS₂ in the cathode), are also presented in this work, since they provide useful information on the performance of the active material (rather than the overall electrode). The gravimetric capacity measured at slow discharge rates is used in basic research to investigate the charge storage reaction inside the active material, and it allows direct comparison with the charge storage performance of other active materials.⁵⁷ In addition to this, gravimetric properties are independent of the electrode size and shape, under the assumption that the transport of charges to the active material particles is not hindered. By comparing the gravimetric performance of electrodes with different geometries (but identical composition), it is possible to highlight ohmic losses or incomplete electrolyte penetration and wetting of the active material. Gravimetric performance can also offer a valid metric for applications requiring lightweight EESD, although the mass of the overall device (electrodes, electrolyte, current collector and separator) should be considered for the normalization.

The performance of EESD can also be normalized by the volume of the device (or electrode) tested. Whole-cell gravimetric and volumetric performance are the key parameters for most EESD applications - though areal performance is important when the available footprint area is limited, as in miniaturized sensors. However, it is important to note that, in the literature, volumetric properties are often measured for thin film electrodes with low mass loading of active material, thus overestimating the performance for real applications.⁸

2. Manufacturing of EESDs *via* 3D Printing

3D printing designates a family of manufacturing techniques characterized by the ability to create complex geometries with customized shape, by the addition and consolidation of successive layers of material.^{47,54} The design freedom offered by 3D printing meets the need for new and adaptable EESDs for wearable systems, which often present unconventional shapes and size limitations.⁴⁷ In terms of electrochemical performance, a tailored control over the electrode geometry ensures higher surface-to-volume ratios and enhanced areal loading of active materials, boosting the areal and volumetric energy density of the printed devices.⁵⁷ Additionally, three-dimensional electrodes with optimized geometry present shorter charge-transport distances, leading to better rate capability and higher specific power even at high areal loading of active material ($> 10 \text{ mg cm}^{-2}$).⁵⁷ Several 3D printing techniques offer the possibility to integrate different materials in a single manufacturing process, tuning the composition and the functional properties of the different sections of the structure, *e.g.* rigidity, conductivity and porosity.^{59,60}

The 3D printing techniques that have been more extensively investigated for the fabrication of EESDs are based on photopolymerization, material jetting and material extrusion processes (Figure 1.9). Stereolithography and other vat polymerization techniques are typically based on the selective curing of a layer of photopolymer by a laser beam. After curing, the build platform is lowered and

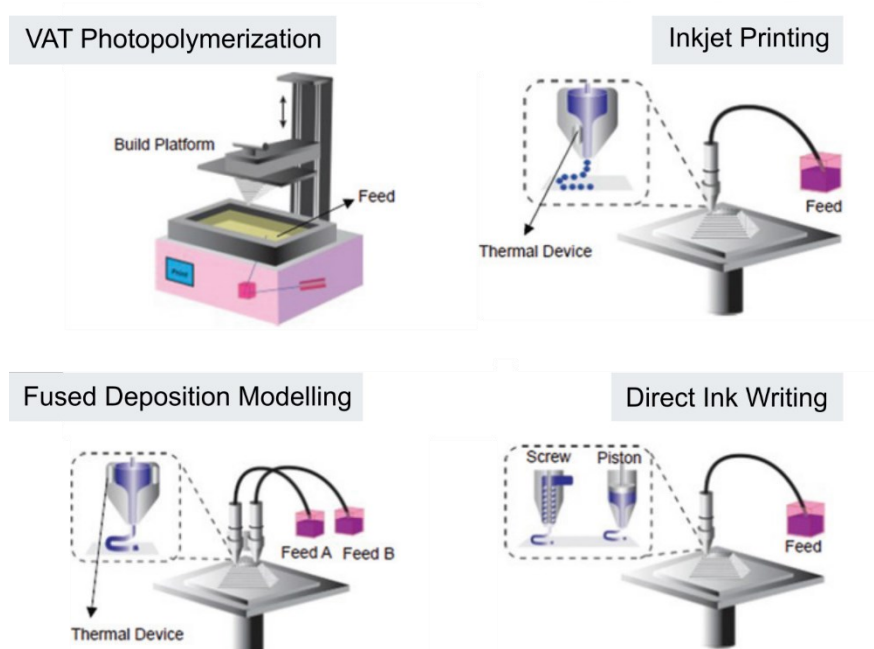


Figure 1.9: Schematic showing the main 3D printing techniques that have been employed for the manufacturing of EESDs (adapted with permission from ref.³⁸⁰)

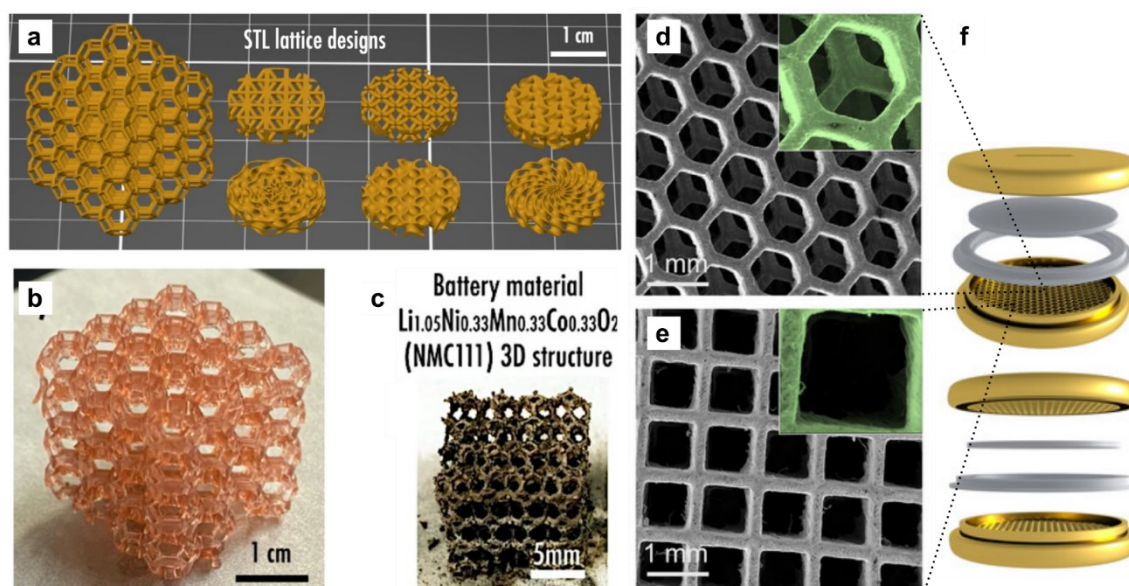


Figure 1.10: (a, b) Lattice design and 3D printed structure obtained from the photocurable precursor for LIB electrodes proposed by Martinez *et al.*⁶³; (c) picture of the electrode after annealing and conversion to $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ (panels a-c adapted with permission from ref. ⁶³); (d-f) 3D model and SEM images of a gold-sputtered 3D printed structure used as a case and current collector for LIBs by Gulzar *et al.*⁶⁴, with diamond cubic (d) and body-centred cubic (e) structure (panels d-f adapted with permission from ref. ⁶⁴).

new photopolymer is added and cured to obtain the successive layer of the structure.⁵⁷ Photopolymerization techniques offer high printing resolution, with the ability to create features as small as 200 nm and structures with arbitrary complexity, since each layer is completely consolidated before printing the subsequent one.⁶¹ Nonetheless, the printing process is constrained to the use of a photocurable resin, which is typically expensive and not electrochemically active. Dispersions of carbon nanotubes ~ 0.2 wt% in a photoresist were demonstrated by Xiong *et al.*⁶² for capacitor applications. Higher concentrations of carbon nanotubes caused significant absorption and scattering of the laser beam, which hindered the polymerization process. In order to avoid scattering from the solid particles in the photoresist, Martinez *et al.*⁶³ developed a photocurable precursor for LIB electrodes based on a photopolymerizable polymer loaded with soluble metal salts (lithium, nickel, cobalt and manganese nitrates), Figure 1.10-a,b. However, the structure required a thermal process to carbonize the resin, which significantly compromised the mechanical properties of the electrodes (Figure 1.10-c).⁶³ Photopolymerization-based 3D printing is more appropriate for the fabrication of customized battery cases, made electrically conductive by gold sputtering to act as a current collectors, as demonstrated by Gulzar *et al.*, Figure 1.10-d,e,f.⁶⁴

Inkjet Printing (IJP) is the main representative of material jetting techniques, and it has received increasing attention for the fabrication of printed electronics. IJP is based on the direct deposition of ink droplets onto a substrate, typically paper or plastic, to form continuous lines with a spatial resolution < 25 μm .^{54,57} The droplets are ejected from a moving print head through a piezoelectric

or thermal mechanism. IJP is typically included in the family of 3D printing processes since it offers control over the thickness of the printed structures; however, electrodes thicker than a few hundreds of microns are difficult to obtain with this process.⁵⁴ The ink formulations for IJP often use water as the dispersing medium for the particles of active material. However, in order to avoid satellite droplets and defects during printing, the inks should possess specific rheological properties that are expressed in term of the Ohnesorge number (Oh), which represents the ratio between the viscous forces and the inertial and surface tension forces acting on the ink. To achieve an adequate value for the Ohnesorge number (*i.e.* between ~ 0.1 and ~ 1) and prevent the sedimentation and aggregation of the particles in the ink, dispersants and other additives must be included in the ink formulation.⁶⁵ Contrary to photopolymerization processes, IJP can be easily adapted to dispersions of different materials, that can be simultaneously deposited *via* a print head fed by multiple ink cartridges. The material versatility of IJP was demonstrated by Choi *et al.*⁶⁶, who fabricated a fully-inkjet-printed activated carbon supercapacitor on paper. A cellulose nanofibers suspension was initially printed onto the paper substrates as a primer, to overcome uncontrolled spreading of the ink droplets and ring-like deposition. The electrodes were fabricated using a dispersion of activated carbon and single wall carbon nanotubes, to which sodium dodecylbenzene sulfonate was added as a dispersing agent. The current collector was fabricated on the carbon electrodes by printing a suspension of silver nanowires, which was UV-sintered after deposition to enhance the electrical conductivity.

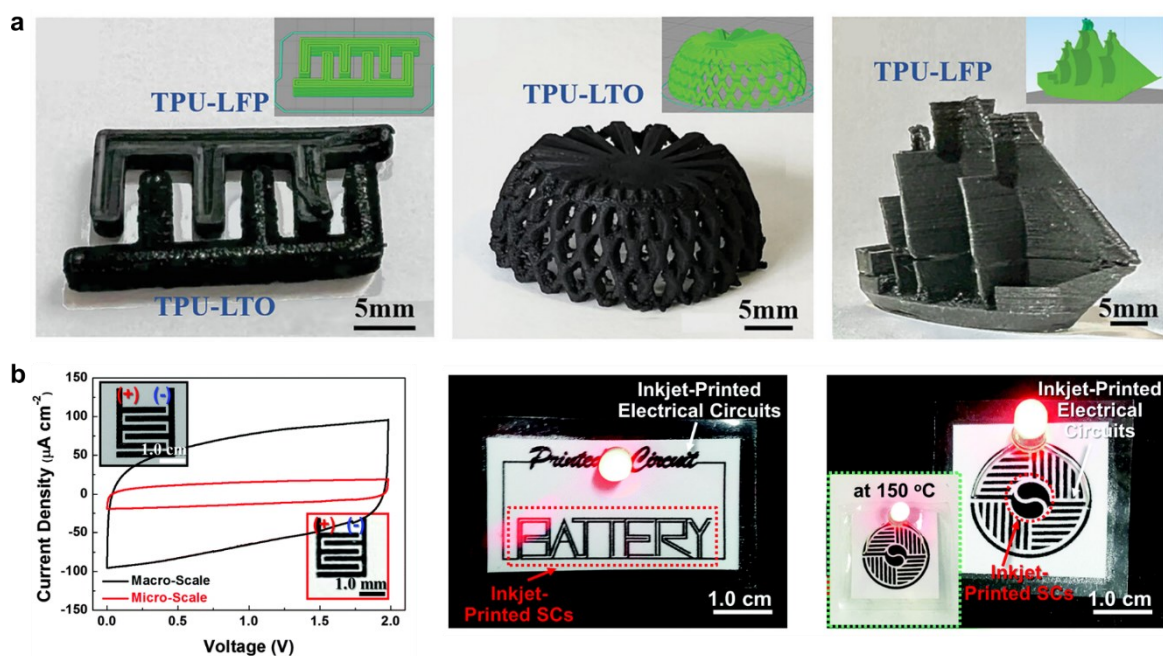


Figure 1.11: (a) Printed electrodes fabricated by Hu *et al.*⁶⁷ using FDM with an interdigitated structure (left), a mesh suspensions bridge structure (centre) and a sailboat structure (right), adapted with permission from ref. ⁶⁷, Copyright 2016, The Royal Society of Chemistry; (b) flexible supercapacitors proposed by Choi *et al.*⁶⁶ using IJP with interdigitated structure and corresponding cyclic voltammetry (left) and customized shapes (centre and right) powering an LED (adapted with permission from ref. ⁶⁶, Copyright 2023, Wiley-VCH GmbH).

Finally, an ionic-liquid electrolyte was printed over the electrodes and UV-crosslinked to form a solid-state electrolyte, obtaining a fully-printed supercapacitor providing a specific energy $\sim 12 \text{ Wh kg}^{-1}$ and a specific power $\sim 23 \text{ W kg}^{-1}$ (Figure 1.11-b).⁶⁶

Material extrusion printing processes, such as Fused Deposition Modelling (FDM) and Direct Ink Writing (DIW), are based on the continuous extrusion of a filament of material from a print head, equipped with an extrusion nozzle usually $\sim 50\text{-}500 \text{ }\mu\text{m}$ in diameter.⁵⁷ The filament is deposited onto a substrate to build a three-dimensional structure layer-by-layer. In FDM the extrudable filament is generated feeding a thermoplastic polymer to the print head, where it is heated to a semi-liquid state. When the filament is deposited onto the build platform at a lower temperature, it quickly solidifies forming a solid structure.⁵⁷ FDM can be used to print functional electrodes by preparing composite filaments containing electroactive particles in a thermoplastic matrix. However, the thermoplastic polymers for FDM (*e.g.* polylactic acid and polycarbonate) are not conductive, which limits the applicability of this technique to battery manufacturing. Hu *et al.*⁶⁷ investigated the use of thermoplastic polyurethane as a polymer matrix to print flexible LIB electrodes *via* FDM. The composite filament was prepared by dissolving thermoplastic polyurethane in dimethylformamide and adding the active materials to the solution (lithium iron phosphate, lithium iron oxide and graphite). The slurry was then dried and converted to filaments for FDM using an extruder, and FDM was then used to fabricate interdigitated electrodes, made of stacked filaments $\sim 150 \text{ }\mu\text{m}$ in diameter (Figure 1.11-a).⁶⁷ The printed batteries exhibited a better cycling performance than 3D printed electrodes based on polylactic acid (99.12% vs. 69.04% capacity retention after 200 cycles), owing to a smaller charge transfer resistance.⁶⁷ The lower flexibility of polylactic acid causes cracks during cycling, with the electrical disconnection of the active particles. FDM has also been studied to fabricate aqueous zinc-ion batteries based on organic PANI cathodes by Gao *et alii*.⁶⁸ A conductive scaffold was printed using a polylactic acid filament loaded with conductive carbon particles. The superficial layer of polylactic acid was then removed by saponification in NaOH solution, and subsequently a composite PANI-polyacrylic acid film was electrodeposited on the printed structure, where the polyacrylic acid layer acted as a proton reservoir for the charge storage processes in PANI. The 3D cathode was able to deliver a specific energy of 212.5 Wh kg^{-1} at a power density of 486.6 W kg^{-1} when tested in a ZnSO_4 electrolyte with a zinc anode.⁶⁸

Figure 1.12 presents a comparison of the main features of FDM, IJP and photopolymerization printing techniques for the fabrication of energy storage devices. Stereolithography and similar photopolymerization processes are characterized by high resolution and high-quality surface finish for the electrodes, but their application to battery manufacturing is hindered by high material costs and long manufacturing times (a few millimetres per hour in the vertical direction), which result in prohibitively high production costs.⁵⁴ In comparison, IJP ensures lower manufacturing costs and has a good multi-material capability, although inkjet-printed electrodes are typically in the form of thin film structures (a few hundred microns in thickness).⁵⁷ Three-dimensional architectures with

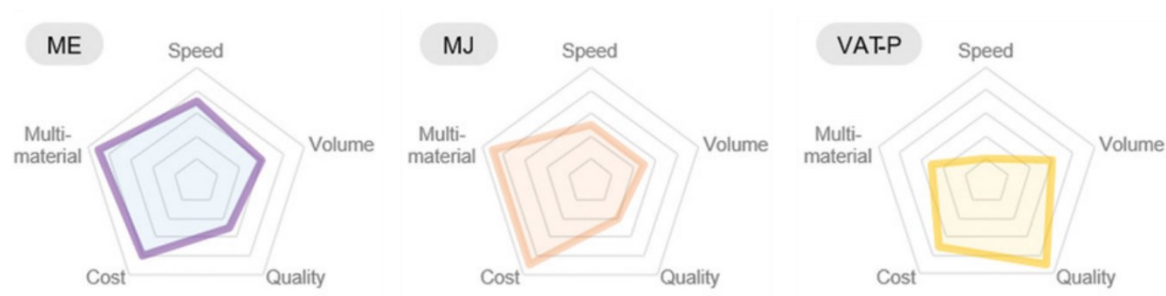


Figure 1.12: Radar charts comparing the main features of 3D printing techniques on a scale from 0 (lowest suitability) to 9 (highest suitability); the techniques considered are material extrusion (ME, such as Direct Ink Writing and Fused Deposition Modelling), material jetting (MJ, such as Inkjet Printing) and VAT photopolymerization (VAT-P). Adapted with permission from ref.³⁸⁰, Copyright 2020 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim).

voids, overhangs and self-supporting pillars cannot be produced using this printing technique.⁵⁴ Extrusion-based processes like FDM have the capability to produce complex architectures in relatively short times, and present favourably low costs compared to photopolymerization. Nonetheless, FDM requires large amount of thermoplastic polymer inside the extrusion filaments, which compromise the electrochemical performance of the printed electrodes. Additionally, composites filaments loaded with electroactive particles are normally prepared by dissolution of the thermoplastic polymer in chlorinated solvents, such as dichloromethane, or toxic dimethylformamide, to ensure the homogenous dispersion of the particles in the polymeric matrix.

Direct Ink Writing (DIW), also known as Robocasting, is an extrusion-based printing process that, unlike FDM, does not require a thermoplastic matrix for extrusion and can rely on aqueous processing for ink preparation. For these reasons it has been widely studied for the additive manufacturing of aqueous energy storage devices, as discussed in the next section.

2.1. Direct Ink Writing

In Direct Ink Writing, an extrusion print head equipped with one or multiple nozzles moves along a predefined path, enabling the continuous deposition of paste-like inks. The printing process is carried out at room temperature, since the solidification of the ink filaments after extrusion relies solely on the rheological features of the inks.⁵⁴ The resolution of the printing process is therefore controlled by the diameter of the extrusion nozzle and by the rheological properties of the ink.⁵⁷ Structures with features as small as $\sim 1 \mu\text{m}$ have been demonstrated printing polymeric dispersions through capillary micronozzles.⁶⁹ However, when dispersions of electroactive particles are used as inks, the size of the smallest printable features is limited by the dimension of the dispersed particles, ranging between $\sim 100 \mu\text{m}$ and $\sim 500 \mu\text{m}$ for particles $\sim 10 \mu\text{m}$ in diameter (as discussed in Chapter 2). DIW is among the most flexible printing processes for multi-material deposition, presenting the ability to fabricate three-dimensional structures made of metals, ceramics, polymers and a wide range of electroactive materials for batteries and supercapacitors.⁷⁰ These materials can either be

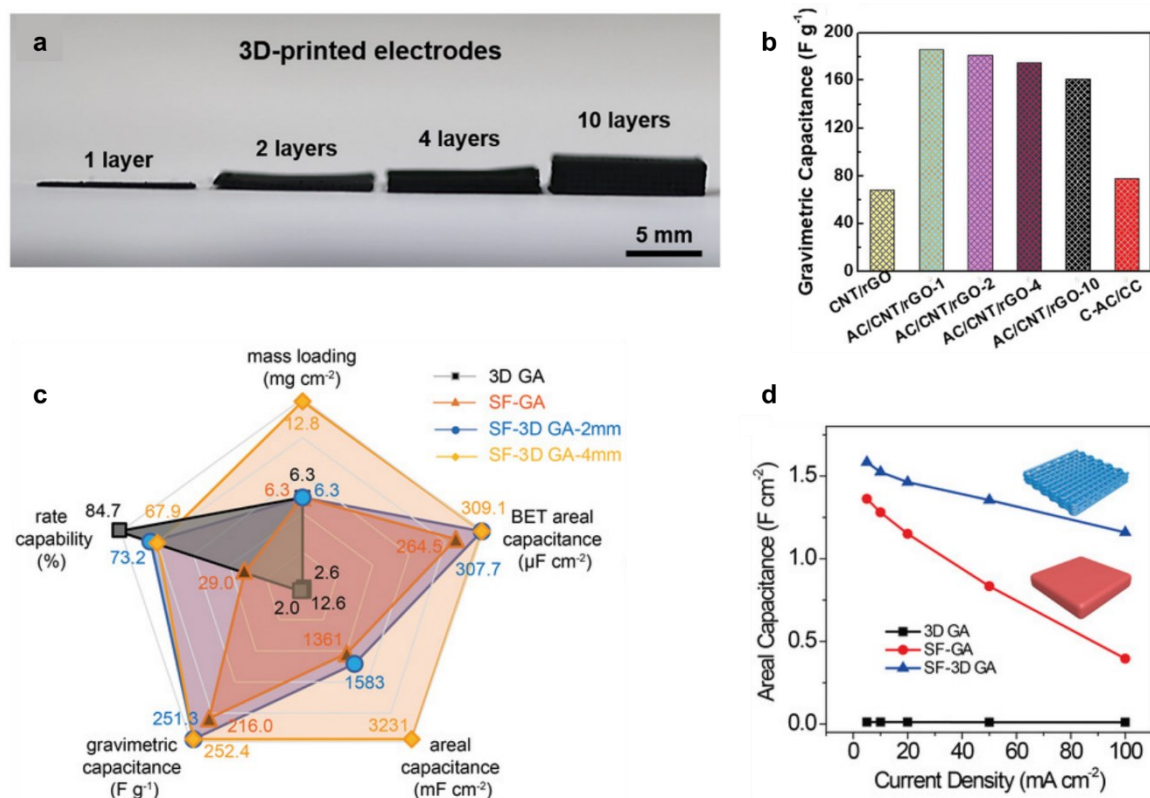


Figure 1.13: (a) Photograph showing the 3D printed activated carbon electrodes proposed by Gao *et al.*⁷¹ with different thickness; (b) comparison of the gravimetric capacitance of the structures in panel (a); panels (a) and (b) were adapted with permission from ref.⁷¹, Copyright 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim; (c, d) radar chart presenting a comparison of the 3D printed graphene aerogel (SF- 3D GA) proposed by Yao *et al.*⁷² (c) and rate capability of the printed structures (d); panels (c) and (d) were adapted with permission from ref.⁷², Copyright 2020 The Authors, Published by WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim)

included in the ink formulation or be deposited on a 3D printed scaffold after printing and consolidation, by electrodeposition or hydrothermal methods. As an example, Gao *et al.*⁷¹ formulated carbon-based inks containing activated carbon as the active material for 3D printed symmetric supercapacitors. Electrodes with high mass loading ($\sim 59.6 \text{ mg cm}^{-2}$, corresponding to 10 printed layers) were obtained through the extrusion of highly concentrated inks, providing an areal capacitance of 9.16 F cm^{-2} (Figure 1.13-a).⁷¹ In order to preserve the rate capability and power density of electrodes several millimetre thick, carbon nanotubes and graphene oxide (thermally reduced after printing) were included in the ink formulation, in order to provide a highly conductive network for the transport of electrons to the activated carbon particles. Carbon nanotubes and reduced graphene oxide also complemented the charge storage capability of activated carbon through electric double layer or surface pseudocapacitive processes. Owing to the high conductivity of the printed structures, the gravimetric capacity of the electrodes only decreased from 186 F g^{-1} to 161 F g^{-1} when the thickness was increased from 1 to 10 layers, coherently with an increase in tortuosity from 1.58 to 1.83 (Figure 1.13-b). The printed electrodes were used to assemble symmetric supercapacitors, achieving an areal energy density of 0.63 mWh cm^{-2} and a gravimetric energy density $\sim 6 \text{ Wh kg}^{-1}$.⁷¹

In a similar study, Yao *et al.*⁷² demonstrated that 3D printed graphene electrodes can retain a capacitance of 1.16 F cm^{-2} at a very high discharge current of 100 mA cm^{-2} (rate capability 73.2%), in contrast to tape casted electrodes with a rate capability $\sim 19\%$ (Figure 1.13-c,d), owing to the accessible channels and fast charge transport in the printed electrodes.⁷²

The advantages of 3D printed LIB electrodes over conventional blade-casted structures were investigated by Wang *et alii.*⁷³ Lithium iron phosphate LiFePO_4 electrodes, consisting of printed filaments $\sim 100\text{-}150 \text{ }\mu\text{m}$ in diameter, were fabricated using DIW. The printed electrodes presented higher surface area, improved mechanical strength and optimized ion diffusion paths in comparison to conventional structures, which resulted in a better cycling stability and higher capacity. In particular, tape-casted electrodes at a mass loading $\sim 10 \text{ mg cm}^{-2}$ achieved an initial discharge capacity of 124 mAh g^{-1} , which faded to 51.8% after 115 cycles.⁷³ In contrast, the 3D printed electrodes presented an initial capacity of 150 mAh g^{-1} (closer to the theoretical capacity of $\text{LiFePO}_4 \sim 170 \text{ mAh g}^{-1}$), without any noticeable fading after 150 cycles at 1C. Increasing the thickness of the printed electrodes from 2 to 8 layers resulted in a high areal capacity of 7.5 mAh cm^{-2} , corresponding to an energy density of 19.3 mWh cm^{-2} at a power density of 2.99 mW cm^{-2} (Figure 1.14-a,b).⁷³ The structure of the printed electrodes, presenting large channels between the printed filaments, allowed for efficient electrolyte penetration and short local Li^+ ion diffusion paths ($< 150 \text{ }\mu\text{m}$), enhancing the areal energy density without sacrificing the power density.

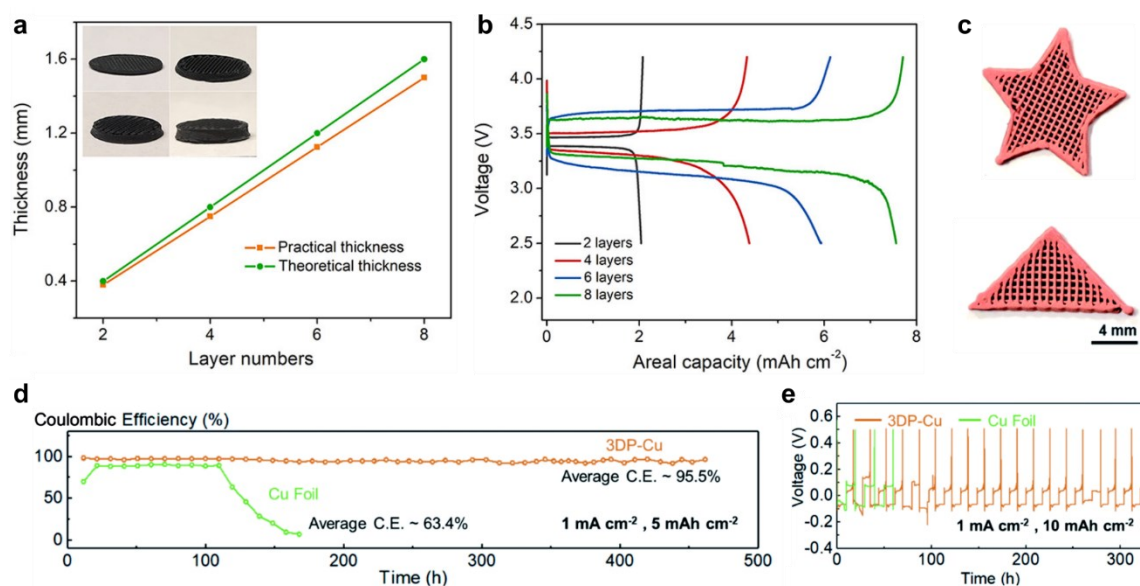


Figure 1.14: (a) Digital photograph and thickness as a function of the number of printed layers for the 3D printed LiFePO_4 electrodes proposed by Wang *et al.*⁷³; (b) discharge curves corresponding to the electrodes in panel (a) at different number of layers; panels (a) and (b) were adapted with permission from ref. ⁷³, Copyright 2018, American Chemical Society; (c) 3D printed copper electrodes for the plating-stripping of lithium proposed by Lim *et al.*⁷⁵; (d, e) coulombic efficiency for the copper structures proposed by Lim *et al.*⁷⁵ and bare copper foil for plating and stripping of lithium (d) and corresponding plating-stripping profiles (e); panels (c-e) were adapted with permission from ref. ⁷⁵, Copyright 2020, The Royal Society of Chemistry.

DIW has found extensive application in the fabrication of three-dimensional current collectors for the electrodeposition of pseudocapacitive and battery-like materials. This approach significantly simplifies the ink preparation step, since the only functional requirements for the printed scaffolds are high electrical conductivity and electrochemical stability in the electrodeposition solution and in the cell electrolyte. Commercial EESDs typically use metallic current collectors, *e.g.* made of copper or aluminium. Nonetheless, the fabrication of conductive metal scaffolds with DIW is challenging, since the deposition of metal particle dispersions does not ensure the same electrical conductivity as the corresponding metal foils, owing to the high contact resistance in the structure. Rocha *et al.*⁷⁴ proposed a dispersion of copper particles in Pluronic F127 (a triblock copolymer commonly used in DIW) as an ink to fabricate copper current collectors for supercapacitors. A similar approach was followed by Lim *et al.*⁷⁵, who printed copper frameworks for the electrodeposition of lithium (Figure 1.14-c). The frameworks were initially annealed in air to remove the polymeric binder, and then reduced at 600°C in Ar/H₂ for 10 h to transform the copper oxide into metallic copper and promote the thermal sintering of the particles. The debinding step was necessary to completely remove the polymer, preventing the formation of carbon residues that would hinder sintering and electron transport in the metallic structure.⁷⁵ The printed copper structures with their high surface area were able to minimize the local current density during operation, resulting in a stable plating and stripping of lithium ions even at fast rates. In particular, the cell presented a low overpotential of ~ 21 mV and could be cycled for ~ 475 h at 1 mA cm^{-2} , maintaining a high coulombic efficiency $\sim 95.5\%$ (Figure 1.14-d,e).⁷⁵ During plating, lithium filled the pores between the copper particles on the surface of the 3D structure, producing a uniform layer, whereas it formed discontinuous deposits on copper foil, causing the growth of dendrites. The conductivity of printed metal current collectors can be enhanced with laser or flash-light sintering, as demonstrated using inks based on nickel particles.⁷⁶ These sintering processes can decompose the binder and promote the formation of sintering necks between the particles, enhancing the electrical conductivity of the structure without the need of a thermal treatment. For this reason, they have been widely used in the post-processing of electronic systems printed on flexible substrates (*e.g.* paper or plastic), which typically present low decomposition temperatures and cannot undergo thermal annealing.^{77,78}

Considering the challenges of printing 3D structures made of metallic particles, carbon-based inks are more often used for the fabrication of conductive scaffolds and current collectors, presenting high conductivity, low cost and stability in a wide variety of chemical environments. Yang *et al.*⁷⁹ created conductive carbon microlattices made of carbon nanotubes and reduced graphene oxide with DIW, which were used for the electrodeposition of MnO₂. The electrodeposition on the printed carbon structure was more uniform and required a smaller overpotential in comparison to carbon cloth and titanium mesh. Additionally, the printed carbon structure could accommodate a high mass loading of MnO₂ (28.4 mg cm^{-2}) without sacrificing gravimetric capacity of 282.8 mAh g^{-1} and

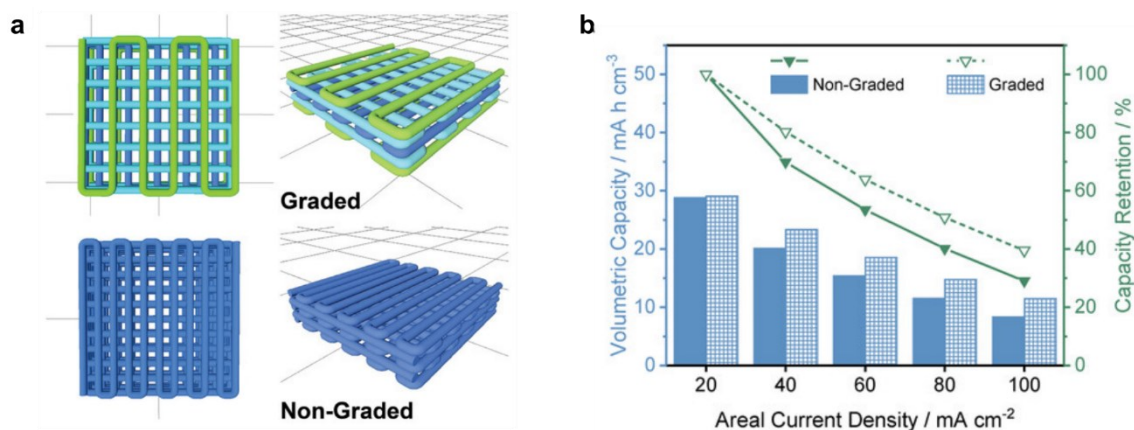


Figure 1.15: (a) Schematic illustration of the graded structure proposed by Lin *et al.*⁸¹ for the uniform electrodeposition of MnO₂ on graphene scaffolds; (b) volumetric capacity and capacity retention for the graded and non-graded MnO₂ electrodes (adapted with permission from ref.⁸¹, Copyright 2023, Wiley-VCH GmbH).

gravimetric energy density (226.2 Wh kg⁻¹) when the structures were tested as ZIB cathodes.⁷⁹ Different electroactive materials (such as nickel cobalt oxide and zinc) can also be electrodeposited on 3D printed carbon scaffolds, and coupled to MnO₂ electrodes to assemble asymmetric supercapacitors or batteries.⁸⁰

In virtue of the design freedom offered by DIW, the geometry of the current collector can be optimized for electrodeposition processes, in order to further increase the loading of active material. Lin *et al.*⁸¹ fabricated a reduced graphene oxide scaffold for MnO₂ electrodeposition, whose structural design was optimized to obtain a uniform layer of active material even at a high mass loading of 70 mg cm⁻². The spacing between parallel filaments was gradually decreased moving from the lower to the upper layer of the printed woodpile electrodes (from 1.2 mm to 0.4 mm in the first 10 layers), and then gradually increased again after the tenth layer (Figure 1.15-a).⁸¹ The large channels at the bottom and at the top of the electrodes would maximized the flux of ions, whereas the densely packed filaments in the central region would provide a high electrochemically active surface area, maximizing the energy density of the electrode. After the electrodeposition process, the graded scaffolds appeared uniformly coated by manganese oxide, whereas in the non-graded structures the MnO₂ was mainly deposited on the exterior regions, owing to the hindrance to Mn²⁺ diffusion towards the inner region.⁸¹ Despite presenting a lower surface area, the lithium-ion hybrid capacitors with graded electrodes achieved the same volumetric capacity as the non-graded electrodes (~ 29.1 mAh cm⁻³ at 20 mA cm⁻²). Additionally, they presented better rate capability at high currents (39.5% vs. 29.0%) and lower diffusion resistance (11.19 Ω vs. 38.25 Ω), Figure 1.15-b.⁸¹

3D printed carbon hosts have also been used for the electrodeposition of zinc to fabricate ZIB anodes with arbitrary geometry. Using a three-dimensional anode is a promising strategy to prevent the growth of dendrites and promote the uniform deposition of zinc, since the 3D structure lowers the local current density and homogenizes the interfacial charge distribution.^{82,83} Zeng *et al.*⁸³

fabricated a nitrogen-doped carbon scaffold with DIW, where the N-doping increased the affinity for zinc during electrodeposition. This led to a reduction in the nucleation overpotential from 23.2 mV to 12.0 mV, owing to the strong interaction of zinc with the graphitic, pyridinic and pyrrolic nitrogen sites, and the formation of a uniform layer of zinc on the structure. The high surface area of the printed scaffold also increased the cycle life of the anode to over 380 h (at 1 mA cm^{-2}), hindering the growth of dendrites in comparison to zinc foil (160 h cycle life).⁸³

In addition to providing deterministic control over the geometry of the electrodes, DIW also offers the possibility to modulate the spatial distribution of the ink components inside the printed structures, in order to obtain electrodes with gradient composition. He *et al.*⁸² proposed a 3D printed porous carbon scaffold made of carbon nanotubes and cellulose nanofibrils presenting a gradient distribution of silver nanoparticles. The lower layers of the structure had a higher concentration of zincophilic silver nanoparticles, promoting the electroplating of zinc in this area. In the absence of a gradient concentration of silver nanoparticles, the zinc ions were preferentially deposited onto the upper region of the electrode, increasing the risk of dendrite growth and short circuits. In comparison to conventional zinc hosts, such as copper and nickel foam, the gradient scaffolds exhibited a much lower deposition overpotential ($< 43.1 \text{ mV}$ after 450 h of cycling) and they were stable for 630 h of continuous plating-stripping at 1 mA cm^{-2} .⁸² A similar approach was followed by Wang *et al.*,⁸⁴ who fabricated printed electrodes with a gradient distribution of alumina nanoparticles as a scaffold for lithium plating. The gradient scaffold could withstand over 1500 h of lithium plating and stripping at a low overpotential of $\sim 40 \text{ mV}$.

Although the recent literature has mainly investigated the fabrication of electrodes for batteries and supercapacitors, some examples of 3D printed electrolytes and passive components, *e.g.* separators, substrates and external encapsulation, have also been reported. McOwen *et al.*⁸⁵ developed a printable solid-state-electrolyte for LIBs, starting from a dispersion of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ in ethanol with a texanol binder. The ink was used to fabricate 3D printed structures with higher aspect ratio than conventional pellet electrolytes, minimizing the surface impedance caused by poor contact between the electrode and electrolyte. This resulted in a low area specific resistance of $22 \Omega \text{ cm}^2$, with an overpotential of only 2.3 mV when the cell was cycled at 0.1 mA cm^{-2} .⁸⁵ The fabrication of the electrodes, electrolyte and passive components in the same printing process reduces the costs and simplifies manufacturing, eliminating the need for multiple assembly steps. Additionally, all-printed EESDs can be directly integrated onto microscale electronics.⁵⁷ Sun *et al.*⁸⁶ pioneered the fabrication of positive and negative LIB electrodes in the same manufacturing process using DIW. A negative $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode and a positive LiFePO_4 electrode were printed on a sputtered gold current collector, to obtain structures with high aspect ratio (~ 11) and interdigitated geometry (Figure 1.16-a). The absence of conductive additives in the ink formulation limited the capacity that could be obtained from the electrodes, therefore an increase the thickness of the LiFePO_4 electrode

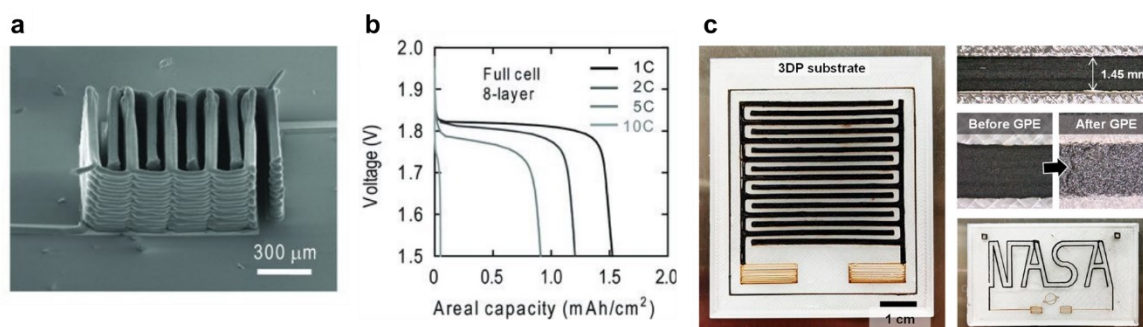


Figure 1.16: (a, b) SEM image of the 16-layer LIB 3D printed by Sun *et al.*⁸⁶ (a) and discharge curves for an 8-layer device (b), adapted with permission from ref.⁸⁶, Copyright 2013, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim; (c) all-printed supercapacitor fabricated by Seol *et al.*⁸⁸ using DIW (adapted with permission from ref.⁸⁸, Copyright 2020, American Chemical Society).

from 8 to 16 layers did not result in any improvement in its areal capacity ($\sim 8.33 \text{ mA cm}^{-2}$). The final battery was nonetheless still able to deliver an areal capacity of 1.5 mA cm^{-2} at a discharge rate of 1C, although the capacity rapidly faded at increasing discharge currents ($\sim 0.9 \text{ mA cm}^{-2}$ at 5C), Figure 1.16-b.⁸⁶ In a follow-up work, the same research group proposed an all-printed battery integrating printed electrodes, a printed separator and printed epoxy resin case.⁸⁷ The fabrication of all battery components with DIW eliminated the need for drying, electrolyte-infilling, calendaring and heat-sealing of the outer case, which are employed in the fabrication of conventional LIBs. Conductive carbon black was included in the electrode inks to overcome the low electrical conductivity of the active materials ($\text{Li}_4\text{Ti}_5\text{O}_{12}$ and LiFePO_4). As a result, the areal capacity increased from $\sim 1 \text{ mAh cm}^{-2}$ to $\sim 14.5 \text{ mAh cm}^{-2}$ increasing the electrode thickness from 0.05 to 1 mm.⁸⁷ To assemble an all-printed battery, a UV-curable separator based on alumina and LiTFSI was printed between the two electrodes, and the device was encapsulated in a printed case made of epoxy resin and silica particles. The all-printed battery delivered an areal capacity of 4.45 mAh cm^{-2} at a discharge current of 0.14 mA cm^{-2} .⁸⁷ An all-printed supercapacitor based on activated carbon electrodes was also proposed by Seol *et alii*.⁸⁸ In this study, all the components of interdigitated supercapacitors were printed using DIW, from the silver current collectors to the activated carbon electrodes and lithium perchlorate electrolyte (Figure 1.16-c). The resulting supercapacitor achieved a relatively low capacitance of $\sim 0.1 \text{ mF cm}^{-2}$ at 1 A g^{-1} , corresponding to a power and energy density of 161 W kg^{-1} and 9.95 Wh kg^{-1} .⁸⁸ These values steeply decreased at higher current densities as a result of the large amount of PVDF binder needed to print the electrodes, highlighting the importance of the ink formulation step for DIW.

As demonstrated by the studies reviewed in this section, DIW is unique in its ability to print multiple functional materials for integrated EESDs with customized shape. However, the most challenging step of the DIW process lies in the development of printable inks, which are able to form structures with the desired geometry and do not require prohibitively high pressures for extrusion.

The next sections (Section 2.2 and 2.3) will introduce the concept of printability for DIW and describe the properties that inks should present to be printable. Section 3 of this chapter will then provide insight into the experimental strategies and formulation methods that have been proposed in the recent literature to achieve printable inks for batteries and supercapacitors.

2.2. Printability

The printability of inks plays a crucial role in DIW to achieve the desired geometry, resolution and electrochemical and functional properties. An ink for DIW is considered printable if it can be continuously extruded through the print nozzle of choice to build a structure that faithfully replicates the original digital model.⁵⁴ Additionally, the printed structure should retain its morphology throughout the deposition, drying, and post-processing stages. The printability of an ink largely depends on the degree of geometric accuracy desired for the features of the printed structure, as defined by its final application. Notably, there has been a growing interest in small-size and miniaturized EESDs with features in the micron range, which require inks that can be stably extruded through micronozzles at a moderate extrusion pressure.

In DIW and similar extrusion-based techniques, the printing process can be divided into three distinct stages, namely (1) the flow of the ink inside the print cartridge and the deposition nozzle; (2) the ejection of the ink out of the deposition nozzle; and (3) the deposition of the ink filament onto the substrate or the underlying layer to obtain a three dimensional structure (Figure 1.17-a).⁵⁴ During the first stage of the printing process, the ink must not form large and hard agglomerates that can block the deposition nozzle, hindering a continuous and smooth flow.^{54,89} It is also crucial that the ink is extrudable at a moderate pressure, particularly when employing capillary nozzles for the fabrication of EESDs with miniaturized features. A decrease in the ink viscosity at increasing shear rates (shear thinning behaviour) can promote the flow throughout micronozzles and reduce the pressure required for extrusion.^{54,90}

The fabrication of a solid, self-standing structure in extrusion-based printing relies on the solidification of the ink after extrusion from the print head. In DIW this is achieved by selecting ink formulations that can turn from shear-thinning liquids during extrusion into solid-like materials at rest.^{54,89,91} From a rheological perspective, inks must be yield-stress fluids, which behave as elastic or viscoelastic solids when they are subjected to a small mechanical stress, resisting deformation and retaining their shape. If the stress applied exceeds a threshold value, known as the yield stress, yield-stress fluids transition to a flowing state with liquid-like properties.⁵⁴ Ideally, the ink should instantly revert to its solid-like properties after extrusion, so to ensure the mechanical stability of the printed filament. Nonetheless, the rheological properties of many yield-stress fluids do not only depend on the instantaneous shear rate and shear forces to which they are subjected, but also on the shear history. This category of yield-stress fluids, known as thixotropic fluids, is generally not suitable for DIW, since the recovery time required to restore the rest properties of the ink might be

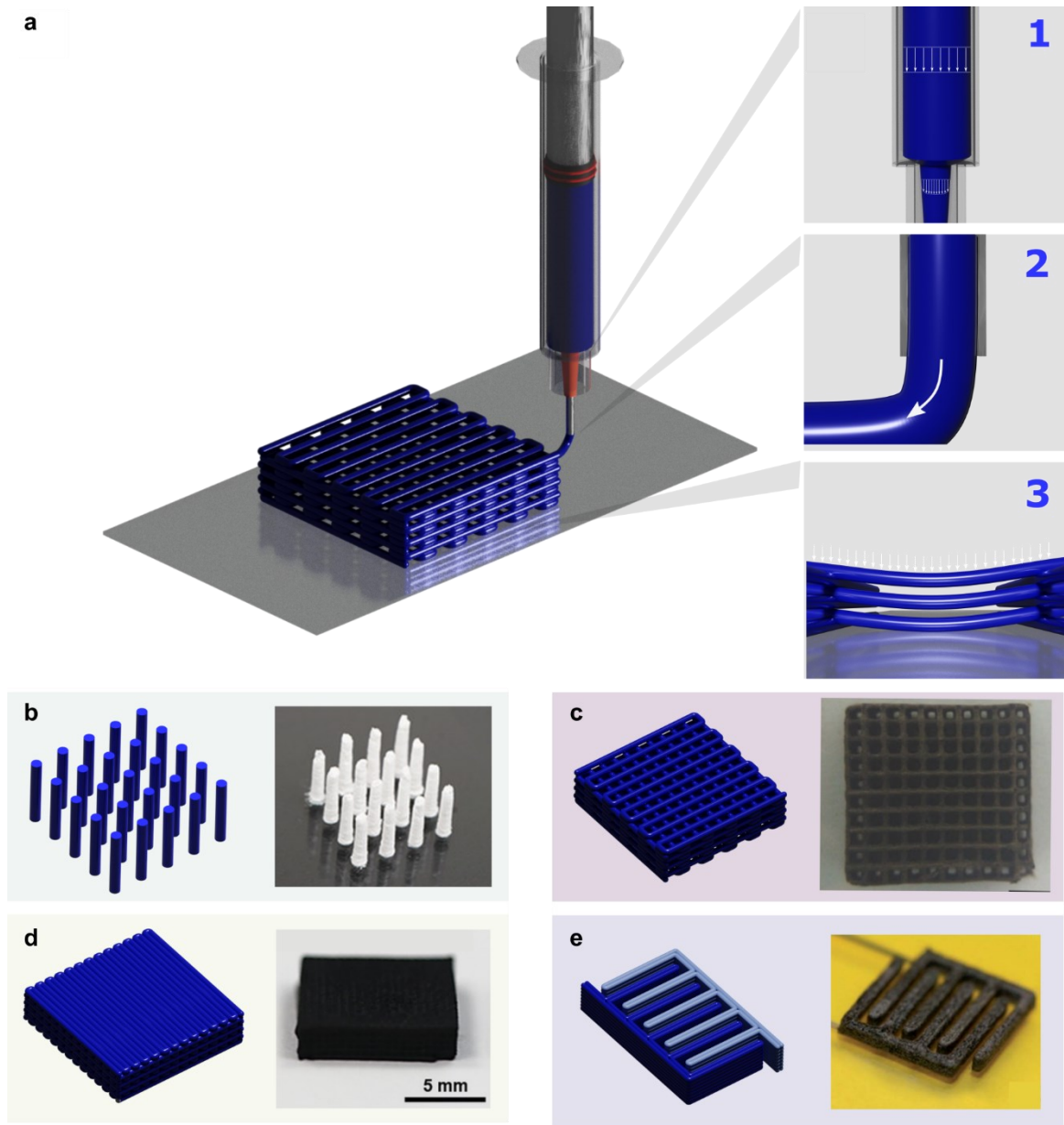


Figure 1.17: (a) Schematic illustrating the main steps of the DIW process: flow of the ink inside the print cartridge (1), ejection from the nozzle (2), deposition onto the substrate (3); (b-e) typical designs for 3D printed electrodes fabricated with DIW for EESDs: pillar design (b); woodpile design (c); compact design (d) and interdigitated design (e); adapted with permission from ref. ⁵⁴

significantly longer than the timescale of the extrusion process, with microstructural changes still occurring inside the ink after deposition.⁵⁴

When the deposition of the three-dimensional structure is completed, it must retain its shape until full consolidation by evaporation of the solvent or freeze-drying. The main electrode geometries used in the fabrication of printed EESDs are presented in Figure 1.17. Woodpile structures are made of layers of uniformly spaced filaments stacked in a crisscross pattern, forming square channels that promote the infiltration of the electrolyte inside the electrode and the diffusion of ions to

the electrode surface (Figure 1.17-c).^{54,92} The interdigitated structure is instead made of closely spaced interlocking fingers presenting high aspect ratio to maximize the area in contact with the electrolyte (Figure 1.17-e). Interdigitated electrodes have shorter ionic diffusion paths, do not require a separator and both electrodes can be simultaneously printed on the same substrate, thus constituting the most suitable geometry for integrated EESDs.^{54,93} Pillared electrodes ensure high surface area, but they are mechanically less stable than interdigitated or woodpile structures (Figure 1.17-b), thus they have not been extensively investigated for energy storage devices. Finally, compact, space-filling electrodes can also be manufactured using DIW, although their low surface to volume ratio and long diffusion distances are detrimental for energy storage processes (Figure 1.17-d). The structures in Figure 1.17 are characterized by overhanging filaments (*e.g.*, in the woodpile design), high-aspect-ratio vertical walls (*e.g.*, in the interdigitated design) or pillars. The rheological properties of the ink should minimize the lateral buckling and slumping of these structural features, under the action of gravity and capillary interactions with the substrate. In particular, the viscoelastic storage modulus of the ink should be sufficiently high to limit the deformation of suspended parts at rest, whereas a high yield stress would prevent structural collapse.⁵⁴ A more detailed discussion on these rheological properties and how they can be optimized for DIW inks will be provided in Chapter 2.

The shape fidelity and dimensional accuracy of the printed electrodes can be verified after printing using non-destructive techniques, such as X-ray computed tomography (XCT). XCT can provide information on the macroscopic geometric features of the printed parts, alongside their complex internal structure, *e.g.* porosity, adhesion between the printed layers and relative distribution of the different phases in multi-component electrodes. Wang *et al.*⁸⁴ used XCT to measure the void surface area, porosity, and morphological complexity of 3D printed graphene framework, parameters that are relevant for the plating of lithium in LIBs. Similarly, Lin *et al.*⁸¹ used XCT to image the structure of 3D printed graphene electrodes with different geometries and investigate how the electrode geometry influenced the distribution of electrodeposited manganese oxide on the electrode surface. X-ray computed tomography can also provide information on the structural and compositional changes occurring in the three-dimensional electrodes under a mechanical load or during charge and discharge, through *in-situ* experiments.^{75,94}

The discussion on printability presented in this section was based on self-supported structures replicating a 3D digital model with high shape fidelity, as is the case for EESD electrodes. Other components, particularly non-structural parts such as the electrolyte, might have different morphological and functional requirements, thus a greater shape variation beyond the original digital model can be tolerated. The printing requirements for electrolytes will be discussed in further detail in Chapter 4.

2.3. Ink design principles

The previous section outlined the rheological properties that an ink should possess to be printable, *i.e.* a yield-stress rheology with a shear-thinning response under flow and a fast recovery of the rest viscoelastic properties after shear.⁵⁴ The ink formulation must be designed to meet these target features, considering the interplay between the ink microstructure and its flow properties, so to achieve the desired printability. In particular, yield stress inks for DIW are characterized by a jammed microstructure, resulting from soft interactions between the ink components.⁹⁵ Depending on the nature of these interactions, yield stress materials can be classified into *colloidal glasses*, which present repulsive forces between crowded particles (typically at high volume fractions); and *gels*, which are dominated by attractive forces acting between the ink components (usually at lower particle concentrations).^{96,97} Attractive and repulsive interactions can also coexist inside the same material, for example in the presence of locally-crowded attractive particles.^{97,98}

The attractive or repulsive interactions result in the existence of a minimum-energy position for every particle inside the ink, from which they can be removed by providing an adequate amount of energy (Figure 1.18).⁹⁵ If the energy imparted to the particles (for example applying a shear stress to the material) is insufficiently high, the particles cannot be extracted from their potential wells, and return to the minimum-energy positions after the stress is released, with no change in the overall microstructure (Figure 1.18). Notably, since the particles are immersed in a liquid phase, the displacement dissipates energy even if the final microstructure is not altered, resulting in a viscoelastic response rather than a purely elastic one. If the applied stress is sufficiently large, all the components of the ink can be extracted from their potential wells leading to the breakdown of the ink

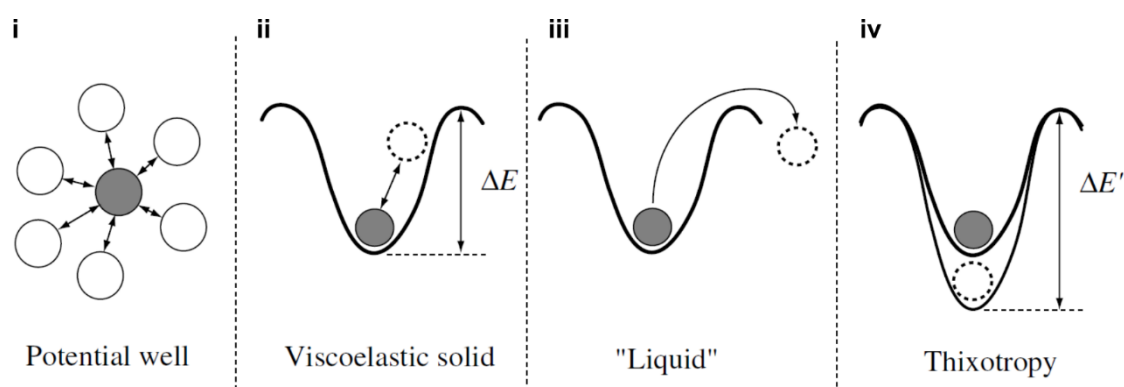


Figure 1.18: Schematic showing the potential well resulting from soft interactions between the particles of a jammed system (i) and its correlation with different macroscopic motions of the system (ii-iv). Panel (ii) illustrates the behaviour of a viscoelastic fluid subjected to a small deformation with negligible hydrodynamic forces, resulting in a purely elastic response (*i.e.* the particles restore their energy after the motion). However, in real systems hydrodynamic forces can cause significant viscous dissipation during motion. Panel (ii) displays the liquid-like behaviour of a jammed system subjected to a sufficiently high shear force, allowing the particles to escape from their potential wells. Panel (iv) illustrates the response of thixotropic systems, in which the local neighbourhood of particles (hence the energy of the potential wells) evolves with time, for example under the action of thermal agitation or colloidal forces. Panel i-iv were adapted with permission from ref.²¹⁴

microstructure.⁹⁵ When a particle is extracted from its original potential well, it encounters new neighbouring particles, whose interactions determine a new potential well. If the applied stress is sufficiently large, the particle will be removed from the new potential well, resulting in an indefinite deformation of the material, *i.e.* in a continuous flow.⁹⁵ Larger values of stress determine a higher degree of structural breakdown of the particle network, causing a shear thinning behaviour during flow.

In inks for the manufacturing of EESDs the network of attractive or repulsive interactions can be directly formed by the particles of active materials,⁹⁹ but more often its formation is aided by processing additives.^{54,74} Inks for DIW consist of functional fillers (*i.e.* the active materials responsible for charge storage processes in the final electrode), binders, additives and solvents. This classification follows the composition of slurries used in the industrial manufacturing of EESDs; however, industrial formulations generally include solid components at concentrations that are too low to form crowded microstructures with a yield-stress rheology.⁹⁵ Functional fillers for printed EESDs generally range from carbon-based materials (such as activated carbon, carbon nanotubes and graphene) to oxides, phosphates and metals.⁵⁴ The role of binders is to hold the solid particles in the ink together and promote adhesion to the substrate after deposition. Conventional binders are inert polymeric materials, *e.g.* PVDF or cellulose, but more recently inorganic and electroactive binders have also been proposed.^{100,101} Polymeric binders can also enhance the stability of the ink and stabilize the particles against sedimentation.⁵⁴ However, since traditional binders are not electroactive, the amount of binder needed for processing must be minimized, considering that inks for EESDs should provide structures with high electrical conductivity, energy density and rate capability.⁵⁴ Solvents are a critical component of DIW inks, providing fluidity to the dispersion and allowing for extrusion and deposition. Owing to the flammability, toxicity and cost of organic solvents, aqueous inks are typically preferred. Finally, additives are often included in the ink formulation to control specific properties, such as the stability or flow properties of the dispersion.⁵⁴ Similarly to binders, inactive additives such as viscosifiers and surfactants aid printability and processing, but they must be removed after printing, increasing the complexity and cost of manufacturing.

In summary, this section has described the typical microstructure that inks for DIW should present to be printable and it has provided a classification of the ink components according to their function. Next section will offer a more detailed discussion on the specific methods and compositions that can be pursued to obtain printable inks for batteries and supercapacitors, in light of the requirements presented here.

3. Overview of ink formulation methods

Inks for DIW are *jammed systems*, characterized by reversible soft interactions between the microstructure components. As discussed above, these interactions can be attractive or repulsive,

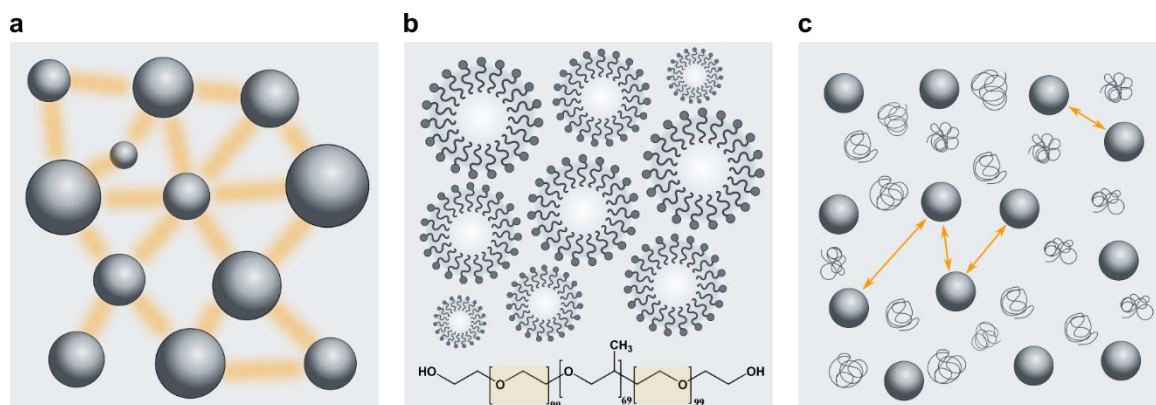


Figure 1.19: (a) Schematic showing the formation of a network of soft interactions (in yellow) between the solid component of the ink; (b) representation of a yield-stress gel made of crowded polymeric micelles (top) and molecular structure of Pluronic F127 (bottom); (c) schematic showing the attractive interactions (yellow arrows) between solid particles, mediated by the depletion of polymeric molecules between the particles.

producing in both cases a percolative network of particles able to bear mechanical stress without yielding (Figure 1.19-a). Several ink compositions are possible to obtain these microstructural features starting from electroactive materials, either by introducing suitable additives, or by taking advantage of the native functional groups on the particle surface.

3.1. Polymer-based inks

Polymeric additives can promote the formation of attractive gels by adsorbing onto the particle surface and bridging different particles together. In the case of non-adsorbing polymers, attractive interactions can be mediated by the formation of polymer-depleted regions between the particles, which cause an imbalance in the local osmotic pressure (Figure 1.19-c).⁹⁵ In addition to the formation of attractive interactions, polymeric additives can increase the viscosity of the liquid component of the ink, stabilizing the dispersion against sedimentation.

Fluorinated polymers have been widely used as binders in conventional battery manufacturing processes, which are based on the casting of a slurry containing the electroactive materials and conductive additives.¹⁰² The composition of these slurries can be easily adapted to the DIW process, by increasing the concentration of solid particles until a jammed system with the desired flow properties is obtained.^{103–105} For example, polymer inks with a polyvinylidene difluoride (PVDF) binder were recently proposed for lithium- and zinc-ion battery electrodes.^{104,105} Printable electrolytes for LIBs were also recently demonstrated using a fluorinated polymeric binder and alumina particles as inert filler.¹⁰⁶ PVDF is unlikely to adsorb onto the solid components of these inks, as demonstrated by studies on carbon black dispersions,¹⁰⁷ but it can enhance the secondary interactions between carbon or alumina particles through a depletion mechanism and increase the viscosity of the inks. Nonetheless, the printability of these inks is not significantly affected by the chemical nature

of the solid particles, owing to a lack of specific interactions between the polymer molecules and the particle surface, making these formulations extremely versatile.¹⁰⁴ Additionally, PVDF is chemically and thermally inert, which prevents unwanted side reactions during the manufacturing process and operation of the electrodes. Despite these advantageous properties, PVDF is usually dissolved in N-Methylpyrrolidone (NMP), a toxic and mutagenic solvent with a high boiling point (~202°C), which complicates the manufacturing process of the electrodes. The use of alternative solvents for the formulation of PVDF-based DIW inks has not been widely investigated, despite the availability of greener substitutes for NMP.¹⁰⁸ In Chapter 5, the use of dimethyl sulfoxide (DMSO) as a non-hazardous solvent for the DIW of vanadium disulfide electrodes is proposed.

Water-dispersible polymers with abundant hydroxy and carboxylic groups, such as cellulose and its derivatives, have better adhesion to battery materials than PVDF. These binders are highly hydrophilic and enhance the contact area between the electrolyte and the active material,¹⁰⁹ ensuring a higher electrolyte uptake by the electrodes. A mixture of hydroxypropyl and hydroxyethyl cellulose was proposed to formulate inks for LIB cathodes and anodes, based on lithium titanate and lithium iron phosphate, respectively.⁸⁶ However, the absence of electrically conductive additives in these polymer inks limited the rate performance and the capacity achievable by three-dimensional electrodes. Conductive components, such as silver nanowires or carbon nanotubes,¹¹⁰ can be included in cellulose-based inks to retrieve good rate performance at high areal loading of electroactive material.

Some polymers are able to self-organize in aqueous dispersions, forming jammed microstructures without the aid of a solid phase. A notable example for DIW is represented by Pluronic F127, a triblock copolymer able to form spherical micelles in water.¹¹¹ At high concentrations, the micelles form a closely packed structure causing the gelation of the system (Figure 1.19-b). Pluronic F127 was recently used to print the current collector and electrodes of a reduced chemically-modified-graphene supercapacitor by Rocha et al.⁷⁴ Similarly to block copolymers, concentrated dispersions of cellulose nanofibres (CNF) can form gels owing to the mechanical contacts between the crowded elongated CNF units, which behave as load-bearing networks of stiff beams.^{112,113} In addition to this simplified mechanical response, CNF gels are also stabilized by the electrostatic repulsion between the negatively charged functional groups on the fibre surface. In the recent literature, CNF were mixed with lithium iron phosphate, providing a viscoelastic ink for the 3D printing of LIB cathodes.¹¹⁴ Symmetric supercapacitors were also fabricated by dispersing carbon nanotubes and an N-doping agent in a CNF hydrogel and printing the resulting ink.¹¹⁵ The main advantage of inks based on gel-forming polymers is that high concentrations of electroactive materials are not required to obtain a suitable rheological response. The network of polymeric micelles or fibrils in the dispersion act as a carrier for the solid particles, dispersing them and controlling the flow properties of the mixture.

Compared to fluorinated polymers, water-dispersible binders are better suited for the printing of aqueous EESDs. The use of organic solvents would significantly aggravate the environmental impact of electrode manufacturing,¹¹⁶ reducing the advantages of aqueous EESD over LIBs. Nonetheless, polymeric additives usually present low electronic conductivity and are unstable in aqueous electrolytes because of their high water solubility. For these reasons, they are often carbonized at high temperatures ($> 500^{\circ}\text{C}$) after printing, which can induce undesirable side reactions or phase transformations in the electroactive material. In Chapter 4, a polyvinyl alcohol (PVA) binder is proposed for zinc-ion batteries, presenting high electrical conductivity without the need for thermal annealing.

3.2. Colloidal and polyelectrolyte inks

A stable colloidal dispersion can be turned into a jammed system by increasing the concentration of colloidal particles, until a glassy phase, characterized by repulsive interactions between crowded elements, is obtained (Figure 1.20-a).⁹⁷ Alternatively, suitable gelating agents can be added to the dispersion to reduce the repulsive interactions and form attractive gels (Figure 1.20-b).¹¹⁷ The latter approach ensures gelation at lower particle concentrations when compared to repulsive glasses, reducing the risk of occlusions inside the printing head.⁵⁴ Dispersions of colloidal oxides, such as Al_2O_3 and SiO_2 , are typically stabilized by the negative surface charge resulting from the ionization of surface -OH groups. If the suspension is acidified, the surface groups get neutralized, flocculating the system. Similarly, flocculation can also be induced by the addition of ions that alter the electrical double layer and screen the negative charge, drawing particle into closer contact. These approaches have been widely used for the DIW of ceramic green bodies, since they do not require additives that might contaminate the system.¹¹⁸ Although silica and alumina are not electrochemically active for the energy storage devices considered in this work, they can be used as inert additives to obtain printable electrolytes. In Chapter 5 the destabilization of silica suspensions by zinc ions to obtain printable electrolytes will be presented.

The literature on DIW has devoted great attention to two highly hydrophilic and electrochemically active materials that can form stable colloidal dispersions at high concentrations: graphene oxide (GO) and MXenes. GO is a graphene derivative characterized by oxygen-containing moieties on the basal plane and edge of the crystals. The ionization of carboxylic and hydroxyl groups on the surface of GO sheets results in a negative charge, that stabilizes GO dispersions in water. Owing to the high aspect ratio of GO sheets, a jammed phase can be obtained at relatively low GO concentrations, as low as 0.05 mg mL^{-1} , depending on the lateral size of the sheets.¹¹⁹ Higher concentrations ($> 100 \text{ mg mL}^{-1}$) are however usually needed to obtain printable inks for DIW, presenting a sufficiently high elastic response and yield stress.^{80,120} GO inks have been used to print high-surface area electrodes, showing a supercapacitive behaviour with high specific capacitance after chemical or thermal reduction.¹²¹ Additionally, GO has also been used as a processing additive to

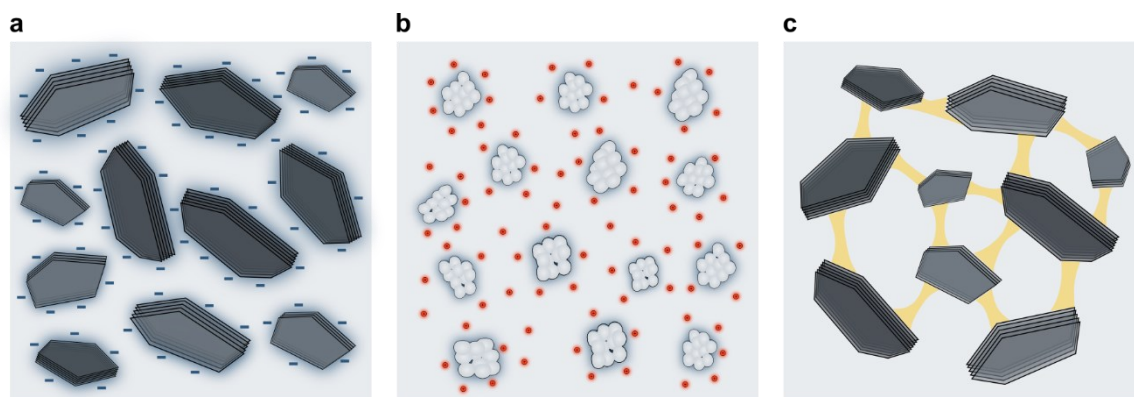


Figure 1.20: Schematic showing different approaches to obtain a yield-stress fluid from a dispersion of solid particles: (a) crowded colloidal dispersion stabilized by electrostatic repulsions (such as graphene oxide dispersions); (b) attractive colloidal gel obtained by shielding the electrostatic repulsion between solid particles with positive ions; (c) capillary suspension showing liquid bridges (in yellow) connecting the solid particles.

control the rheology of inks based on other active materials, such as sulfur or nickel-cobalt sulfide.^{122–124} Although graphene oxide can be printed without any additional binders, preparing highly concentrated dispersions is time consuming, and printed GO structures require intensive post-processing to obtain high-performance electrodes. This typically involves freeze-drying to enhance the electrochemically active surface area, and chemical or thermal reduction in toxic reducing agents (*e.g.* hydrazine) or at high temperatures ($> 1000^{\circ}\text{C}$), to improve the electrical conductivity.¹²⁵ The critical GO concentration to obtain a printable ink can be lowered adding Ca^{2+} ions to the dispersion, which form coordination bonds with the negatively charged moieties on the surface of the sheets reducing the repulsion interactions.^{126,127} Highly conductive carbonaceous materials, such as graphene and carbon black, can also form colloidal gels at sufficiently high concentrations.¹²⁸ However, the absence of charged functionalities and high hydrophobicity of these materials limit the dispersibility in water; thus organic solvents must be used instead, such as NMP or mineral oil. The rheology of carbon black suspensions in DMSO will be discussed in detail in Chapter 5.

Similarly to graphene oxide, MXenes have negatively charged surface functionalities ($-\text{F}$, $-\text{OH}$ and $=\text{O}$) and can form stable dispersions in water.¹²⁹ Concentrated pastes containing $> 1.8 \text{ mg mL}^{-1}$ of $\text{Ti}_3\text{C}_2\text{T}_x$ have a suitable flow behaviour for extrusion-based printing techniques.¹³⁰ Unlike GO, MXenes are already highly conductive and pseudocapacitive, thus printed MXene structures can be directly used as aqueous supercapacitor electrodes.⁹⁹ Nonetheless, the preparation of MXenes inks poses safety concerns for the use of hydrofluoric acid in the exfoliation process, and recent studies have demonstrated the instability of MXenes in aqueous environment and in air.¹³¹

Polyelectrolytes molecules are characterized by ionizable moieties in their polymeric backbone, such as carboxylic, sulfonic or amine groups, which control the stability of the suspension *via* electrostatic interactions.¹³² When ions with opposite charge are introduced in the suspension, they can

induce attractive forces between the charged moieties of the molecules, causing gelation. Complexes of polyacrylic acid (negatively charged) and polyethylenimine (positively charged) can form printable inks for DIW when the ratio between opposite moieties is non-stoichiometric, as shown by Gratson *et alii*.⁶⁹ However, polyelectrolytes tend to have complex phase diagrams in the presence of multivalent salts, often resulting into phase segregation which complicates the preparation of homogeneous inks. Stable suspensions of electrochemically active polyelectrolytes, such as PEDOT:PSS, can be turned into gels after the addition of multivalent ions, *e.g.* Fe^{3+} or Sn^{4+} .^{133,134} The gelation of PEDOT:PSS using Zn^{2+} ions for the printing of zinc anodes will be discussed in Chapter 4. Printable PEDOT:PSS inks can also be obtained by a controlled dry-annealing of the conductive polyelectrolyte suspensions to form a connected network of PEDOT-rich nanofibrils in a hydrophilic PSS matrix.^{135,136} The nanofibrils can then be redispersed in water at high concentrations (> 4 wt%) to obtain hydrogel inks for supercapacitors.

3.3. Capillary inks

Suspensions of solid particles can be transformed into attractive gels by introducing a small amount of a secondary liquid, immiscible with the bulk liquid phase.¹³⁷ If the secondary liquid presents a suitable surface tension, it can form bridges between the solid particles resulting in attractive capillary forces (Figure 1.20-c). Inks based on capillary suspensions are thus characterized by a reticulate network of particles connected by attractive pendular bridges of the secondary liquid.¹³⁸ This microstructure is comparable to Pickering emulsions, in which the solid particle stabilize the interface between two immiscible liquids.¹³⁹ However, capillary suspensions are typically formed at low volume fractions of the secondary liquid (~ 0.2 vol%), minimizing the use of non-aqueous solvents in the electrode processing and the risk of contaminations in the final device. Capillary bridges can be used to obtain aqueous pastes from hydrophobic particles, such as graphite or silicone microbeads,^{140,141} without the need for surface modifications. Chapter 3 will demonstrate the use of capillary suspensions to print aqueous dispersion of pristine graphene nanoplatelets. Graphene capillary inks showcase notable advantages when compared to GO dispersions, having significantly higher electrical conductivity without the need of thermal or chemical reduction.

Chapter 2

Experimental Methodology and Characterization Techniques

In this chapter the experimental methodologies used for the synthesis of the electroactive materials, for the formulation of DIW inks and for the characterization of the inks and electrodes will be presented. In particular, section 1 and 2 will discuss the experimental methods employed for the synthesis of vanadium disulfide and manganese oxide and for the preparation and printing of the inks. Section 4, 5 and 6 will focus on the characterization of the inks and the electrodes, providing a description of the rheological, physical, and electrochemical characterization methods used in this work.

1. Synthesis of active materials for 3D Printed EESD

1.1. Hydrothermal synthesis of vanadium disulfide

Hydrothermal synthesis was used as a low-cost and scalable method for the production of vanadium disulfide for ZIB cathodes. In a typical reaction process, thioacetamide (TAA) and sodium orthovanadate, acting respectively as the sulfur and vanadium source, are dissolved in water and heated to the final reaction temperature in a pressure reactor. During the synthesis, TAA hydrolyses releasing HS^- , which reacts with the orthovanadate to form VS_2 .¹⁴² This process can be easily scaled up to produce several grams of VS_2 in one synthesis, meeting the demand of large amounts of active material for high-mass-loading 3D printed electrodes.

In a typical synthesis, ~ 11.2 mmol of sodium orthovanadate ($\geq 90\%$, Sigma-Aldrich) were dissolved in 100 mL of deionised water ($\sim 18 \text{ M}\Omega \text{ cm}$) in the PTFE liner of a 200 mL stainless-steel autoclave at room temperature. After complete dissolution, ~ 56 mmol of TAA (98%, Sigma-Aldrich) were added, together with 40 mL of ethylene glycol (EG, $>99\%$ Sigma-Aldrich). EG was added as a co-solvent and reducing agent, controlling the morphology of the VS_2 crystals and preventing the re-oxidation of V^{4+} to V^{5+} . The autoclave was heated to 160°C for 24 h and then cooled naturally to room temperature. The reaction products were washed three times with ethanol and stored as a dry powder in air.

1.2. Electrodeposition of manganese oxide

Manganese oxide was grown on conductive substrates and printed scaffolds *via* a potentiostatic electrodeposition process from a solution of manganese(II) acetate. During the electrodeposition process, the Mn^{2+} ions in the electrolyte migrate towards the conductive scaffold (working electrode), where they are oxidized to an Mn^{3+} intermediate:^{143,144}



Mn^{3+} causes hydrolysis, forming a continuous film of MnOOH on the surface of the electrode. Finally, MnOOH is oxidized to MnO_2 :



In a typical electrodeposition process, a three electrode cell was set up in a 100 mL beaker filled with ~75 mL electrolyte. The electrolyte was obtained dissolving 0.1 M $\text{Mn}(\text{CH}_3\text{COO})_2$ (manganese acetate tetrahydrate, $\geq 99\%$ from Sigma-Aldrich) and 0.1 M Na_2SO_4 (anhydrous, $\geq 99.0\%$ from Sigma-Aldrich) in deionized water ($\sim 18 \text{ M}\Omega \text{ cm}$). A printed graphene scaffold was used as the working electrode for the potentiostatic electrodeposition process, performed with a VMP-3 workstation (Bio-Logic Science Instruments), with a piece of graphite foil ($\sim 2 \text{ cm}^2$) as the counter electrode and a commercial Ag/AgCl (3 M KCl) reference electrode (BASi MF-2056). Preliminary linear sweep voltammetry tests were performed to choose the electrodeposition potential, as detailed in Chapter 5. The electrodeposition of manganese oxide was carried out at an oxidative potential of 0.7 V vs. Ag/AgCl for an electrodeposition time between 15 and 75 min. After electrodeposition the structures were rinsed with deionized water and dried on a hotplate at 60°C .

2. Ink preparation and Direct Ink Writing

2.1. Graphene inks

The formulation of capillary inks was adapted from previous works on capillary suspensions of carbon-based materials.^{140,145} Graphene capillary inks were formulated by dispersing 1 g of sodium carboxymethylcellulose (average Mw $\sim 250,000$, degree of substitution 1.2, Sigma-Aldrich) in 19 g of deionized water ($\sim 18 \text{ M}\Omega \text{ cm}$) to obtain a cellulose concentration of 5 wt%. Subsequently, 4.2 g of graphene nanoplatelets (5 μm particle size, surface area $120\text{-}150 \text{ m}^2 \text{ g}^{-1}$, Sigma-Aldrich) were added to 21 g of the cellulose solution to a final composition of 16.7 wt% graphene and 4.2 wt% carboxymethylcellulose. Sodium carboxymethyl cellulose acted as a viscosifier for the graphene suspension, promoting the colloidal stability of the nanoplatelets. The graphene dispersion was

transferred to a 150 mL polypropylene jar and homogenized using a planetary mixer (Thinky ARE-250) at 2000 rpm for 10 min. After mixing, the dispersion was cooled to room temperature and ~ 0.4 mL of 1-octanol ($\geq 98\%$, Sigma-Aldrich) were gradually added as a secondary liquid phase to form bridges between the graphene platelets. The ink was homogenized at 2000 rpm after each addition and then stored at $\sim 4^{\circ}\text{C}$ before printing.

Composite graphene-carbon nanotubes ink were formulated by dispersing 4.2 g of graphene nanoplatelets (5 μm particle size, surface area 120-150 $\text{m}^2 \text{g}^{-1}$, Sigma-Aldrich) and 1 g of sodium carboxymethylcellulose (average Mw $\sim 250,000$, degree of substitution 1.2, Sigma-Aldrich) in 20 mL of a commercial aqueous suspension of carbon nanotubes (Tuball BATT H₂O, 0.4 wt% of single-wall carbon nanotube stabilized by 0.6% CMC, OCSiAl). The carbon nanotube used in this study have a nominal length $> 5 \mu\text{m}$ and diameter of $1.6 \pm 0.4 \text{ nm}$, with a G/D ratio > 90 (determined by Raman spectroscopy at 532 nm). The final cellulose:graphene:nanotubes mass ratio was 10:42:0.8. The suspension was homogenized using a planetary mixer (Thinky ARE-250) at 2000 rpm for 5 min and then stored at $\sim 4^{\circ}\text{C}$ before printing.

2.2. PEDOT:PSS inks

PEDOT:PSS ($\sim 1.3 \text{ wt\%}$ dispersion in water, Sigma-Aldrich) was used as a polyelectrolyte binder for zinc particles. Two grams of PEDOT:PSS dispersion were weighed in a 150 mL polypropylene jar, and 2 g of zinc dust ($< 10 \mu\text{m}$, $\geq 98\%$, Sigma-Aldrich) were added to the dispersion to formulate a 50 wt% ink (or alternatively 0.57 g of zinc dust for the 78 wt% ink). The mixture was homogenized at 1400 rpm for 10 min using a planetary mixer (Thinky ARE-250). The acidic pH of the PEDOT:PSS suspension promotes the leaching of Zn^{2+} ions from zinc, which destabilizes the polymer forming a gel. The PEDOT:PSS inks were cooled to room temperature after mixing and then directly printed.

2.3. Zinc inks

Inks for zinc anodes were formulated transferring 2 g of a 10 wt% polyvinyl alcohol solution, obtained dissolving 10 g of polyvinyl alcohol (Mowiol 56-98, Mw $\sim 195,000$, Sigma-Aldrich) in 90 g of deionised water (resistivity $\sim 18 \text{ M}\Omega \text{ cm}$) at 120°C , to a 150 mL polypropylene jar. Fifteen grams of zinc dust ($< 10 \mu\text{m}$, $\geq 98\%$, Sigma-Aldrich) were then added to the solution, and the mixture was homogenized in a planetary mixer (Thinky ARE-250) for 2 min at 1800 rpm to obtain the pure zinc ink (0% ink). Different amounts of carbon black (acetylene, $> 99.9\%$, 75 m^2/g surface area, Alfa Aesar) were gradually added to the zinc slurry to a final carbon-to-zinc mass ratio of 1:100, 3:100 and 5:100 to formulate the 1%, 3% and 5% ink, respectively. After each addition of carbon black, the inks were homogenized again at 1800 rpm for 2 min. The final ink was cooled to room temperature and loaded in a 3 mL plastic cartridge for printing.

Printable zinc electrolytes were formulated dispersing 0.1 g of silicon dioxide (silica, fumed, 370-420 m² g⁻¹ from Sigma-Aldrich) in 1.9 g of deionised water (~ 18 MΩ cm) in a 150 mL polypropylene jar. Zinc sulfate heptahydrate (99%, Sigma-Aldrich) was added to the dispersion to a final concentration of 2 mol L⁻¹, forming a colloidal gel. The suspension was homogenized in a planetary mixer (Thinky ARE-250) at 1800 rpm for 2 min and left to rest overnight before characterization or printing.

2.4. VS₂ inks

VS₂ inks for ZIB cathodes were formulated dispersing 0.2 g of carbon black (acetylene, > 99.9%, 75 m²/g surface area, Alfa Aesar) in 1.8 g of dimethyl sulfoxide (≥ 99.5%, Sigma-Aldrich) in a 150 mL polypropylene jar, to obtain a 10 wt% concentration slurry. The carbon slurry was homogenized using a planetary mixer (Thinky ARE-250) at 1800 rpm for 2 min. Subsequently, 0.2 g of polyvinylidene fluoride (PVDF, M_w ~ 350, #44080 from Alfa Aesar) were added to the mixture and the resulting slurry was further homogenized for 2 min at 1800 rpm. Finally hydrothermal VS₂ (synthesized as detailed in Section 1.1) was manually ground for 5 min using an agate mortar and mixed into the carbon slurry, homogenizing it again at 1800 rpm for 2 min. The final composition of the ink was 6:2:2 (VS₂:PVDF:carbon black) by mass.

2.5. 3D Printing setup

The inks were printed using a commercial extrusion 3D printer (2019 Robocasting System, 3DInks LLC, Stillwater, US), consisting of a gantry robot with three linear actuators which control the movement of the printing head along the x-, y- and z- directions (Figure 2.1). The printing head consists of a plastic cartridge containing the ink, connected to a stainless-steel plunger (Figure 2.1-b). The vertical motion of the plunger, which determines the extrusion of the ink from the barrel tip, is controlled by a linear actuator (Figure 2.1-a). RoboCAD software (3DInks LLC, Stillwater, US) was used to design the parts to print, generating a CAD file with the electrode geometry. The CAD file was then sliced by RoboCAD and translated into instructions for the motion controller, coded in Aerobasic G-code (A3200 Motion Composer, Aerotech, UK), with the path to follow, the printing speed and the extrusion rate. During the slicing process, an extrusion nozzle diameter between 100 μm and 410 μm (as specified in the experimental chapters) and a printing speed of 6 mm s⁻¹ were selected. The extrusion rate of the ink from the nozzle was set equal to the printing speed (6 mm s⁻¹) to avoid filament breakup or accumulation of excess ink along the printing path. Alternatively, the CAD files for the printing process were drawn in SolidWorks (Dassault Systèmes) and then sliced in RoboCAD (3DInks LLC, Stillwater, US). The CAD files used throughout this work for the fabrication of the electrodes (woodpile and interdigitated geometry) are presented in Figure 2.1-c,d. The woodpile geometry presents alternating layers of equally spaced struts, forming open channels that ensure the diffusion of the electrolyte and provide high mechanical stability against

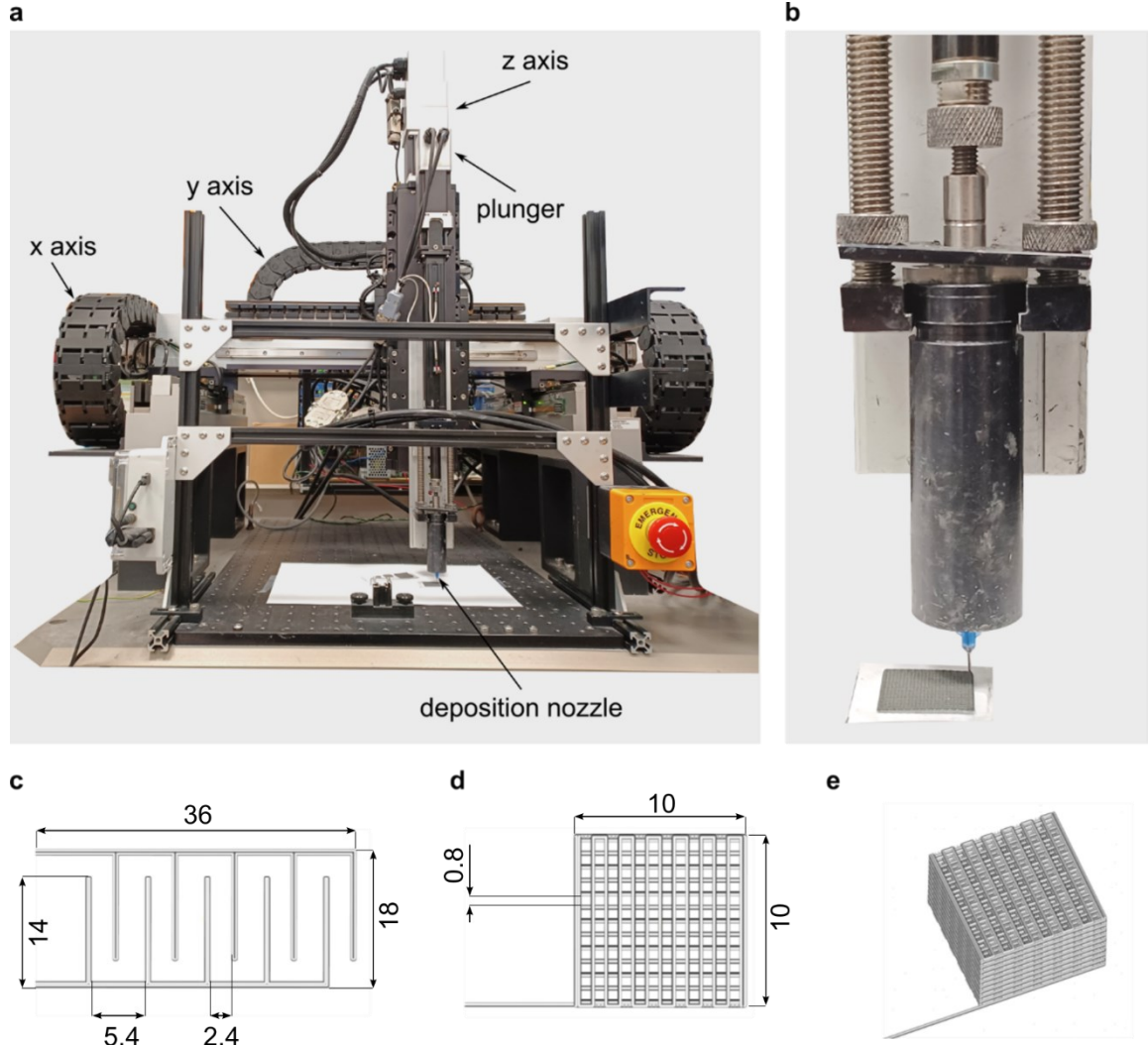


Figure 2.1: (a) Picture of the 3D printer used throughout this work, showing the linear actuators controlling motion in the x-, y- and z- direction and the extrusion plunger; (b) zoomed-in view of the deposition nozzle during printing of a woodpile electrode; (c,d,e) visualization of the CAD files used to print interdigitated devices (c) and woodpile electrodes (d,e), dimensions in millimetres.

lateral buckling. On the other hand, the interdigitated geometry allows the simultaneous fabrication of the negative and positive electrodes on a single substrate, simplifying the integration of printed EESD in electronic systems.

The printing process was carried out at room temperature on graphite foil substrates (for single woodpile electrodes) and on alumina substrates with pre-patterned gold current collectors (for interdigitated batteries). Around 1.5 mL of the selected ink was manually loaded into a 3 mL syringe barrel using a stainless steel spatula. The printer plunger was inserted into the barrel and the ink was pushed to the syringe tip. The barrel was then mounted onto the moving head of the printer. It should be noted that manually loading the ink into the barrel induces an uncontrollable shear history, which can affect the reproducibility of the printing process. The majority of the inks studied in this work are not thixotropic, therefore the shear applied during the ink loading process does not influence the properties of the ink at the beginning of extrusion. However, the zinc inks discussed

in Chapter 4 present a certain degree of thixotropy. The barrel loading process could be standardised by pre-loading the ink into a secondary syringe and extruding it into the primary barrel used for printing at a constant shear rate (*e.g.* using an automatic syringe pump).

Gel electrolytes were either drop-casted or printed between the fingers of the interdigitated devices, and the devices were subsequently encapsulated with parafilm or epoxy resin. Graphene interdigitated supercapacitors were printed on glass and paper substrates (100% cellulose paper, Canson).

2.6. Electrode postprocessing

Printed structures were dried in air at room temperature after the printing process. Vanadium disulfide and zinc electrodes were further heated to 70°C in a vacuum oven under dynamic vacuum for 1 h to completely remove the residual solvent and promote the solidification of the binder. Graphene electrodes were thermally annealed in a tubular furnace at 350°C for 30 min (Ar atmosphere ~ 0.5 mbar) to carbonize the carboxymethyl cellulose binder. Graphene electrodes on paper substrates were either directly tested after drying in air or annealed using a continuous-wave CO₂ laser before testing (Synrad Firestar F201, 10.6 μm). The CO₂ laser annealing was performed at 10-20% of the maximum laser power (250 W) by Prof Francesca Brunetti and Dr Giuseppina Polino at the Department of Electronic Engineering, University of Rome Tor Vergata.

3. Rheological characterization and simulation

The printability of inks for Direct Ink Writing depends on their rheological properties as discussed in Chapter 1. Rotational rheometry was used to characterize the flow behaviour of the inks and optimize their composition in order to obtain the desired morphological features. The rheometric analysis presented throughout this work was conducted within the theoretical framework of continuum mechanics, assuming that the inks behave as continuous bodies, *i.e.* the average physical properties of an ink do not change abruptly from one point to the neighbouring ones.¹⁴⁶ Although inks are highly heterogeneous systems, this assumption generally holds true because the characteristic flow length, *i.e.* the diameter of the printing nozzle ($> 100 \mu\text{m}$), is significantly larger than the size of the particles dispersed in the ink ($\sim 1 \mu\text{m}$), as shown in Figure 2.2-a. Wall slip and shear localization can determine discontinuities of velocity on a larger length scale,¹⁴⁷ causing artifacts during the characterization of the inks. To prevent these issues, roughened plates and other experimental setups are typically used,¹⁴⁸ as discussed in Chapter 3 for the characterization of graphene inks.

The majority of rheometric techniques relies on *simple shear* flows to measure the constitutive properties of fluids and slurries. In a simple shear flow, the components of the fluid velocity have the following form:

$$v_x = \dot{\gamma} y, \quad v_y = 0, \quad v_z = 0 \quad ; \quad (2.4)$$

where $\dot{\gamma}$ is the shear rate, and it is in general a function of time $\dot{\gamma}(t)$. Examples of simple shear flows that are relevant for this discussion are the steady flow of an ink between two rotating plates (Couette flow) and the flow inside a cylindrical conduit (Poiseuille flow). It can be shown that for simple shear, the stress tensor inside the fluid has the form:¹⁴⁹

$$\boldsymbol{\Sigma} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & 0 \\ \sigma_{xy} & \sigma_{yy} & 0 \\ 0 & 0 & \sigma_{zz} \end{pmatrix} , \quad (2.5)$$

where $\sigma_{xy} = \tau(\dot{\gamma})$ is the shear stress.* The apparent viscosity η of the material, defined as

$$\eta(\dot{\gamma}) = \frac{\tau}{\dot{\gamma}} , \quad (2.6)$$

is a measure of the resistance to flow under the action of a shear force, associated with the internal interactions between the fluid particles.¹⁵⁰ As anticipated in Chapter 1, inks for Direct Ink Writing are yield stress fluids, thus they can flow steadily only if the shear stress τ applied to the material

* This discussion is only rigorous for simple fluids, *i.e.* fluids in which the current stress is a functional of the deformation history.

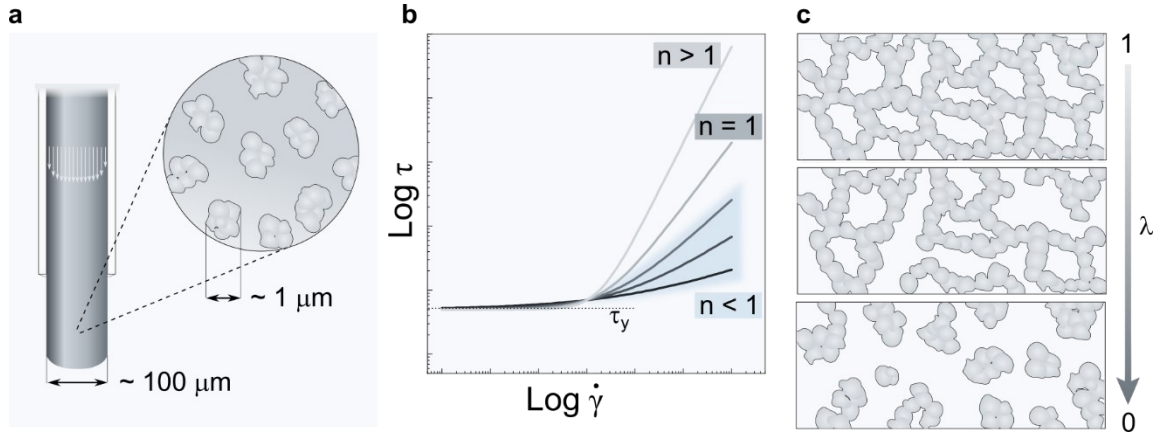


Figure 2.2: (a) Schematic showing the characteristic dimension of the extrusion nozzle and of the particles in the ink, justifying the continuous body assumption; (b) flow curves for a Herschel-Bulkley model, showing a shear thickening behaviour ($n > 1$), a Bingham behaviour ($n = 1$) and a shear thinning behaviour ($n < 1$), decreasing values of n from top to bottom curve; (c) schematic representing the inner structure of an ink at different values of the structure parameter λ .

is higher than the yield stress τ_Y . In the liquid regime ($\tau > \tau_Y$), the rheological properties of the material are completely determined by the relationship between shear stress and shear strain, as represented by apparent viscosity $\eta(\dot{\gamma})$ (a discussion of normal stresses σ_{ii} is beyond the scope of this work). The flow behaviour of DIW inks usually follows an empirical law, known as the Herschel-Bulkley model:^{89,151}

$$\tau = \tau_Y + K \dot{\gamma}^n, \quad (2.7)$$

where K is the viscosity parameter and n is the flow index. The Herschel-Bulkley model assumes that the ink acts as a solid material below the yield stress and that it has a rate-dependent viscosity during flow, which can be either shear-thinning ($n < 1$) or shear-thickening ($n > 1$), Figure 2.2-b. Even though this model provides a satisfactory description of the ink flow in most circumstances, it is unable to account for the elastic or viscoelastic properties of the ink at rest (*i.e.* below the yield stress) and the thixotropic recovery of the ink microstructure and physical properties after flow. Thixotropic effects, *i.e.* the time-dependant change of rheological properties induced by flow,¹⁵² can be taken into account assuming that the viscosity $\eta(\dot{\gamma}, \lambda)$ and the yield stress $\tau_Y(\lambda)$ are functions of an additional parameter λ , known as the structure parameter.¹⁵³ This describes the degree of aggregation, bonding or jamming of the particles that make up the microstructure of the ink (Figure 2.2-c). Since λ can be related to measurable rheological properties, *e.g.* the viscosity, the yield stress or the viscoelastic moduli,¹⁵⁴ it is possible to determine the kinetic of ink restructuring by measuring the evolution of these rheological properties over time, for example *via* three-interval thixotropy tests.

3.1. Rotational rheometry

Several rheometric techniques have been proposed to characterize the properties of the solid regime, liquid regime, and the transition between the two in yield-stress fluids.^{91,155,156} Rotational rheometry, in particular, can provide a comprehensive characterization of yield-stress inks for Direct Ink Writing in the two flow regimes. In a parallel-plate rotational rheometer (Figure 2.3-a), the fluid of interest is sheared between two stainless-steel plates of same symmetry axis, one fixed (stator) and one free to rotate (rotor). When a torque T is applied to the rotor, it results in a rotation around the symmetry axis at angular velocity Ω . Assuming no-slip boundary conditions at both plates, the shear stress can be calculated from the measured angular velocity as:¹⁵⁷

$$\dot{\gamma}(r) = \frac{r}{H} \Omega \quad . \quad (2.8)$$

Equation 2.8 shows that for the parallel-plate geometry the shear is not uniform in the radial coordinate. For simplicity, in the computation of shear rate it is usually assumed that the shear rate is constant and equal to the value at $r = R$. Additionally, in a parallel plate geometry the exact value of shear stress cannot be directly calculated from the measured torque. Therefore, most commercial

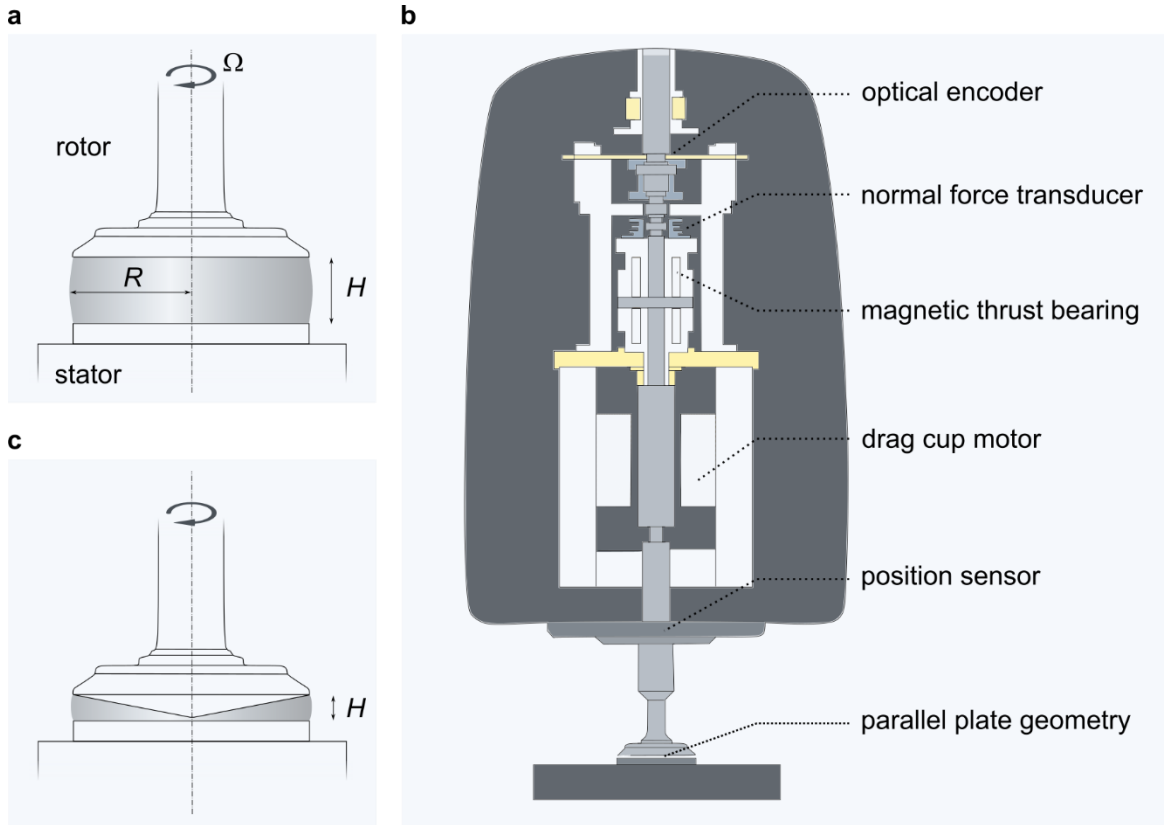


Figure 2.3: (a) Schematic of a parallel-plate geometry, showing the stator and rotor of the rheometer; (b) schematic showing the main components of the rotational rheometer used in this work (Discovery Hybrid HR1, TA Instruments); (c) schematic of a cone-and-plate geometry.

rheometers make the following approximation, which will also be also used in this work for the calculation of shear stress:^{150,157}

$$\tau(R) \approx \frac{2}{\pi R^3} T \quad , \quad (2.9)$$

where R is the radius of the plate. Compared to a parallel-plate geometry, a cone-and-plate geometry (Figure 2.3-c) ensures more homogeneous shear conditions, since the shear rate is constant in the gap between the plates. Nonetheless, this geometry is unsuitable for dispersions containing solid particles, owing to the vicinity the conical plate to the surface of the stator.

The rheological properties of the inks formulated in this work were measured using a Discovery Hybrid HR1 rotational rheometer (TA Instruments), equipped with 40 mm stainless-steel plates (setup schematized in Figure 2.3-b). The ink temperature was kept at 25°C throughout the experiments using a Peltier plate as the stator. A commercial solvent trap was also employed during the measurements to minimize the evaporation of the liquid component of the inks (Peltier Solvent Trap, TA Instruments). It consisted of an insulating cover around the rotor, which created a local environment saturated with the ink solvent, slowing down evaporation. Roughened plates were obtained by applying disks of sandpaper (600 grit) to the stainless steel plates and calibrating the inertia, friction and gap of the instrument. After loading the ink onto the rheometer stator, the rotor was lowered to a gap of 1050 μm , the excess ink was trimmed away using a spatula and the rotor was subsequently lowered to the final gap of 1000 μm .[†] Three types of experiments were performed to characterize the printability of the inks: flow tests, oscillatory tests and thixotropy tests. In a typical testing procedure, oscillatory frequency-sweep tests were always performed first, followed by amplitude tests or flow tests on the same sample. Oscillatory frequency-sweep tests were performed at low oscillatory strain (within the linear viscoelastic region, as discussed below), therefore it was assumed that they did not alter the microstructure and rheological properties of the ink tested. Additionally, since DIW inks typically have constant viscoelastic moduli in the range of frequency probed, the initial oscillatory test also acted as a conditioning step, which ensured the equilibration of the ink after loading and the stability of the rheological response over time. The specifics of the rheological tests performed in this work are presented below.

Flow tests: The flow properties of the inks were measured in controlled shear rate mode, applying a logarithmic shear rate ramp in the range 0.1-100 s^{-1} and measuring the corresponding shear stress. The resulting flow curves $\tau(\dot{\gamma})$ and $\eta(\dot{\gamma})$ provided information on the shear-thinning behaviour of the inks, which was quantified by fitting the $\tau(\dot{\gamma})$ curve with Equation 2.7 (Herschel-Bulkley

[†] All the rheological tests were performed under the assumption that the shear history does not significantly influence the rheological properties of the inks (*i.e.* a steady-state is reached almost instantaneously). Therefore, an initial conditioning was not necessary before starting the experiments, and continuous shear ramps were used in place of constant shear sweep tests. The validity of this assumption was confirmed by thixotropy tests.

model). Lower values of the flow index n correspond to a steeper reduction of viscosity with shear rate and a smaller extrusion pressure. Although it is also possible to determine the yield stress τ_Y from the Herschel-Bulkley fitting of the flow curve, the literature on DIW relies more often on oscillatory tests, since it is difficult to reach a steady state at low rates for an accurate fitting.¹⁴⁷ It has been shown¹⁵⁸ that oscillatory measurements provide a higher estimate of τ_Y than flow tests; thus, for a meaningful comparison with values reported in literature, the yield stress was also determined from oscillatory measurements in this work.

Oscillatory tests: In oscillatory measurements the fluid is subjected to a sinusoidal shear strain $\gamma(t)$, where:

$$\gamma(t) = \gamma_0 \sin \omega t \quad . \quad (2.10)$$

In the limit of small strain amplitudes ($\gamma_0 \ll 1$), the microstructure of the material is not significantly disturbed by the deformation, and the resulting response of the material is linear.¹⁵⁷ The range of strain amplitudes at which the material has a linear response is known as the linear viscoelastic (LVE) region. Inside the LVE region, the measured shear stress is also sinusoidal, but it is shifted of a phase angle δ :

$$\tau(t) = \tau_0 \sin(\omega t + \delta) = \tau'_0 \sin \omega t + \tau''_0 \cos \omega t \quad . \quad (2.11)$$

It is possible to introduce two dynamic moduli, an in-phase dynamic modulus G' known as the storage modulus:

$$G' = \frac{\tau'_0}{\gamma_0} \quad , \quad (2.12)$$

and an out-of-phase modulus G'' , known as the loss modulus:

$$G'' = \frac{\tau''_0}{\gamma_0} \quad . \quad (2.13)$$

The storage modulus accounts for the elastic effects during shear, *i.e.* the reversible storage of energy resulting from the deformation of the material. On the other hand, the loss modulus is a measure of the irreversible changes in the microstructure of the material during shear, resulting in the viscous dissipation of the deformation energy, for example by frictional forces between partially mobile fluid domains.¹⁵⁹ A similar discussion is valid if a sinusoidal stress is applied to the material and the material strain response is measured.

Oscillatory tests were used to characterize the viscoelastic properties of the inks in the solid regime ($\tau < \tau_Y$) and the transition to the liquid regime ($\tau = \tau_Y$). During frequency-sweep tests, a small-amplitude sinusoidal strain ($\gamma_0 \approx 0.1\%$) was applied to the sample and the frequency of the oscillation $f = 2\pi\omega$ was swept between 0.1 and 100 Hz, while measuring the dynamic moduli as a function of f . The value of γ_0 was sufficiently small to fall within the LVE region of the inks (as confirmed by amplitude-sweep tests), but to still retain a good noise-to-signal ratio for the stress measurements. Since the microstructure of the inks is not significantly altered by frequency-sweep tests, they were used to probe the dynamic properties in the solid regime. Conversely, amplitude-sweep tests provided information on the limit of the LVE region and the value of yield stress. In amplitude-sweep tests, a sinusoidal stress at a fixed frequency $f = 1$ Hz was imposed on the sample, sweeping the oscillation amplitude between 1 and 10^4 Pa. When the imposed stress becomes sufficiently large, the microstructure of the ink starts breaking down, and the storage modulus departs from a constant plateau, indicating the transition from a linear to a nonlinear response.¹⁶⁰ The crossover point of the viscoelastic moduli in amplitude-sweep tests, $G'(\tau_0) = G''(\tau_0)$, is usually interpreted as the yield stress of the material, indicating the transition from a solid to a liquid regime.¹⁴⁷ However, since this crossover point often falls beyond the limit of the LVE region, the yielding process has typically already started and the data measured are highly nonlinear. For this reason oscillatory tests tend to overestimate the value of yield stress, even though they are more

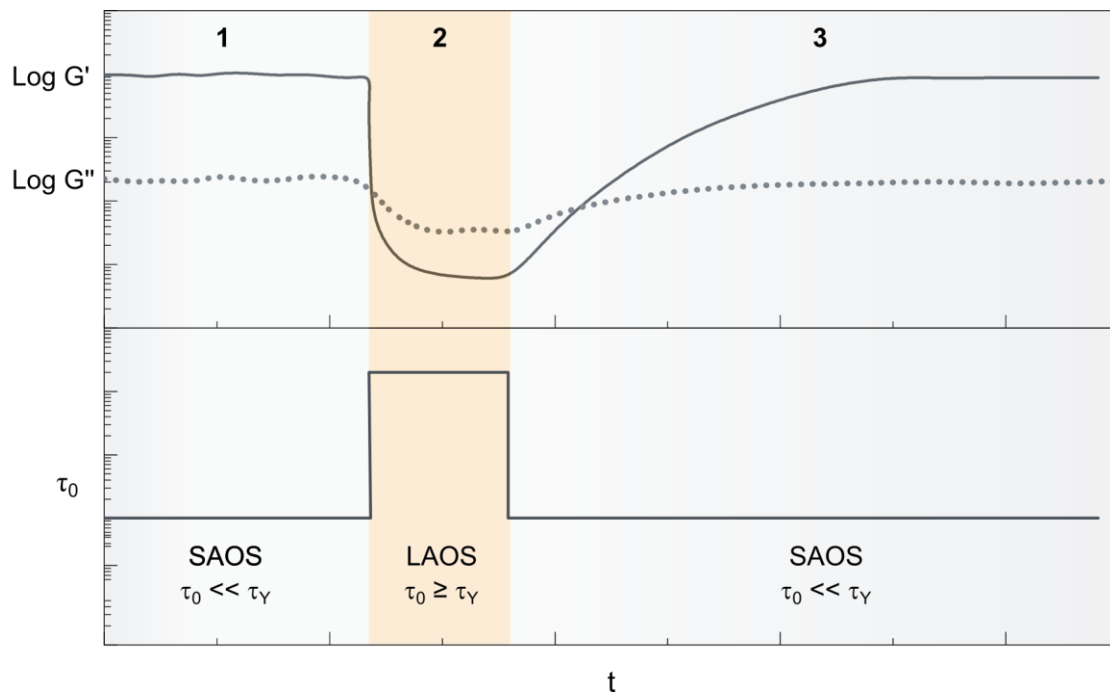


Figure 2.4: Three-interval thixotropy test consisting of three steps: (1) equilibration step at small amplitude oscillatory shear (SAOS); (2) destructuring step at a large amplitude oscillatory shear (LAOS); (3) recovery step at small amplitude oscillatory shear.

reliable and provide more consistent results when compared to other techniques.^{158,160} Outside the LVE region, *i.e.* in the proximity of the yield point, the conventional definitions of storage and loss moduli provided in this section do not hold true, because the material response is not sinusoidal. Nonetheless, even outside the LVE region, it is still possible to define first-harmonic moduli considering the fundamental frequencies in the Fourier expansion of the non-linear response.¹⁶¹

Thixotropy tests: Since small amplitude oscillatory measurements are non-destructive, they can be used to study the degree of structure λ of the inks over time. In particular, three-interval thixotropy tests (3ITTs) were used in this work to study the recovery kinetic of the inks after a destructive shearing process.¹⁶² The storage modulus $G'(t)$ was monitored at a fixed frequency of 10 Hz over time to probe the degree of structure of the fluid. The 3ITTs performed in this work consisted of three steps (Figure 2.4): (1) an initial reference interval during which a small amplitude oscillatory stress (τ_0 within the LVE region of the ink) is applied for ~ 120 s; (2) a high shear interval, during which a large amplitude oscillatory stress ($\tau_0 \geq \tau_Y$) is applied for ~ 60 s; (3) a regeneration interval at the same oscillatory conditions as the initial step.^{150,162} In the initial step, the microstructure of the ink is equilibrated and the reference value of G' at rest is recorded. The aim of the second step is to destroy the dynamic bonds that make up the microstructure of the ink, resulting in a sudden drop in G' . This step simulates the high-shear conditions that DIW inks experience during extrusion. Finally, in the last step a non-destructive oscillatory stress is used to probe the recovery rate of the dynamic bonds and the return to the initial level of structure. These conditions are similar to the rest state of the ink after extrusion, when the ink is only subjected to gravity and to the capillary interactions with the substrate. 3ITTs can also be conducted imposing a continuous shear flow and monitoring the viscosity $\eta(t)$ over time. When continuous flow 3ITTs were performed, a low shear

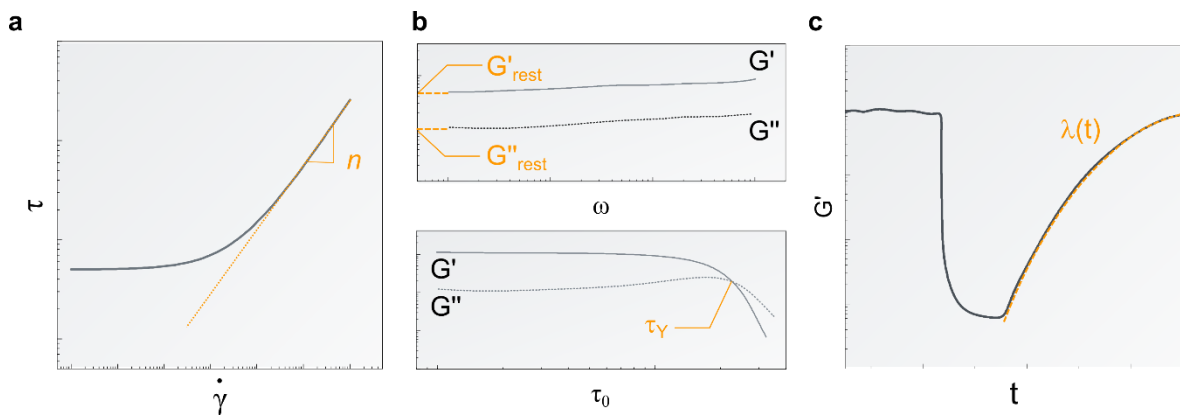


Figure 2.5: Schematic showing the tests to determine the main rheological parameters that describe the printability of DIW inks: (a) flow curves, which provide information on the flow index n ; (b) oscillatory tests, providing information on the viscoelastic moduli at rest and on the yield stress; (c) three-interval thixotropy tests, providing information on the thixotropy of the inks and the restructuring kinetic.

rate of 0.1 s^{-1} was applied in step 1 and 3, whereas a high shear rate of 100 s^{-1} was applied in step 2. The same experimental conditions for 3ITTs were applied when comparing different inks (either oscillatory or flow tests), since the restructuring process can follow different paths depending on the shear condition applied to the material in step 2.¹⁶³

A schematic showing the rheological properties that can be determined from the tests discussed in this section and typical experimental trends for DIW inks are presented in Figure 2.5.

After rheological analysis, the printability of the graphene inks was also assessed measuring the printability index from SEM pictures of the woodpile structures, following the procedure described by Kyle *et al.*¹⁶⁴ For this purpose, a 6-layer woodpile structure (design presented in Section 2.5) was imaged after drying and the printability index was measured for each central square holes of the structure. The holes adjacent to the external side were excluded because they present geometric distortion associated with the sudden change of printing direction, which are not directly related to the rheological properties of the ink during extrusion. The average of the printability indices obtained with this procedure was taken as the printability index of the structure.

3.2. CFD simulation

The extrusion of DIW inks throughout the printing head is not a simple shear flow, because at least two components of the velocity vector are non-zero. Therefore, to simulate the flow of DIW inks during extrusion, a more general form of the Herschel-Bulkley model (Equation 2.7) was considered:

$$\boldsymbol{\Sigma} = \left(\frac{\tau_Y}{|\dot{\boldsymbol{\gamma}}|} + K|\dot{\boldsymbol{\gamma}}|^{n-1} \right) \dot{\boldsymbol{\gamma}} \quad , \quad (2.14)$$

where $\dot{\boldsymbol{\gamma}}$ is the shear rate tensor and $\boldsymbol{\Sigma}$ the stress tensor. This is the form of the Herschel-Bulkley model that was used for CFD simulations throughout this work, with a Papanastasiou regularization to avoid discontinuities in the viscosity function.¹⁶⁵ The values for the yield stress τ_Y , the viscosity parameter K and the flow index n were obtained from a Levenberg-Marquardt least square fitting of the experimental flow curves $\tau(\dot{\gamma})$. No-slip boundary conditions were assumed for the lateral walls of the syringe barrel, whereas a constant-velocity inlet (corresponding to a printing speed of 6 mm s^{-1}) was set at the plunger surface. Steady-state flow conditions were considered, since flow initiation transients only affect the initial part of the printed structure, usually a dummy line removed during postprocessing. The CFD simulations were performed with Ansys Fluent 2021 R1 software with a maximum iteration/time step of 200.

4. Physical characterization

The electroactive materials used to formulate the inks and the 3D printed structures were analysed using a combination of physical characterization tools, including electron microscopy, X-ray diffraction, X-ray computed tomography, Raman spectroscopy and X-ray photoelectron spectroscopy. Additional physical properties that are relevant for the integration of the 3D printed structures into electrochemical cells, *e.g.* specific surface area, conductivity and mechanical properties, were also measured. This section will provide the basic principles behind these characterization techniques and describe the methods for sample preparation and analysis.

4.1. Scanning electron microscopy and cryo-SEM

Scanning electron microscopy (SEM) is an imaging technique that relies on the scattering of a focussed electron beam by the atoms of the sample to produce a magnified view of the sample topography. The electron beam is typically produced inside an electron gun by a thermionic or Schottky emitter or by a field emission tip (Figure 2.6-b).¹⁶⁶ The emitted electrons are accelerated by an electric field (V_{EHT} in Figure 2.6-b), producing a beam with energy between 0.1 and 30 keV parallel to the optic axis. Before impacting onto the sample, the electron beam is modified by a series of electrostatic and magnetic condenser lenses and focussed onto the sample surface by an objective lens, providing an electron probe with a final diameter around 1-10 nm.¹⁶⁶ To form an image, the electron probe is deflected by two magnetic coils and scanned in two perpendicular orientations in a raster pattern. The image is built by assigning to each position of the raster pattern a greyscale value, corresponding to the intensity of the signal detected from that position.

The interaction of the primary beam with the atoms of the sample results in both elastic and inelastic scattering events. The former alter the trajectory of the primary electrons but preserve their energy; whereas the latter transfer part of the energy of the primary beam to the atoms of the specimen. The electrons that emerge from the specimen surface after elastic scattering events are known as *backscattered electrons* (BSE). They typically present high energies and they can therefore escape from deeper regions inside the specimen (Figure 2.6-a). Although the deep escape volume of BSE is unfavourable to achieve high spatial resolution, these electrons carry important information on the chemical composition of the specimen, since the probability of elastic scattering strongly depends on the nuclear charge, *i.e.* on the atomic number Z , of the scattering atoms.¹⁶⁷ Unlike elastic scattering, in inelastic scattering events the energy of the primary beam is transferred to the atoms of the sample, causing the ejection of weakly-bound electrons from outer shells, known as *secondary electrons* (SE), or the ejection of inner-shell electrons, usually followed by the emission of characteristic X-rays. Additional inelastic scattering events that typically occur inside the specimen are the deceleration of primary electrons, which causes the emission of a continuum X-ray radiation,

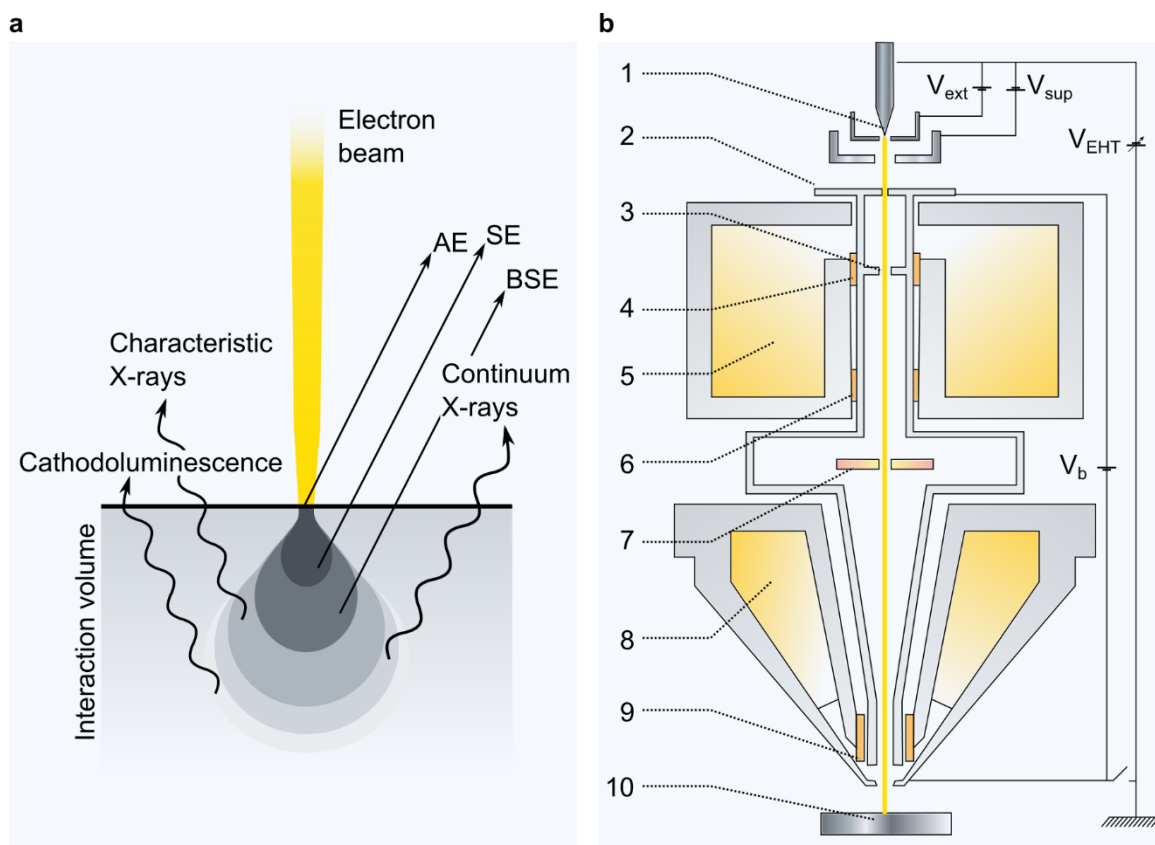


Figure 2.6: (a) Diagram showing the results of the interaction of an electron beam with a thick specimen, including secondary electrons (SE), backscattered electrons (BSE) and Auger electrons (AE), adapted from ref.³⁸¹ (Copyright Ponor, CC BY-SA 4.0, via Wikimedia Commons); (b) schematic of the cross-section of the SEM used throughout this work: (1) Schottky field emitter; (2) anode; (3) multi-hole aperture; (4) gun alignment system; (5) condenser lens; (6) stigmator; (7) in-lens detector; (8) electromagnetic objective lens; (9) scan coils and stigmator; (10) specimen.

and the generation of plasmons and phonons. Secondary electrons are ejected at low kinetic energy (< 50 eV), thus only the ones produced in the proximity of the surface can escape the specimen (Figure 2.6-a).¹⁶⁷ Owing to the low escape depth of secondary electrons (only a few nanometres vs. 100-1000 nm for backscattered electrons), they provide topographical contrast and enable high-resolution imaging of the surface structure of the sample.^{166,167} In particular, the surface features that are oriented towards the detector appear brighter, since the probability that the SE emitted by these surfaces reach the detector is higher. The secondary electrons leaving the sample are typically captured by an Everhart-Thornley detector, consisting of a scintillator that converts the electrons into visible photons and a photomultiplier tube that converts the photons into an electric signal corresponding to the initial SE intensity.¹⁶⁶ In high resolution SEM, the specimen lies within the magnetic field generated by the objective lens (*in-lens* SEM, Figure 2.6-b), therefore the secondary electrons spiral up through the objective field to reach the detector, which is usually positioned above the objective lens. In-lens detectors achieve higher spatial resolution and lower directional shadowing, by filtering out BSE and low-resolution SE generated far from the optical axis.¹⁶⁷

The characteristic X-rays produced by the inelastic interactions between the primary beam and the sample atoms carry information on the elemental composition of the sample. These characteristic X-rays can be detected by an energy dispersive X-ray spectrometer (EDS), usually consisting of a semiconductor detector. When the X-rays are absorbed in the detector, they excite electron-hole pairs resulting in a current pulse that can be measured by an external circuit.¹⁶⁷ The number of electron-hole pairs generated is proportional to the energy of the absorbed photon. It is thus possible to track the EDS spectrum as a histogram, reporting the number of photons detected per energy interval. The EDS spectrum typically contains peaks at characteristic energies, which allow the identification of the elements present in the sample at the location of the electron probe, and a continuous background, originating from the braking radiation. EDS spectra can also be used to quantitatively assess the chemical composition of the sample under investigation. However, quantification in SEM is complicated by the reabsorption of the X-rays inside the interaction volume and by the consequent emission of X-rays at lower energy (X-ray fluorescence), which depends on the unknown composition of the sample.¹⁶⁶ Considering these complications, EDS analysis was only employed in this work to qualitatively determine the elemental distribution inside the specimens.

The samples for SEM analysis were prepared by cutting the specimen, *i.e.* the printed electrodes or metal foil anodes, with a razor blade and mounting them on aluminium stubs using conductive carbon tape. The powders of active materials were either dried and fixed on the stub using carbon tape or dispersed in ethanol and directly drop-casted on the stub surface. Insulating specimens were coated with a thin layer of chromium (~ 10 nm) by sputter deposition immediately before the analysis, in order to prevent charging artifacts. The imaging and elemental analysis were performed on a Leo Gemini 1525 field-emission SEM and on a Zeiss Auriga field-emission SEM (Carl Zeiss), equipped with an Oxford Instruments INCA EDS detector. Imaging was performed at an accelerating voltage of 5-10 kV and at a working distance 5-7 mm, using an in-lens secondary electron detector. Elemental EDS mapping and point analysis were acquired at an accelerating voltage of 10 kV.

Conventional scanning electron microscopy requires high vacuum conditions ($< 10^{-4}$ Pa) to avoid the scattering of electrons by gas molecules. As a consequence, it is not possible to study the microstructure of the inks in the wet state, *i.e.* before removing the liquid phase that disperses the particles of active materials and the other solid components. The microstructure of wet DIW inks is directly related to their rheological properties and printability, and it can provide insight into the processes that occur during flow and deposition, as discussed in Chapter 4. For this reason, the water-based inks formulated in this work were also analysed using cryo-SEM. Cryo-SEM allows the imaging of hydrated samples after freezing in ultra-low temperature. The samples are typically plunged into slush nitrogen (*i.e.* a mixture of solid and liquid nitrogen $\sim -200^\circ\text{C}$), causing the solidification of water to an amorphous glass-like state.¹⁶⁸ The growth of ice crystals, that might alter

the morphology of the sample microstructure is therefore prevented. The samples are then fractured with a blade to expose the internal structure, the topmost layer of water is sublimated, and they are vacuum-transferred to the SEM chamber for imaging.¹⁶⁹

Samples for cryo-SEM were prepared using a Quorum preparation chamber (PP3010T, Quorum Technologies, UK), following the procedure described by Constantinou *et alii*.¹⁶⁹ The inks were frozen in slush nitrogen (produced with the freeze-thaw method by reducing the pressure of liquid nitrogen) and then transferred to the preparation chamber, where they were fractured and the surface water was sublimated for 5 min at -90°C. The samples were transferred to a Zeiss Auriga field-emission SEM (Carla Zeiss) and imaged at 5 kV at a working distance of ~ 5 mm. The cryoSEM measurements were performed at the centre for electron microscopy (Department of Materials, Imperial College London) with the help of Dr Martina Cihova and Ms Victoria Garcia Giner.

4.2. Transmission electron microscopy

Transmission electron microscopy (TEM) is a microscopy technique that provides morphological, compositional and crystallographic information about the specimen, relying on the interaction of the specimen atoms with a high energy electron beam. Similarly to SEM, the beam is generated by a thermionic or Schottky emitter, and goes through a series of electromagnetic lenses, apertures and stigmators before hitting the specimen. The electrons of the primary beam present however higher energy than SEM (~ 100-300 keV), so they can be transmitted through the sample, usually having a thickness < 100 nm.

During transmission, the electrons of the primary beam can undergo elastic or inelastic scattering with the specimen atoms, similarly to what happens in SEM. The contrast in TEM images is produced either from variations in the amplitude of the incident electron beam or from variations in its phase after scattering.¹⁷⁰ Amplitude contrast typically arises from differences in the atomic mass or thickness of the sample, resulting in a different probability of electron absorption in different regions of the specimen. Phase contrast is instead determined by the interference between electrons that have travelled along different paths in the material, and it is typically used for high-resolution transmission electron microscopy (HR-TEM).¹⁶⁶ In crystalline materials, the contrast arising from the elastic scattering of electrons can be better described in terms of Bragg's diffraction (discussed in the next section). In this case, the angular probability of a scattering event is not continuous, but it presents sharp peaks corresponding to the orientation of those crystallographic planes that satisfy Bragg's law. In selected area electron diffraction (SAED), a portion of the beam corresponding to a certain area of the specimen is selected using an appropriate aperture. The resulting electron diffraction pattern provides information on the crystal structure and orientation of the selected area.

In this work, TEM was used to obtain morphological and crystallographic information about graphene nanoplatelets, vanadium disulfide and manganese oxide, used as active materials for DIW inks. TEM samples were prepared by dispersing the dried powders in ethanol and drop-casting them

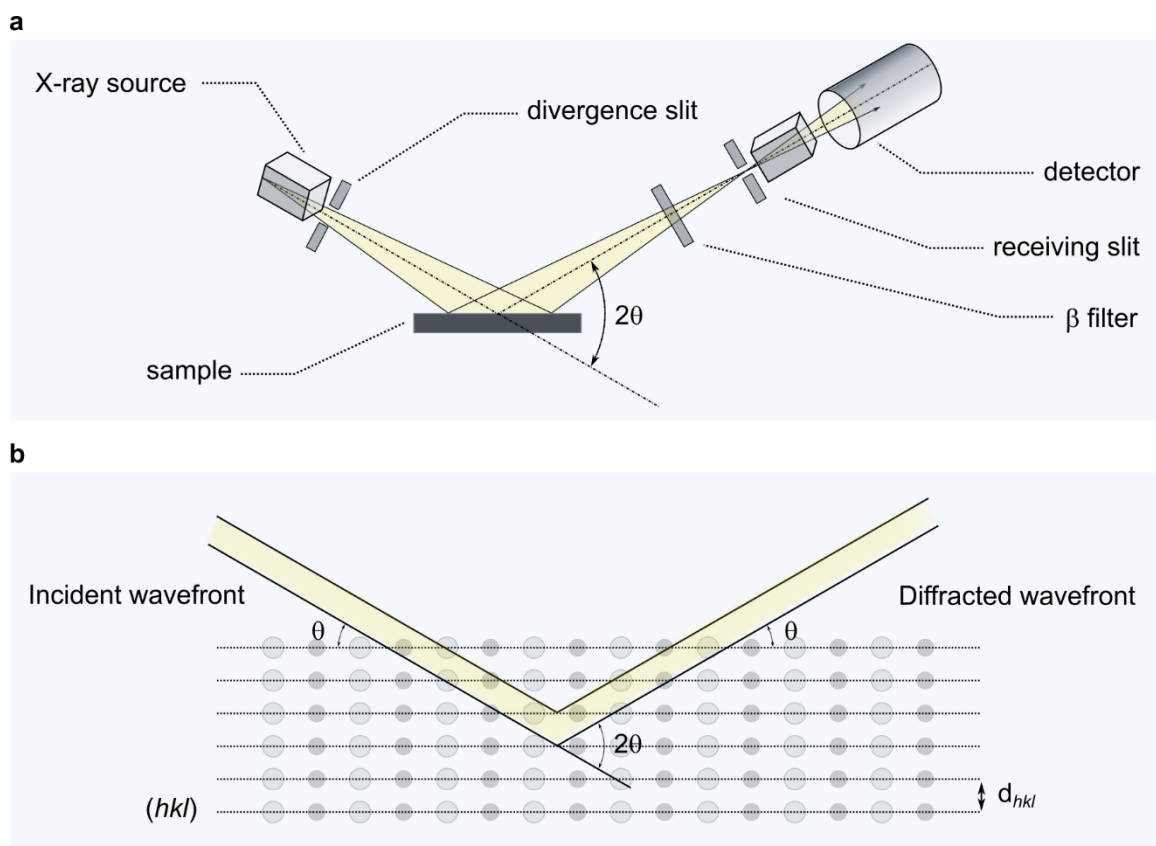


Figure 2.7: (a) Schematic of an X-ray powder diffractometer equipped with a point detector; (b) diffraction of an incident X-ray wavefront by the (hkl) crystallographic planes of the sample, assuming that atomic planes behave as semi-reflecting mirrors.

on carbon-coated copper grids (Agar Scientific). The samples were imaged using a JEOL JEM-2100F TEM with a field emission gun operated at a 200 kV accelerating voltage. Dr Maria Sokolikova and Mr Gang Cheng assisted with the TEM measurement performed in this work.

4.3. X-ray diffraction

X-ray diffraction (XRD) provided information on the crystal structure of the electroactive materials and, in combination with EDS, it was used for the *ex-situ* analysis of the electrodes after electrochemical cycling. In powder diffraction experiments, a monochromatic X-ray beam hits a powder sample or a flat polycrystalline film, which diffracts the incident photons. The intensity of the diffracted beam is measured as a function of the angle between the primary beam and the detector (2θ in Figure 2.7-a). The diffraction of X-rays from a crystalline specimen can be described as a specular reflection by a set of crystallographic planes with Miller indices (hkl) , presenting a spacing d_{hkl} .[‡] A diffracted beam is produced when the reflections from the set of planes (hkl) interfere constructively (Figure 2.7-b), namely when:¹⁷¹

[‡] The simplified assumption that atomic planes behave as semi-reflecting mirrors for X-rays leads to the same results as a more rigorous discussion, requiring that the X-rays scattered from each atom in the plane interfere constructively.

$$2d_{hkl} \sin \theta = n\lambda \quad , \quad (2.15)$$

where n is an integer and λ is the incident radiation wavelength. This condition is known as Bragg's law.

In a typical diffractometer, the X-ray beam is produced by an X-ray tube, either a conventional sealed tube or a rotating anode tube. In the former, a stationary anode (usually a tungsten filament) and a metallic cathode are sealed under vacuum inside a ceramic container, presenting a beryllium window transparent to X-rays. The cathode is electrically heated, resulting in the emission of electrons that are accelerated towards the cathode by a high electric potential (30-60 kV).¹⁷² When the electrons hit the metal cathode they generate X-rays, that escape the tube through the beryllium window. The anode must be continuously cooled with water to avoid meltdown. The radiation generated when the electron beam hits the anode consists of a continuous background (braking radiation) and intense and sharp peaks associated with the characteristic transitions of outer-shell electrons to vacant lower-energy levels.¹⁷² The $K\alpha$ radiation (corresponding to the transition from L to K shells) is usually considered for X-ray diffraction, while the other components can be filtered out using a monochromator. The $K\alpha$ radiation consists of two distinct lines $K\alpha_1$ and $K\alpha_2$ at characteristic wavelengths as a consequence of spin-orbit splitting.

The diffracted X-rays are collected by an X-ray detector, usually a solid-state detector consisting of a high purity silicon crystal doped with lithium. The absorption of an X-ray photon from the detector generates a number of electron-hole pairs proportional to the energy of the photon. If an electric potential is applied across the crystal, this results in an electric current in the external circuit that is proportional to the number of the electron-hole pairs.

A Bruker D2 diffractometer was used for the XRD analysis of the active materials and electrodes. The diffractometer was equipped with a Cu X-ray tube, producing a radiation with wavelength 1.54184 Å (Cu $K\alpha_{1,2}$ radiation). The other spectral lines were eliminated using a digital monochromator. Powder samples were loaded into a cavity holder and the surface of the specimen was flattened using a glass slide, whereas film specimens were directly attached to a zero-background silicon holder. The diffractogram were recorded in the 2θ range 6-60°, with a step size of 0.034°. Peak identification and phase analysis was performed using HighScore Plus (Malvern Panalytical), comparing the position and intensity of the experimental diffraction peaks with the diffractograms in the ICDD PDF-4 database.

4.4. X-ray computed tomography

X-ray computed tomography (XCT) is a non-destructive imaging technique that provides information on the three-dimensional structure of a specimen. XCT was employed here to visualize the

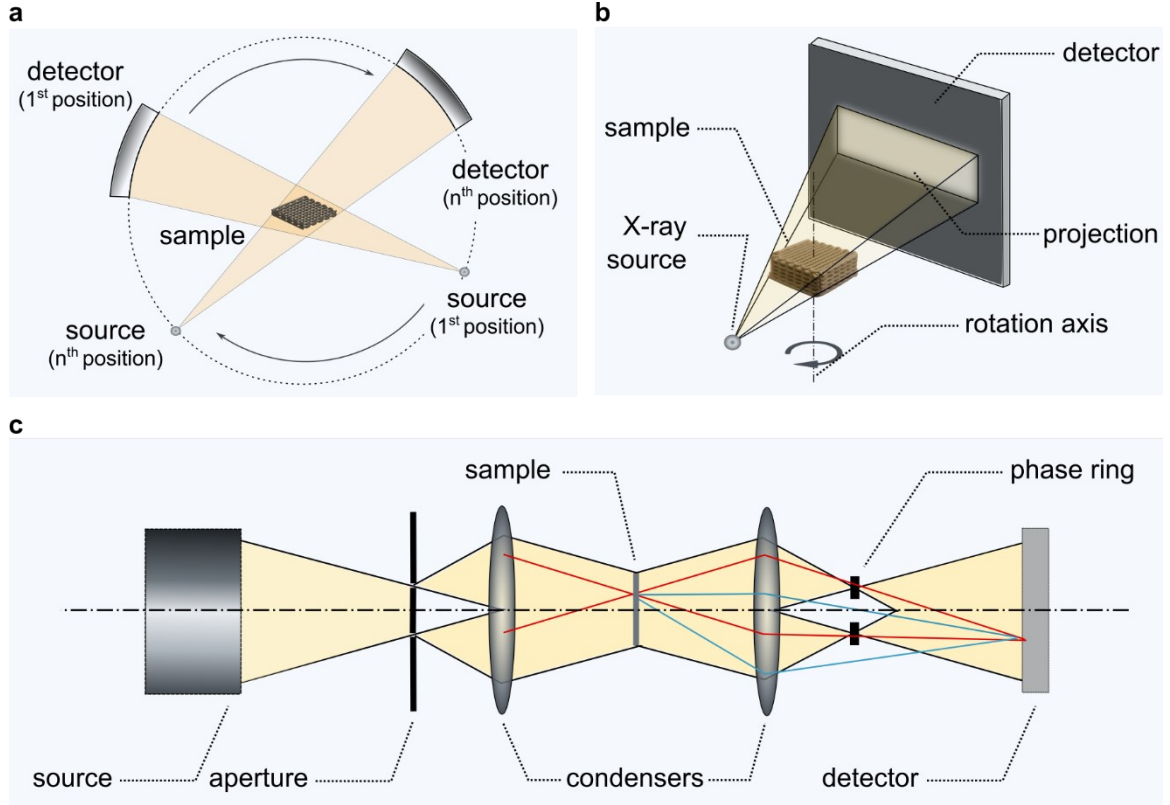


Figure 2.8: (a,b) Schematics showing the acquisition of X-ray projections at different angular positions in an X-ray Computed Tomography experiment; (c) principle of Zernike phase contrast, showing an undiffracted X-ray beam (red) that is phase-shifted with respect to a diffracted beam (green) by the phase ring, causing a modulation in the radiation intensity reaching the detector (adapted with permission from ref.¹⁷⁶, Copyright 2010, Springer Nature Limited).

internal structure of the printed electrodes and obtain quantitative information on the size, distribution and morphology of their features.

In a typical XCT analysis, the specimen is irradiated with X-rays from different viewing directions, producing a set of 2D radiographic projections (Figure 2.8-a). The 3D structure of the specimen is then reconstructed from the projections by a computed algorithm.¹⁷³ Typical XCT instruments use a cone-beam acquisition setup, consisting of three main components: (i) an X-ray source, (ii) a detector and (iii) a set of mechanical axes that control the position and orientation of the sample (Figure 2.8-b). When the X-rays generated by the source pass through a sample, they are refracted and absorbed depending on the nature of the material, as described by its complex refractive index n :¹⁷³

$$n = 1 - \delta + i\beta \quad . \quad (2.16)$$

Here β accounts for the attenuation of the radiation caused by absorption and δ describes the phase shift when the X-rays pass from one medium to the other. In attenuation contrast XCT, the contrast in each radiographic projection is the result of the attenuation of the beam by the different material phases in the specimen. This type of imaging can be used for specimens containing phases with

great difference in electron density, since the attenuation coefficient strongly depends on the atomic number.¹⁷³ For lighter elements with similar absorption coefficients, for example carbon-based materials, phase-contrast XCT can provide better contrast and more detailed projections. If the X-ray source is sufficiently coherent, it is possible to detect the phase shift of the incoming X-rays when they pass through regions with different electron density.¹⁷⁴

In conventional XCT systems, the transmitted X-rays are generated by X-ray tubes, similar to the ones described in Section 4.3. Since X-ray tubes emit a conical radiation, the geometrical magnification of the final tomogram can be changed by moving the sample closer to the source (Figure 2.8-b).¹⁷³ MicroCT X-ray tubes are usually able to provide a radiation that is coherent enough to perform phase-contrast imaging. After passing through the specimen, the X-rays are collected by an area detector, and attenuation or phase contrast are exploited to produce a 3D tomogram. The detectors used in XCT for attenuation imaging are usually scintillation detectors, which convert the X-rays into visible light and detect the visible photons with a photomultiplier.^{174,175} Several techniques can be used to detect the phase shift of the X-ray beam for phase-contrast imaging. In the Zernike phase contrast method, a ring is placed inside the beam to impart a phase shift to the unscattered beam (Figure 2.8-c). The interference between the phase-shifted unscattered beam and the scattered beam transforms the phase shift into a modulated intensity image.¹⁷⁶ After collecting a set of radiographic projections, the spatial distribution of the absorption coefficient $\beta(x, y, z)$ – or of $\delta(x, y, x)$ for phase contrast XCT – is determined using computed reconstruction methods, often based on iterative algorithms or deep learning methods. Iterative algorithms start from an initial 3D model of the system that is used to build estimated projections. At each iteration these estimated projections are compared with the real projections measured by the instrument, and the 3D model is refined to reduce the difference between the two sets.¹⁷⁷

The samples for X-ray tomography were prepared by cutting small sections of the 3D printed electrodes with a surgical blade and attaching them to graphite or aluminium rods (Figure 2.9).



Figure 2.9: (a) Printed graphene sample attached to a graphite rod (0.5 mm in diameter) for X-ray tomography (scale bar 500 μm); (b) Printed zinc sample attached to an aluminium rod for X-ray tomography (scale bar 2.5 mm).

Printed graphene electrodes were analysed using a Zeiss Xradia 810 Ultra (Carl Zeiss) in a large-field-of-view mode (65 μm width). The projections were collected in Zernike phase-contrast mode with a 63 nm voxel resolution (central region of the filament) and a 126 nm voxel resolution (outer region of the filament). The XCT experiments on the Zeiss Xradia 810 Ultra were performed by Dr Francesco Iacoviello at the Department of Chemical Engineering, UCL (London), with subvention from the National Research Facility for lab X-ray CT (NXCT). The porosity of the filament was calculated from the high-resolution scan after segmentation by voxel value with Avizo software (Thermo Fisher Scientific), by approximating the void space to a spherical occupancy. The orientation of platelets was computed on the sections of the tomogram perpendicular to the 3D filament axis, using the OrientationJ plugin for ImageJ (FiJI), based on the computation of the gradient structure tensor of the greyscale images. Printed zinc electrodes were analysed using a Zeiss Xradia 620 Versa with a field of view of 961 μm . The radiographic projections were acquired in attenuation contrast, with a 0.48 μm voxel resolution. The XCT experiments on the Zeiss Xradia 620 Versa were performed at the Henry Moseley X-ray Imaging Facility (University of Manchester) with help from Dr Tristan Lowe and under the subvention of the National Research Facility for lab X-ray CT (NXCT)

4.5. X-Ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was used to study the surface composition and the chemical environment of the elements in the cathode active materials. XPS is based on the emission of photoelectrons by the atoms of a sample irradiated with monochromatic soft X-rays, *e.g.* the Al K α radiation (1486.6 eV).¹⁷⁸ When an X-ray photon with sufficient energy is absorbed by the material, it determines the ejection of an electron at a kinetic energy KE (Figure 2.10):^{170,178}

$$\text{KE} = h\nu - \text{BE} - \phi_s \quad , \quad (2.17)$$

where $h\nu$ is the energy of the photon, BE is the binding energy of the orbital from which the electron was ejected and ϕ_s is an instrumental correction factor (the spectrometer work function). Auger electrons are also normally observed in an XPS spectrum, resulting from the electron relaxation of an ion produced by photoemission (Figure 12, left).¹⁷⁰ Since each element has a characteristic set of binding energies, XPS spectra can be used for the elemental identification and quantification of the species in the sample. Additionally, the chemical environment of the atoms can determine a shift in the binding energy of photoelectrons, hence XPS also provides information on the chemical state of the compound analysed. Even though the X-rays used in conventional XPS analysis can penetrate several microns inside the material, only the photoelectrons that are produced a few angstroms below the surface can emerge without significant energy loss.

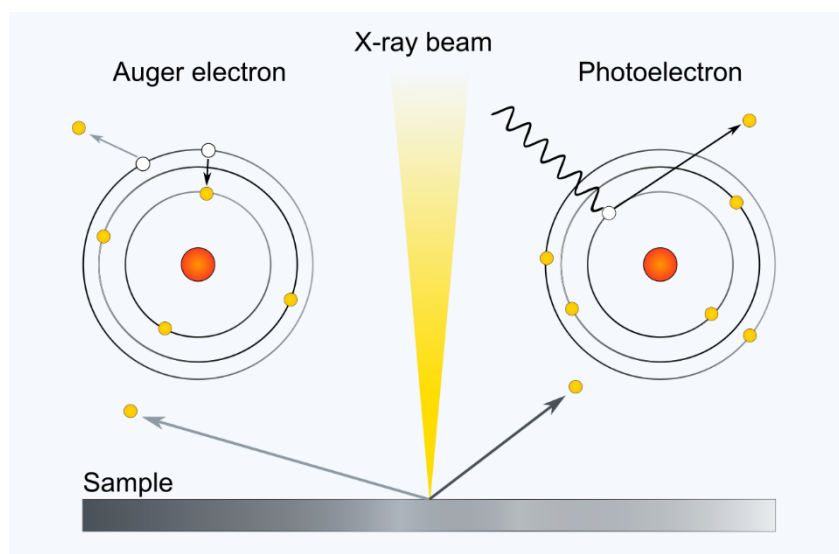


Figure 2.10: Schematic showing the generation of photoelectrons and Auger electrons when an X-ray beam hits the surface of the sample.

The XPS spectra were collected on a Thermo Fisher K-Alpha+ system with an Al K α X-ray source. The samples for the analysis were dispersed in ethanol, drop-casted onto Si/SiO₂ substrates and dried at ambient conditions. Manganese oxide was directly grown on a graphite foil conductive substrate *via* electrodeposition, forming a compact layer ~ 100 μm in thickness. The acquired spectra were analysed using the Avantage software package. Dr Mauro Och assisted with the XPS measurements performed for this work.

4.6. Raman spectroscopy

Raman spectroscopy provided information on the chemical nature and structure of the electrode materials used in this work. In conventional Raman spectroscopy, the sample is irradiated with an intense monochromatic radiation, usually produced by a laser.¹⁷⁹ The incident photons can be scattered either at the same energy of the incident photons (Rayleigh scattering) or at a different energy, *e.g.* when part of the energy is transferred to a phonon (Raman scattering).¹⁷⁹ Following the conservation of energy, the energy difference between the incident and scattered radiation corresponds to the energy difference between the initial and the new vibrational state of the sample, *i.e.* to the energy of the phonon generated. The new vibrational state can have higher energy than the initial one (Stokes scattering), or lower energy (anti-Stokes scattering) when an existing phonon transfers its energy to the scattered photon. However, Stokes lines have higher intensity than anti-Stokes lines, since the probability of Stokes scattering events is higher; therefore only Stokes scattering was considered in this work. In a single scattering process (*first-order* Raman process) the

wavevector of the phonon generated is negligible as a consequence of the conservation of momentum; therefore only phonons near the Γ point of the dispersion relation can be Raman active in first-order processes.¹⁸⁰

In Raman spectra, the intensity of the scattered radiation is conventionally plotted as a function of the Raman wavenumber $\Delta\tilde{\nu}$:

$$\Delta\tilde{\nu} = \frac{1}{\lambda_0} - \frac{1}{\lambda_s} \quad , \quad (2.18)$$

where λ_s is the wavelength of the scattered radiation and λ_0 is the wavelength of the excitation laser. The intensity, position, and shape of the peaks in the Raman spectrum of a material provide information on its crystal structure and composition. Only specific vibrational states can be observed in Raman spectroscopy, determined by selection rules that are obtained from crystallographic or molecular symmetry and quantum mechanics. For example, the polarizability for a Stoke transition should be non-zero to be observed in Raman spectroscopy. In graphite and graphene, only the phonon modes with E_{2g} symmetry (*i.e.* the vibrational modes along the graphene plane) are Raman active, leading to an intense band around 1585 cm^{-1} (G band) associated with first-order processes.¹⁸⁰ A two phonon second-order Raman band (G' band or 2D band) is typically observed around 2700 cm^{-1} , as a result of the emission of two phonons with opposite wavevector. A second-order band is also observed around 1350 cm^{-1} (D band), resulting from a defect-activated scattering process involving one-phonon and one-elastic inter-valley process.¹⁸⁰ The ratio between the intensity of the D and G bands provides information on the concentration of defects in sp^2 carbon materials.

Raman spectra were acquired on a Renishaw inVia Qontor confocal Raman microscope at a wavelength of 532 nm and at a laser power of 0.5 mW, performing 10 consecutive acquisitions to reduce the noise. The samples were dispersed in ethanol and then drop-casted on Si/SiO₂ substrates. The Raman spectra were calibrated with respect to the peak of crystalline Si at 520 cm^{-1} . The Raman peaks of graphene nanoplatelets were fitted using a Lorentzian model in OriginPro 2020 (OriginLab Corporation). Ms Rachael Quintin-Baxendale and Dr Mauro Och assisted with the Raman measurements performed in this work.

4.7. Mechanical tests

The mechanical properties of the printed structures were determined *via* compression tests performed on a universal testing machine (UTM). In a UTM a platen or a clamp connected to the instrument frame is moved at a controlled rate, exerting a load onto the specimen. The load is measured using a strain-gauge load cell, which translates the force detected into an output voltage signal.¹⁸¹ In compression tests an increasing compression load is applied to the specimen, until break or until a predefined level of load is reached.

The mechanical tests were performed on a Zwick/Roell Z010 universal testing machine equipped with stainless steel compression platens. Compression tests were performed at a constant displacement rate of $\sim 0.5\text{-}1\text{ mm min}^{-1}$ until break on freestanding woodpile structures ($\sim 1\text{ cm}^2$ footprint area). A preload of 10 N was applied before starting the measurements.

4.8. Nitrogen adsorption

Gas adsorption was employed to evaluate the specific surface area and the pore size distribution of the active materials for printed energy storage systems. Nitrogen gas (N_2) can be physically adsorbed on the surface and into the pores of a specimen, owing to the attractive dispersion forces and other molecular interactions between the adsorbent and the solid specimen.¹⁸² According to the Brunauer-Emmett-Teller (BET) theory, at constant temperature the volume of adsorbed nitrogen v is related to the equilibrium adsorption pressure p by the equation:

$$\frac{p/p_0}{v(1 - p/p_0)} = \frac{c - 1}{v_m c} \frac{p}{p_0} + \frac{1}{v_m c} \quad , \quad (2.19)$$

where p_0 is the saturation pressure of nitrogen at the temperature of adsorption, v_m is the volume of an adsorbed monolayer and c is a constant that depends on the energy of adsorption. In a typical nitrogen adsorption experiment, the adsorbed volume of nitrogen v is measured as a function of the pressure p at 77 K. The experimental data are then fitted with Equation 2.19 in order to determine the monolayer volume v_m . The BET surface area can be calculated as:

$$S_{BET} = \frac{v_m}{v_{N_2}} N_A \sigma \quad , \quad (2.20)$$

where N_A is the Avogadro number, v_{N_2} is the molar volume of nitrogen and σ is the cross-section of nitrogen molecules (0.162 nm^2).^{183,184} The BET surface area only provides a rough estimate of the real surface area of the specimen, since the molecular cross sectional area σ depends on the nature of the adsorbent-adsorbate interaction.¹⁸⁴

Nitrogen adsorption experiments were performed on an Autosorb iQ-AG static chemisorption analysis station (Quantachrome instruments). The powder materials were directly loaded in a glass bulb and a glass rod was inserted into the bulb to minimize the dead volume. Dr Alessandra Pinna provided support with the BET measurements performed for this work.

4.9. Thermogravimetric analysis

Thermogravimetric analysis (TGA) gave insight into the decomposition temperature of the polymeric binder used for the 3D printing inks. In TGA, a controlled temperature program is applied to the specimen while monitoring its mass with a microbalance. The specimen is continuously purged

with a gas flow, which determines the type of atmosphere surrounding the specimen during the analysis (inert, reducing or oxidising). The mass loss observed at a certain temperature can be attributed to the removal of volatile components, *e.g.* absorbed moisture, to the formation of reaction products or to the degradation of the specimen.¹⁸⁵

A Netzsch STA 449C was used to perform TGA analysis in inert nitrogen atmosphere. The inks were dried at room temperature and then ground to a powder using an agate mortar. Around 50 mg of the dried powder were loaded in a platinum crucible for the analysis.

4.10. Electrical conductivity measurements

The electrical conductivity of the inks was determined with four probe measurements. The inks were tape casted on glass substrates and dried overnight at room temperature. Four equally spaced contacts were made on the films using conductive silver paint (RS Components). A current ramp was applied between the two outer contacts and the potential fall between the inner contacts was measured using a Gamry Interface 1000 potentiostat. Ten I-V curves were acquired for each measurement. The conductivity of the ink σ was calculated as:

$$\sigma = \frac{L}{A} R \quad , \quad (2.21)$$

where R is the resistance of the film determined from the I-V curves, L is the distance between the inner contacts and A is the film cross-sectional area.

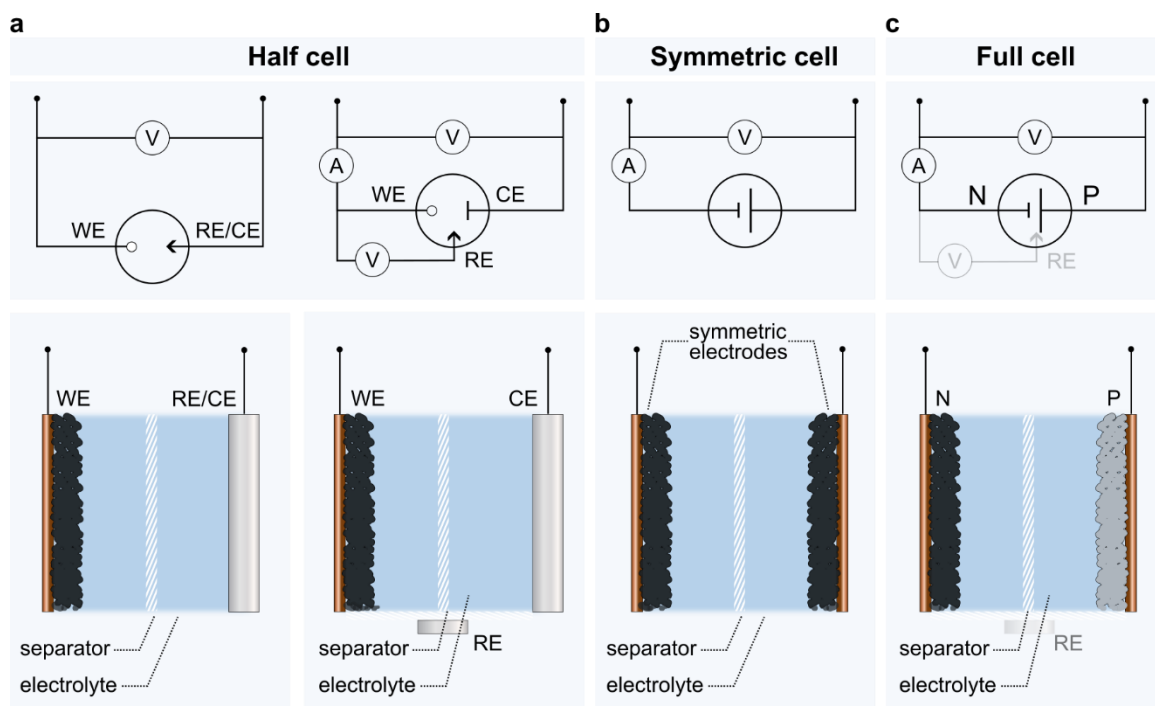


Figure 2.11: Schematic showing the setups employed in this work for electrochemical characterization: (a) half-cell setup, in a two-electrode (left) and three-electrode (right) configuration; (b) symmetric cell setup; (c) full cell setup (a three-electrode cell is possible for this setup but only two-electrode tests were carried out in this work).

5. Electrochemical characterization

The electrochemical properties of the 3D printed structures were characterized for application as electrodes in aqueous batteries and supercapacitors. This section will discuss the experimental setup and testing methods employed to assess the performance of individual electrodes and full cells.

5.1. Cell setup

Three types of cell setups are possible to test the electrochemical properties of energy storage systems: *half cells*, *symmetric cells* and *full cells* (Figure 2.11).¹⁸⁶ Half cells are used to characterize the electrochemical behaviour of active materials and of electrodes of interest, such as their intrinsic capacity, their charge storage mechanism or the electrochemical potential of a certain redox process. Half-cell tests are usually carried out in a *three-electrode configuration*, in which the current flows between the electrode of interest (working electrode) and a counter electrode, while the potential of the working electrode is measured against a suitable reference (Figure 2.11-a, right).¹³ The reference electrode must have a constant and reproducible potential, which is achieved maintaining the activity of all the redox-active species constant near the electrode/electrolyte interface. For example, in a silver/silver chloride (Ag/AgCl) reference electrode, a silver wire is in equilibrium with silver chloride in a potassium chloride solution (typically 3M KCl). The potassium chloride solution stabilizes the activity of the chloride ions, providing a constant potential of 0.210 V vs. SHE (at 25°C).

For the characterization of metal-ion batteries, half-cell measurements are often conducted in a *two-electrode configuration* (Figure 2.11-a, left), where a piece of metal foil is simultaneously used as the counter and reference electrode.[§] Half-cell measurements were used in this work to characterize the capacity, rate capability, reaction kinetics and operating potential of cathode materials and the capacitance, rate capability and operating potential of graphene electrodes for supercapacitors.

In symmetric cell measurements, two identical electrodes are tested in a two-electrode configuration, acting as the positive and negative electrode, respectively (Figure 2.11-b). A symmetric-cell setup was used in this work to characterize the stability and ageing mechanisms of zinc electrodes and the ionic conductivity of zinc electrolytes.

Full-cell measurements are used to assess the properties of electrochemical energy storage devices for practical applications. In a full-cell setup, the potential of both the negative and the positive electrode changes during electrochemical testing, depending on the charge and discharge conditions.¹⁸⁶ Although a reference electrode can be used to monitor the potential variation of the positive and negative electrode, full-cell measurements are more often carried out in a two-electrode configuration, directly measuring the cell voltage (Figure 2.11-c). In the case of symmetric supercapacitors, *i.e.* supercapacitors consisting of electrodes made of the same active material, the full-cell and symmetric-cell setup are equivalent, at least for the purpose of this work. It should be noted that, even in symmetric supercapacitors, the mass ratio between the positive and negative electrodes can be optimized to enhance the device capacitance. In particular, the size of hydrated anions and cations in the electrolyte is typically different, hence the surface area accessible to each species also differs.⁸ Nonetheless, in this work we decided to test symmetric supercapacitors made of identical electrodes (*i.e.* same mass and geometry for the positive and negative electrode). Our rationale for adopting this approach was to ensure the direct comparability of our results with those reported in the literature on 3D printed symmetric supercapacitors, where electrodes with the same mass are employed.

3D printed graphene electrodes were tested in a half-cell setup with a three-electrode beaker cell, consisting of an Ag/AgCl (3M KCl, RE-5B from BASi) reference electrode and a 1 cm² graphite foil (0.01in, 99.8%, Alfa Aesar) counter electrode. The electrochemical properties of the graphene electrodes were measured in different electrolytes, namely 1 M LiOH, 1 M KOH, 1 M NaOH, 1 M Li₂SO₄. Full-cell symmetric supercapacitors were tested in a two-electrode beaker cell, using two identical 3D printed woodpile structures as the positive and negative electrodes, respectively (Figure 2.12-a). For application in wearable devices, graphene electrodes were further characterized in a full-cell interdigitated setup, where two interdigitated electrodes were simultaneously printed

[§] Despite the widespread application of this testing method, the potential of the metal counter/reference electrode can be considered constant only at small current densities, owing to the ohmic drop in the electrolyte and other sources of overpotential at the metal electrode. Therefore, this setup does not allow accurate control over the potential of the working electrode.

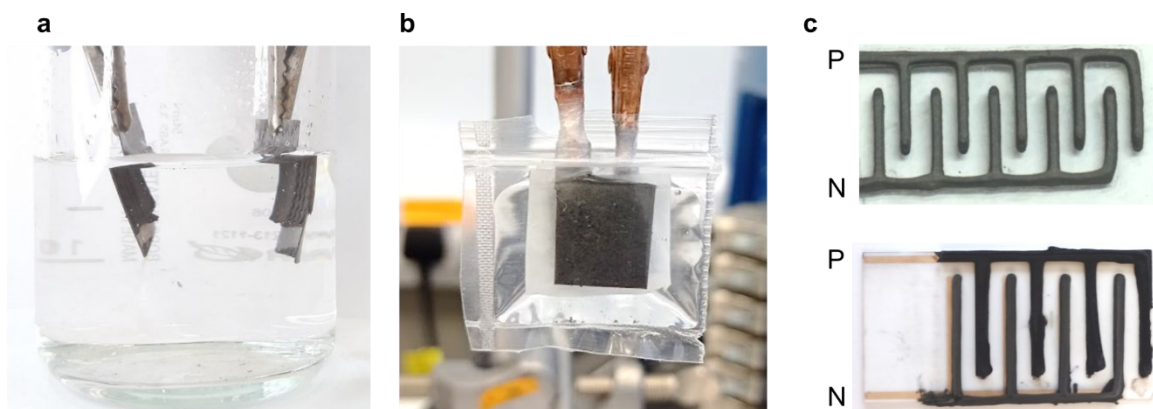


Figure 2.12: (a) Testing of graphene electrodes in a symmetric setup (beaker cell); (b) testing of a zinc hybrid capacitor in a full cell setup (pouch cell); (c) interdigitated symmetric graphene supercapacitor (top) and zinc ion battery (bottom).

on an insulating glass substrate (Figure 2.12-c, top). The interdigitated electrodes were contacted using conductive silver paint (RS PRO Silver Conductive Lacquer, RS Components), which was applied on the side of the interdigitated structures and covered with Kapton tape (Hi-Bond HB830 Amber Polyimide Film, RS components) to avoid contact with the electrolyte. A gel electrolyte was prepared dissolving polyvinyl alcohol (Mowiol 56-98, Mw ~ 195,000, Sigma-Aldrich) and LiOH (98%, Sigma Aldrich) in deionized water (~18 MΩ cm) in a 2:1:20 mass ratio. The gel electrolyte was poured between the interdigitated electrodes and the cells were sealed with parafilm to avoid water evaporation

The 3D printed electrodes for zinc-ion batteries were characterized in a two-electrode pouch-cell configuration, consisting of LDPE pouch bags filled with the electrolyte (2 M ZnSO₄ or 30 m ZnCl₂), Figure 2.12-b. Molality (m, *i.e.* the number of moles of solute per mass of solvent in kg) is used for the concentration of the ZnCl₂ water-in-salt electrolyte instead of molarity (M), following the standard convention in the literature, owing to the difficulty to accurately measure the volume of concentrated electrolytes with high viscosity. Glass microfiber separators (Whatman) were employed to avoid short-circuits between the electrodes. Symmetric-cell measurement using two zinc electrodes (either 3D printed electrode or commercial zinc metal foils, 99.98% from Alfa Aesar) were used to determine the plating-stripping overpotential and stability of the zinc anodes. The cathode materials for ZIBs (manganese oxide and vanadium disulfide) were initially tested in a half-cell configuration, with a zinc foil reference/counter electrode (thickness 0.25mm, 99.98%, from Alfa Aesar). The practicality of 3D printed electrodes for real applications was then assessed by assembling full-cells consisting of a 3D printed zinc anode coupled with a 3D printed cathode. For the characterization of full zinc-ion batteries, unbalanced full-cells with excess anodic mass were employed following the literature on zinc-ion batteries.¹⁸⁷ The choice of oversized anodes in aqueous zinc batteries increases the Coulombic efficiency of the cell,¹⁸⁸ without causing the safety issues observed in unbalanced lithium-ion batteries.¹⁸⁹ Zinc ion batteries were also tested in a full-

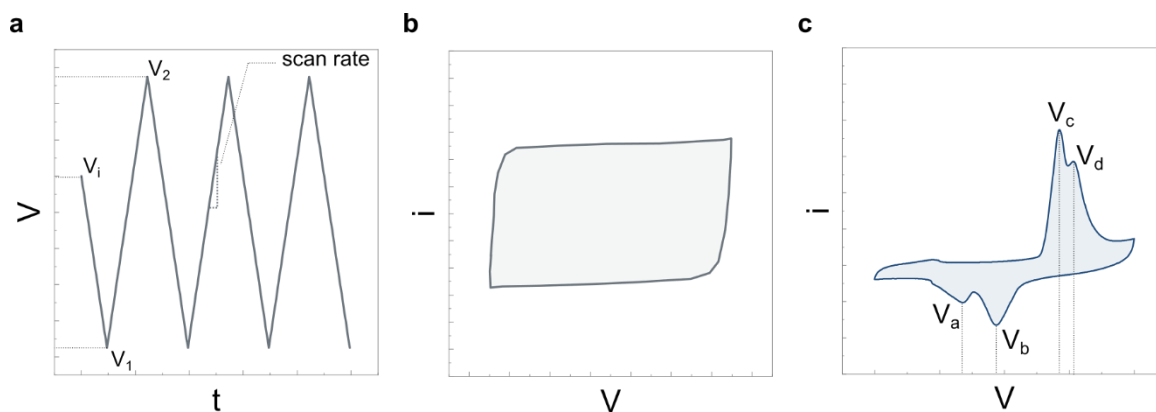


Figure 2.13: (a) Voltage profile in a typical cyclic voltammetry experiment; (b) typical quasi-rectangular cyclic voltammogram of a capacitive material; (c) typical cyclic voltammogram of a battery-like material, showing clear redox peaks.

cell interdigitated geometry, by printing a manganese oxide cathode and a zinc anode on a gold interdigitated current collector (Figure 2.12-c, bottom). The gold current collector were purchased from Metrohm (Metrohm DropSens Interdigitated Gold Electrodes), and consisted of a conductive gold film sputtered on an alumina substrate. The electrolyte ink (2 M ZnSO_4 in a 5wt% fumed silica suspension) was 3D printed in the space between the electrodes and the devices were encapsulated using epoxy resin (RS Components). All the electrochemical tests were performed on a multichannel VMP-3 workstation (Bio-Logic Science Instruments) and on a Gamry Interface 1000 potentiostat/galvanostat. Dr Nagaraju Goli provided support for the electrochemical measurements performed in this work.

5.2. Cyclic and Linear Sweep Voltammetry

Cyclic voltammetry (CV) is an electrochemical characterization technique based on the application of a triangular potential wave to an electrochemical cell, while recording the cell current response (Figure 2.13-a).^{13,190} CV was employed in this work to determine the nature of the charge storage processes (pseudocapacitive or diffusion-limited), the reversibility of the electrode reactions and the stability window for the aqueous electrolytes.

The measured current response is usually plotted against the applied potential, providing a cyclic voltammogram (Figure 2.13-b,c). It can be shown that for ideal capacitors, electrical double layer capacitors and some pseudocapacitive materials the current response is independent of the applied potential and proportional to the scan rate;⁸ therefore, the cyclic voltammogram presents a rectangular shape (Figure 2.13-b). On the contrary, the cyclic voltammograms of battery-like materials show well-defined peaks, each associated with a characteristic redox reaction (Figure 2.13-c). In the proximity of the reversible potential for each redox reaction, the current starts rapidly increasing but it is limited by the progressive depletion of reactants near the electrode surface, reaching a

maximum.^{9,190} For battery materials, the current response associated with redox processes in the bulk of the electrode is linearly proportional to the square root of the scan rate. Additionally, oxidation peaks and the corresponding reduction peaks typically exhibit a significant potential separation in battery materials, caused by the slow diffusion of charge carriers in the electrode bulk.¹⁹¹ In order to quantify the contribution of supercapacitive and battery-like behaviour to charge storage, the Trasatti method was used in this work. The current i measured in a CV scan can be expressed as:^{8,192}

$$i = i_{SC} + i_B = k_1 \nu + k_2 \nu^{1/2} \quad , \quad (2.22)$$

where ν is the scan rate, $k_1 \nu$ represents the supercapacitive contribution i_{SC} (proportional to the scan rate) and $k_2 \nu^{1/2}$ represents the diffusion-limited battery-like contribution i_B (proportional to the square root of the scan rate). At each potential, the cyclic voltammograms measured at different scan rates were fitted using Equation 2.22 to determine the predominant charge storage mechanism. Alternatively, the current can be expressed as:

$$i = a \nu^b \quad , \quad (2.23)$$

where a and b are experimental parameters. If the b -value is close to 0.5, the charge storage is mainly supercapacitive, whereas if b approaches 1 the current response becomes diffusion-controlled.¹⁹¹ When the charge storage mechanism is mainly supercapacitive, the cell specific capacitance can be calculated in a three-electrode configuration as:

$$C_s = \frac{\oint i(V) dV}{2x \nu \Delta V} \quad , \quad (2.24)$$

where the integral is extended to the whole voltammogram, ΔV is the potential window and x is either the area, the volume or the mass of the electrode. However, Equation 2.24 does not account for possible asymmetries between the positive and negative branch of the CV, that can result from parasitic side reactions, high internal resistance or a leakage current between the electrodes.¹⁹³ Therefore, capacitance can be more accurately calculated from galvanostatic discharge tests.

Cyclic voltammetry was also used throughout this work to determine the maximum operating potential window for the electrochemical systems investigated. Voltammograms with progressively larger potential limits were recorded, until a rapid increase in current associated with the decomposition of the aqueous electrolyte or irreversible degradation of the electrodes could be observed at either side of the scan window.

Similarly to cyclic voltammetry, in linear sweep voltammetry (LSV) tests a linear potential ramp is applied to the electrode. LSV was used in this work to investigate the corrosion kinetic of zinc electrodes in a half-cell configuration, with an Ag/AgCl (3M KCl, RE-5B from BASi) reference

electrode and a graphite foil (0.01in, 99.8%, Alfa Aesar) counter electrode. In a mildly acidic electrolyte, two reactions take place simultaneously at the zinc electrode:



For each of these reactions, the charge transfer at the electrode-electrolyte interface obeys the Butler-Vomer equation. The partial current densities can thus be expressed as:¹⁹⁴

$$i_{Zn} = i_{a,Zn} + i_{c,Zn} = i_{0,Zn} \exp\left(\frac{E - E_{0,Zn}}{\beta_{a,Zn}}\right) + i_{0,Zn} \exp\left(-\frac{E - E_{0,Zn}}{\beta_{c,Zn}}\right) \quad , \quad (2.27)$$

$$i_H = i_{a,H} + i_{c,H} = i_{0,H} \exp\left(\frac{E - E_{0,H}}{\beta_{a,H}}\right) + i_{0,H} \exp\left(-\frac{E - E_{0,H}}{\beta_{c,H}}\right) \quad ; \quad (2.28)$$

where i_a is the partial anodic current density, i_c is the partial cathodic current density, i_0 is the exchange current and β_a and β_c are the anodic and cathodic Tafel coefficients. $E_{0,Zn}$ and $E_{0,H}$ are the equilibrium potentials for the zinc and hydrogen half reactions, respectively. In the proximity of the open-circuit potential for the zinc electrode (known here as the corrosion potential, E_{corr}) $i_{c,Zn}$ and $i_{a,H}$ are negligible,** thus the measured current density can be expressed as:

$$i = i_{a,Zn} + i_{c,H} = i_{corr} \exp\left(\frac{E - E_{corr}}{\beta_{a,Zn}}\right) + i_{corr} \exp\left(-\frac{E - E_{corr}}{\beta_{c,H}}\right) \quad , \quad (2.29)$$

where i_{corr} represent the rate of corrosion of the zinc anode.

In order to quantify the corrosion of the zinc electrode, LSV tests were performed in the proximity of the electrode open-circuit potential (between -0.25 V and 0.25 V vs. OCV). Equation 2.29 was used to fit the experimental curves to determine the corrosion current, corrosion potential and the Tafel coefficients. The fitting was performed in Echem Analyst software (Gamry Instruments).

5.3. Chronopotentiometric methods

In chronopotentiometric tests a controlled current signal is applied to the electrochemical cell, while measuring the potential response over time. Two types of chronopotentiometric tests were used in this work: constant-current chronopotentiometry with potential limitation (also known as galvanostatic charge-discharge tests, GCD), in which a constant current is applied to the cell until a pre-set potential is reached and then the sign of the current is switched; and constant-current

** This hypothesis, commonly made to analyse LSV curves for the corrosion of metal electrodes, is not valid in concentrated zinc sulfate electrolytes, as will be discussed in Chapter 4.

chronopotentiometry with time limitation (plating-stripping tests), in which a constant current is applied for a pre-set time interval and then switched.

Galvanostatic charge-discharge tests provided information on the capacity (or capacitance), efficiency, energy density and power density of the electrochemical energy storage devices developed in this work. The stability and rate capability of printed batteries and supercapacitors were assessed by measuring the capacity (or capacitance) at different current densities and over repeated charge-discharge cycles. In a three electrode configuration, for each charge-discharge cycle at a current i , the specific capacitance of a supercapacitive electrode can be calculated as:⁸

$$C_s = \frac{i \Delta t_d}{x \Delta V} \quad , \quad (2.30)$$

where Δt_d is the discharge time, ΔV is the difference between the initial and final potential during discharge and x is either the mass, volume or area of the electrode. It can be shown that the capacitance of a symmetric supercapacitor tested in a full-cell configuration C_{dev} is related to C_s by:^{8,195}

$$C_s = 4 C_{dev} \quad . \quad (2.31)$$

This relation only holds true for volumetric and gravimetric capacitance (*i.e.* when x in Equation 2.30 is the volume or mass of the electrode). For areal capacitance $C_s = 2 C_{dev}$. The energy and power densities of a symmetric supercapacitor can be determined from full-cell GCD tests as:⁸

$$E_{dev} = \frac{1}{2} C_{dev} \Delta V^2 \quad , \quad (2.32)$$

$$P_{dev} = \frac{E_{dev}}{\Delta t_d} \quad . \quad (2.33)$$

Specific capacitance is a meaningful figure of merit to describe the electrochemical performance of supercapacitive devices only if the measured potential is proportional to the charge stored, *e.g.* in electrical double layer capacitors.¹⁹³ For hybrid capacitors and batteries, the specific capacity Q_s is generally considered instead. It can be calculated from GCD tests in half- or full-cell configuration as:

$$Q_s = \frac{i \Delta t_d}{x} \quad . \quad (2.34)$$

For such devices, presenting a non-linear discharge curve, the energy density can be calculated as:¹⁹³

$$E_{dev} = \frac{i}{x} \int_{t_0}^{t_f} V(t) dt \quad , \quad (2.35)$$

where the integral is extended to the whole discharge curve. The power density can, also in this case, be determined according to Equation 2.33.

The main figures of merit describing the performance of supercapacitors and batteries, *i.e.* capacitance/capacity, energy and power density, can be normalized either by the mass, volume or footprint area of the device (x in Equations 2.30-2.35). A comparison of the three different normalizations, and the advantages and uses of each, was provided in Section 1.3 of Chapter 1.

The coulombic efficiency (CE) of a supercapacitive or battery-like electrode can be defined as the ratio between the discharge and charge capacity, representing the fraction of the stored charge that can be reversibly extracted during the discharge step.⁸ In a GCD test:

$$CE = \frac{\Delta t_d}{\Delta t_c} \quad , \quad (2.36)$$

where Δt_d is the discharge time and Δt_c is the charge time.

GCD tests were employed in this work to determine the capacitance, energy density, power density and the coulombic efficiency of graphene supercapacitors in half- and full-cell configuration. They also provided the specific capacity, rate capability and cycling stability of zinc ion batteries in half-cell and full-cell configuration. For the determination of the stability and reversibility of 3D printed zinc anodes, chronopotentiometric tests with time limitation were performed. Symmetric cells were repeatedly charged and discharged at different current densities with a time limitation of 1 h (*i.e.* 1 h charge followed by 1 h discharge) in 2 M ZnSO₄, monitoring the plating and stripping overpotential during repeated cycling. The coulombic efficiency of 3D printed zinc anodes in a 2 M ZnSO₄ electrolyte and of zinc foil anodes in a hybrid electrolyte was assessed with the *reservoir half-cell method* (Figure 2.14).¹⁹⁶ A half-cell consisting of a zinc working electrode and a copper counter electrode was assembled in a LDPE pouch cell filled with 2 M ZnSO₄. A zinc reservoir was created by plating a capacity of 2.5 mAh cm⁻² on the copper counter electrode by a time-limited chronopotentiometric technique. A fraction of this zinc reservoir (0.5 mAh cm⁻²) was then cycled between the working and counter electrodes n times. Finally, the zinc left on the copper electrode was stripped to a cut-off voltage of 500 mV. The coulombic efficiency was calculated as:

$$CE = \frac{n Q_C + Q_S}{n Q_C + Q_R} \quad , \quad (2.37)$$

where Q_R is the capacity plated on the copper electrode to form the zinc reservoir, Q_C is the capacity cycled between the working electrode and the reservoir and Q_S is the final zinc capacity that can be stripped from the reservoir before the cut-off voltage is reached.

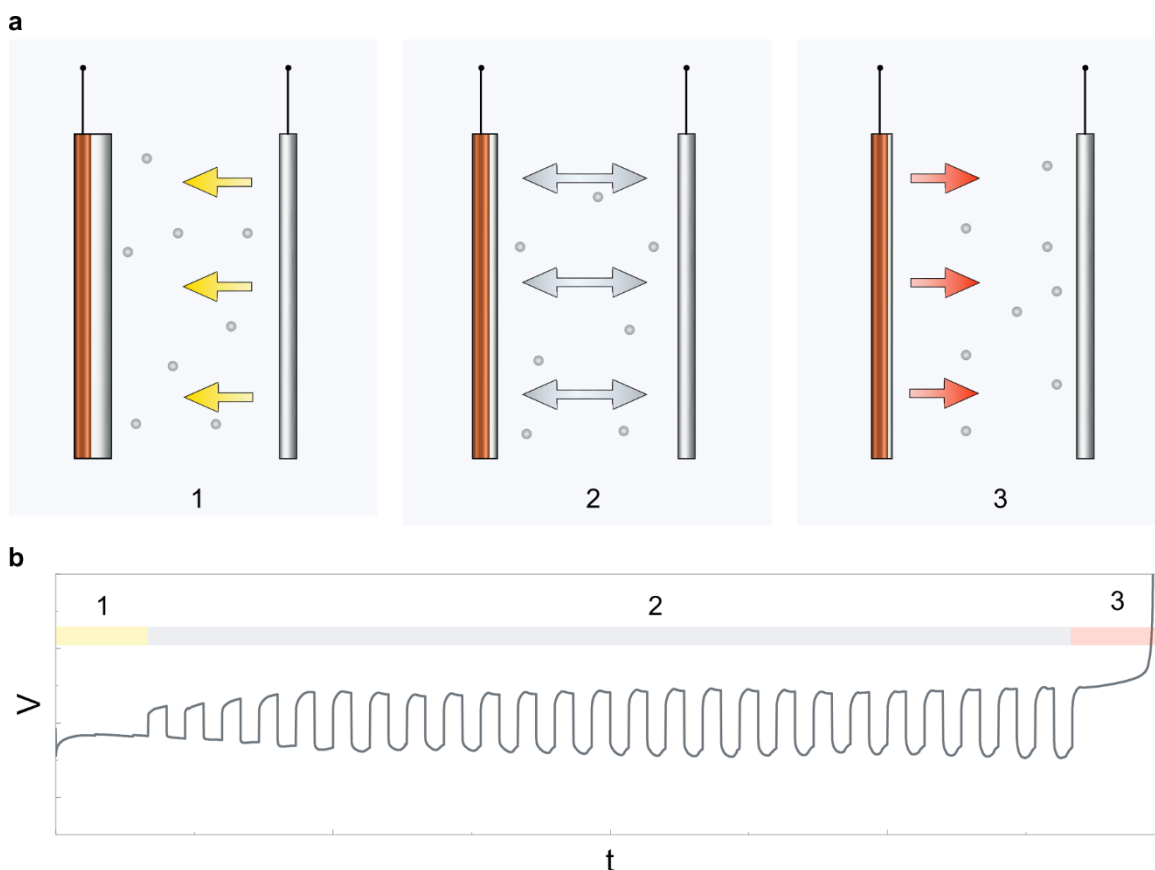


Figure 2.14: (a) Schematic showing the three steps of the reservoir method to measure coulombic efficiency: (1) formation of the reservoir, (2) cycling, (3) stripping of the residual reservoir; (b) corresponding potential profile in a typical test.

5.4. Chronoamperometric methods

In chronoamperometric (CA) techniques a potential step is applied to the cell and the cell response in terms of current is recorded. The degradation of the 3D printed graphene electrode during operation was assessed *via* voltage-holding tests, a particular type of chronoamperometric methods in which the full cell is kept at the nominal voltage and the capacitance retention is determined over time by occasional charge-discharge.¹⁹⁷ 3D printed symmetric graphene supercapacitors were kept at the cell voltage of 1 V while measuring the leakage current. The supercapacitors were discharged and recharged every 30 min at a constant current (2 mA cm^{-2}) to determine the capacitance retention.

Chronoamperometric tests were also studied as a faster alternative to GCD to assess the rate capability of zinc hybrid capacitors. Pouch-cell zinc hybrid capacitors consisting of a 3D printed graphene cathode and a zinc foil anode in a hybrid $2 \text{ M ZnSO}_4 - 2 \text{ M NaCl}$ electrolyte were charged to their maximum operating voltage (1.8 V) at a constant current. The capacitors were completely

discharged at a constant potential, measuring the discharge current $i(t)$. The capacity $Q(t)$ and the corresponding rate $R(t)$ were calculated as:¹⁹⁸

$$R(t) = \frac{i(t)}{\int_0^t i(\tau) d\tau} \quad , \quad (2.38)$$

$$Q(t) = \int_0^t i(\tau) d\tau \quad . \quad (2.39)$$

5.5. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is an alternating current technique which relies on the application of a small-amplitude sinusoidal potential to an electrochemical cell.^{13,199} If the amplitude of the applied signal is sufficiently small, the electrochemical cell exhibits a linear current response. The AC impedance of the cell can therefore be calculated as:

$$Z(\omega) = \frac{\tilde{E}(\omega)}{\tilde{I}(\omega)} \quad , \quad (2.40)$$

where $\tilde{E}(\omega)$ is the phasor representing the applied potential and $\tilde{I}(\omega)$ is the phasor representing the current response. By measuring impedance in a wide range of frequencies (MHz to mHz), EIS allows the study of charge transfer processes inside the cell. In particular, the electrochemical cell can be modelled as a linear equivalent circuit, whose parameters are determined fitting the experimental data. The parameters of the equivalent circuit provide information on the electrolyte ionic resistance, the capacitance of the double layer at the electrode interface and the charge transfer resistance. Impedance data are usually presented in a Nyquist plot, displaying the imaginary part of impedance vs. the real part as a parametric function of frequency.

Electrochemical impedance spectroscopy was carried out on 3D printed graphene electrodes in half-cell and full cell configuration between 10^5 and 10^{-2} Hz at an AC voltage of 5 mV rsm. EIS was also performed on 3D printed zinc anodes in a symmetric cell configuration, between 10^5 and 10^{-2} Hz at an AC voltage of 5 mV. The experimental data were fitted to linear circuits using EC-Lab 11.3 (BioLogic).

EIS tests were also used to determine the ionic conductivity of zinc electrolytes. A symmetric cell made of two stainless steel blocking (non-faradaic) electrodes was set up in a square glass container. Impedance spectra were collected between 10^5 and 10^{-1} Hz at an AC voltage of 5 mV rsm. The electrolyte conductivity was determined from the high-frequency intercept of impedance with the real axis in a Nyquist plot R , representing the resistance to charge transport in the electrolyte. The conductivity σ was calculated as:

$$\sigma = \frac{L}{A} R \quad , \quad (2.41)$$

where L is the distance between the electrodes and A the area of the electrodes immersed in the electrolyte.

Chapter 3

Printed Graphene Supercapacitors

This chapter will present the fabrication of printed electrodes using aqueous dispersions of graphene nanoplatelets (GNPs). Graphene is among the most desirable carbon materials for EDL supercapacitors, owing to its high electronic conductivity, good intrinsic capacitance and mechanical and chemical stability.^{200,201} The high aspect ratio of graphene aids the formation of a three-dimension percolative network of conductive platelets, which provides high discharge capacitance and excellent rate capability. Nonetheless, the stabilization of graphene in aqueous inks is challenging, because of the high hydrophobicity and strong van der Waals interactions between the platelets.²⁰² Most DIW inks developed for graphene supercapacitors contain graphene oxide (GO), an oxidized form of graphene which is highly stable in water owing to negatively-charged surface functionalities. As discussed in Chapter 2, concentrated GO dispersions do not require any further additives to be printable, and can be used to manufacture low-density electrodes with high specific capacitance. However, GO is an electrical insulator, thus the printed structures must be converted to reduced-GO (rGO) to obtain conductive electrodes.¹²⁶ Thermal annealing at high temperatures ($> 1000\text{ }^{\circ}\text{C}$) and chemical reduction in hydrazine are the most common methods to defunctionalize the basal plane of the platelets, partially restoring the sp^2 bonds.^{72,121,203,204} These postprocessing steps are significantly more energy demanding than the conventional manufacturing of carbon-based supercapacitors and involve toxic reducing agents.²⁰⁵ Additionally, even after reduction, the platelets remain highly defective, with residual oxygen moieties and topological defects that hinder the transport of charges.²⁰⁶

Recently, the possibility to disperse graphite and graphene nanoplatelets in concentrated aqueous pastes *via* the formation of a capillary suspension has been demonstrated.^{140,145} The advantage of these formulations lies in the use of pristine graphene in place of graphene oxide, which eliminates the need for post-printing reduction and provides highly conductive electrodes. The first section of this chapter will investigate the use of capillary suspensions as inks for the DIW of symmetric supercapacitors, offering a discussion on the rheological behaviour of the suspensions, the structural properties of the printed electrodes and their electrochemical performance in aqueous electrolytes. Section 2 will propose an alternative ink formulation, integrating carbon nanotubes into the graphene dispersion, and discuss the use of 3D printed graphene-carbon nanotube electrodes as cathodes for zinc hybrid capacitors.

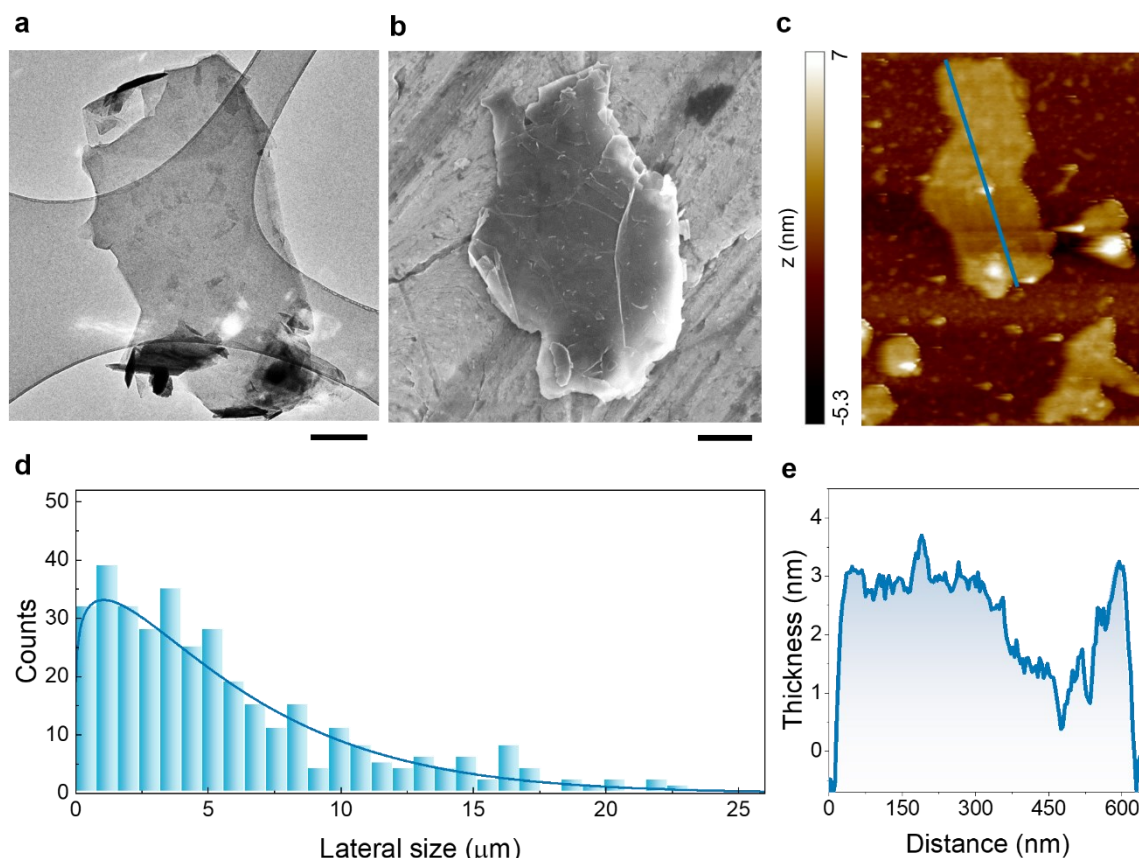


Figure 3.1: (a) TEM imaging of an individual graphene nanoplatelet (scalebar 0.5 μm); (b) SEM imaging of an individual graphene nanoplatelet (scalebar 1 μm); (c) AFM imaging of a graphene nanoplatelet on a silicon substrate; (d) lateral size distribution for the graphene nanoplatelets obtained from SEM imaging; (e) height profile corresponding to the blue line in panel (c).

1. Symmetric graphene supercapacitors

The inks for symmetric graphene supercapacitors were formulated starting from commercial graphene nanoplatelets. The morphological features and chemical structure of the nanoplatelets were first characterized with microscopy and spectroscopy techniques, since these properties play a major role in the stability of the inks and the mechanical and electrochemical performance of the final electrodes. The graphene platelets present an average lateral dimension of $\sim 6 \mu\text{m}$, as evidenced by the TEM and SEM analysis in Figure 3.1-a,b. The lateral size of the platelets follows a Weibull distribution, as expected for particles obtained from random fragmentation processes (mechanical milling), Figure 3.1-d.^{207,208} The thickness of the platelet imaged in AFM analysis (Figure 3.1-c,e), is $\sim 3.5 \text{ nm}$, corresponding to ~ 10 stacked graphene layers. The high aspect ratio of the platelets ($> 10^3$) promotes the formation of a network of interlocked particles, providing high mechanical stability to the 3D graphene structures and reducing the risk of cracks, which would electrically disconnect part of the electrode from the current collector. Additionally, the high aspect ratio allows

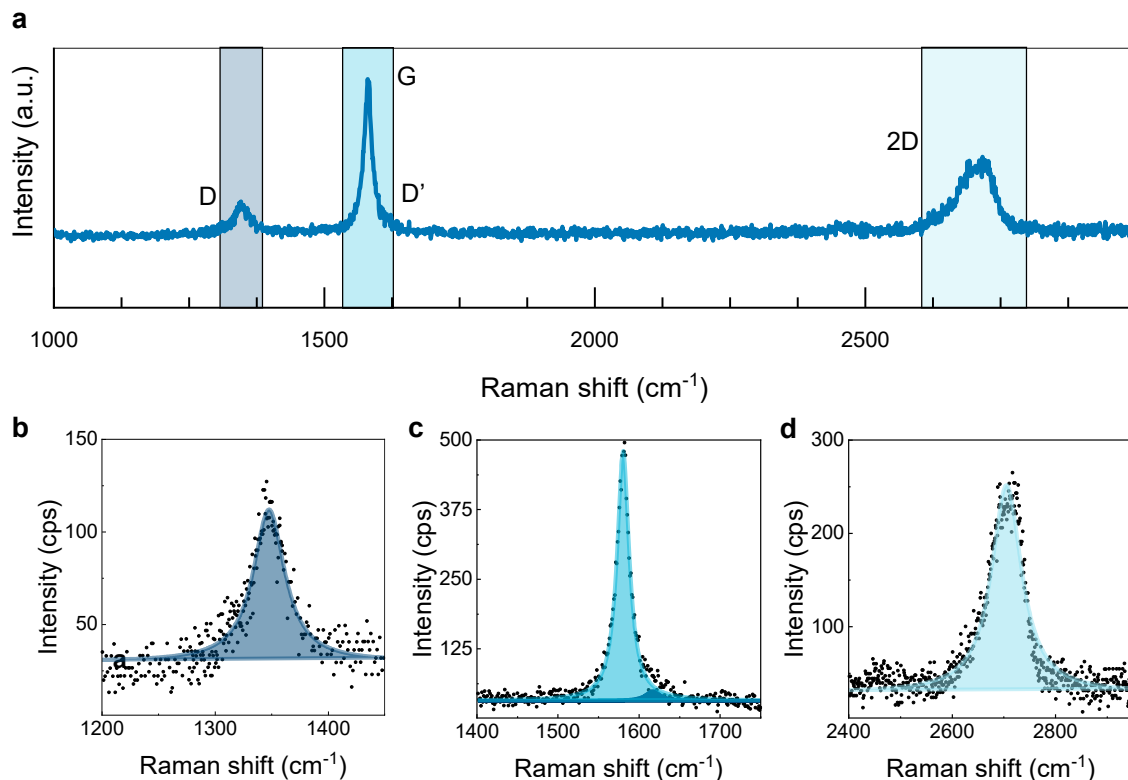


Figure 3.2: (a) Raman spectrum of the graphene nanoplatelets, displaying the four characteristic bands of graphitic materials; (b-d) Lorentzian fittings of the D band (b), the G and D' band (c) and the 2D band (d).

for abundant conductive paths and high specific surface area, which are beneficial for the electrochemical properties of the printed electrodes.

The presence of defects in the crystal structure of the graphene nanoplatelets was investigated with Raman spectroscopy (Figure 3.2-a). The Raman spectrum shows three main bands in the range 1200-2800 cm^{-1} , corresponding to the characteristic features of graphitic materials.^{209,210} The intense band at $\sim 1581 \text{ cm}^{-1}$ (Figure 3.2-a,c) is activated by the E_{2g} in-plane phonon mode at the Brillouin zone centre (G-band), whereas the weaker band at $\sim 1348 \text{ cm}^{-1}$ (Figure 3.2-a,b) is associated with the breathing mode of the sp^2 carbon atoms in the graphene plane (D-band). The breathing mode becomes active at the edge of the crystallites, as a result of the absence of translational symmetry, and it is commonly related to the presence of defects in graphitic materials.²¹¹ The band at $\sim 2705 \text{ cm}^{-1}$ (Figure 3.2-a,d) is activated by second order phonons (G'-band), whereas the small shoulder present in the G-band at $\sim 1617 \text{ cm}^{-1}$ can be associated with the D'-band of graphitic materials, also resulting from second-order processes.²¹¹ The bands in the Raman spectrum of the graphene nanoplatelets were fitted using a Lorentzian distribution to determine the intensity (I) and full width at half maximum (FWHM) of each band. The low I_D/I_G ratio (~ 0.18) indicates the chemical purity of the platelets and the absence of structural defects, which is also supported by the position of the G-band (close to 1580 cm^{-1}).^{212,213} Although the shape of the 2D band can provide information on the

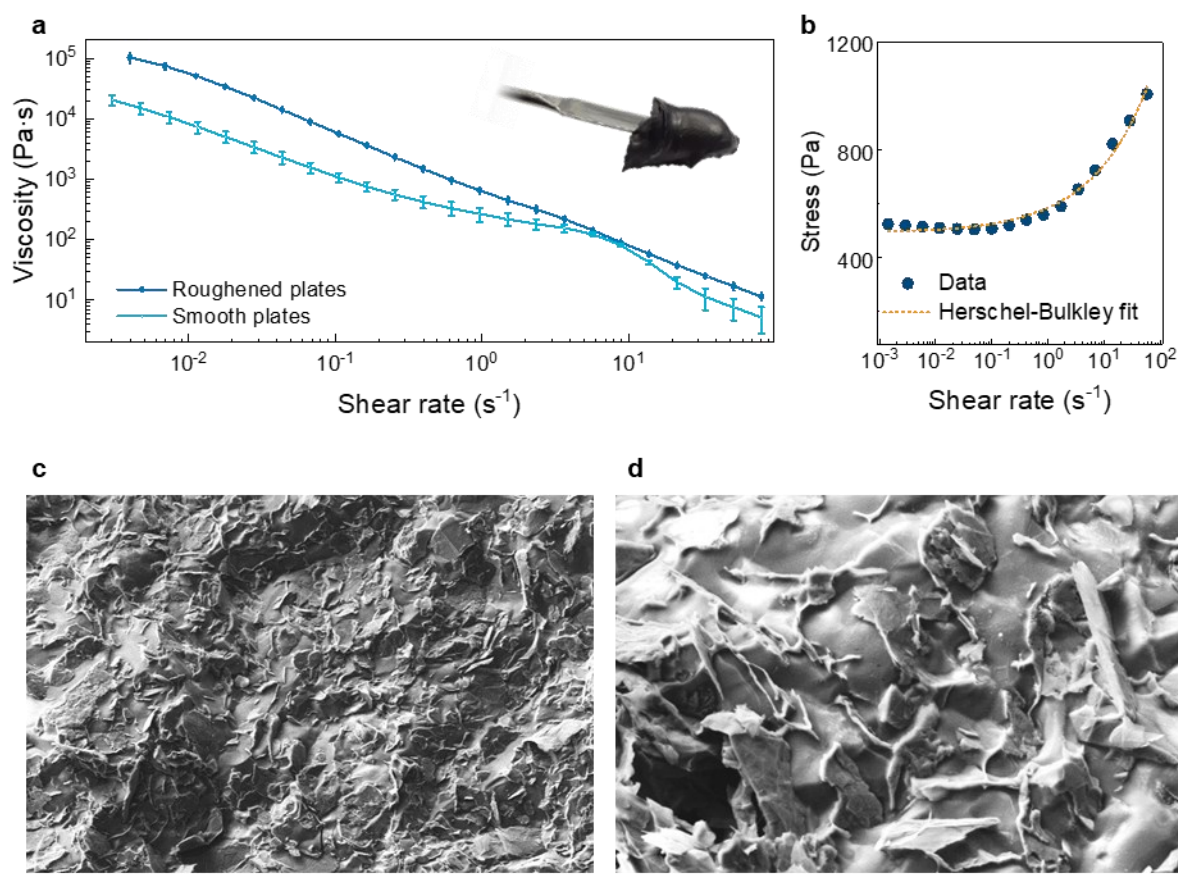


Figure 3.3: (a) Flow curve of the graphene ink obtained from rotational rheometry with (dark blue) and without (light blue) roughened plates and digital photograph of the ink (inset); (b) Herschel-Bulkley fitting of the shear stress-shear rate curve for the graphene ink; (c,d) cryo-SEM on the graphene capillary ink (scale bars 20 μm and 5 μm , respectively).

thickness of few-layer graphene, it becomes almost indistinguishable from bulk graphite for more than ~ 5 layers.

1.1. Ink formulation and printability assessment

The graphene inks were formulated by dispersing the graphene nanoplatelets in water with a small amount of cellulose viscosifier, as detailed in Chapter 2. Octanol was added to form capillary bridges between the hydrophobic particles, resulting in a paste-like dispersion (inset in Figure 3.3-a). Cryo-SEM imaging provided insight into the ink microstructure (Figure 3.3-c,d), displaying well-dispersed graphene platelets forming a continuous network. The voids of the network are filled with a liquid phase (vitrified during sample preparation), made of water and cellulose (Figure 3.3-d). The flow behaviour of the ink was investigated using rotational rheometry, in order to assess its printability for DIW and to determine its rheological properties, namely the Herschel-Bulkley parameters, for CFD simulations. The rotational tests were performed using roughened plates to avoid artifacts in the measurements, in particular the formation of a particle-depleted layer of liquid in the

Table 3.1: Results of the Herschel-Bulkley fitting for the flow curve of the graphene ink.

K (Pa s ^{n})	n	τ_Y (Pa)
94	0.43	60

proximity of the plates (wall slip) and the ejection of the ink from the gap between the plates at high shear rates, which are commonly observed in yield-stress materials.²¹⁴ Because of these effects, measurements with smooth plates underestimate the viscosity of the ink, and the resulting experimental data are significantly less reproducible (Figure 3.3-a). The difference between the two experimental curves in Figure 3.3-a is probably determined by wall-slip effects in the low-rate region (10^{-3} - 10^0 s⁻¹) where the applied shear stress is close to the yield stress, whereas in the high-rate region (10 - 10^2 s⁻¹) the high centrifugal force can determine the lateral ejection of the ink. The flow curve obtained with roughened plates shows a power-law drop in viscosity at increasing shear rate, as expected from a Herschel-Bulkley material. The degree of shear thinning of the inks was quantified fitting the flow curve with the Herschel-Bulkley model (Equation 2.7), as shown in Figure 3.3-b. The low value of the flow index n (~ 0.43 , Table 3.1) indicates a strongly shear-thinning response, which facilitates the extrusion of the ink throughout fine printing nozzles, allowing for the fabrication of miniaturized features. The shear-thinning behaviour stems from the progressive breakdown of the capillary bridges during the shear flow, and the consequent formation of graphene flocs with smaller hydrodynamic volume.²¹⁵

The transition of the ink from a solid-like behaviour at rest to a liquid-like behaviour during flow was investigated with oscillatory measurements. In the linear viscoelastic region, *i.e.* at low oscillatory stress, the ink presents the response of a predominantly elastic material ($G' \gg G''$), with a high storage modulus $\sim 10^5$ Pa (Figure 3.4-a). The viscoelastic moduli are substantially independent of the oscillation frequency, as typically observed in physical gels made of a three-dimensional network of bonded particles, presenting a similar microstructure to the capillary graphene ink (schematized in Figure 3.4-c).¹⁵⁰ When the oscillatory stress is increased, a progressive drop in the storage modulus becomes evident starting from a stress ~ 20 Pa, signifying the onset of yielding and the disruption of the first capillary bridges (Figure 3.4-b). At ~ 60 Pa the storage modulus curve crosses the loss modulus curve ($G' = G''$); the crossover point represents the yield stress of the material. Above ~ 60 Pa the viscous response becomes predominant ($G'' > G'$), indicating the destruction of the three-dimensional network and the onset of flow. The graphene ink presents a comparable yield stress to previously reported GO and MXene inks (Figure 3.4-d), but a significantly larger storage modulus in the LVE region, which prevents sagging and lateral buckling under the effect of gravity and capillary interactions with the substrate.¹¹⁸

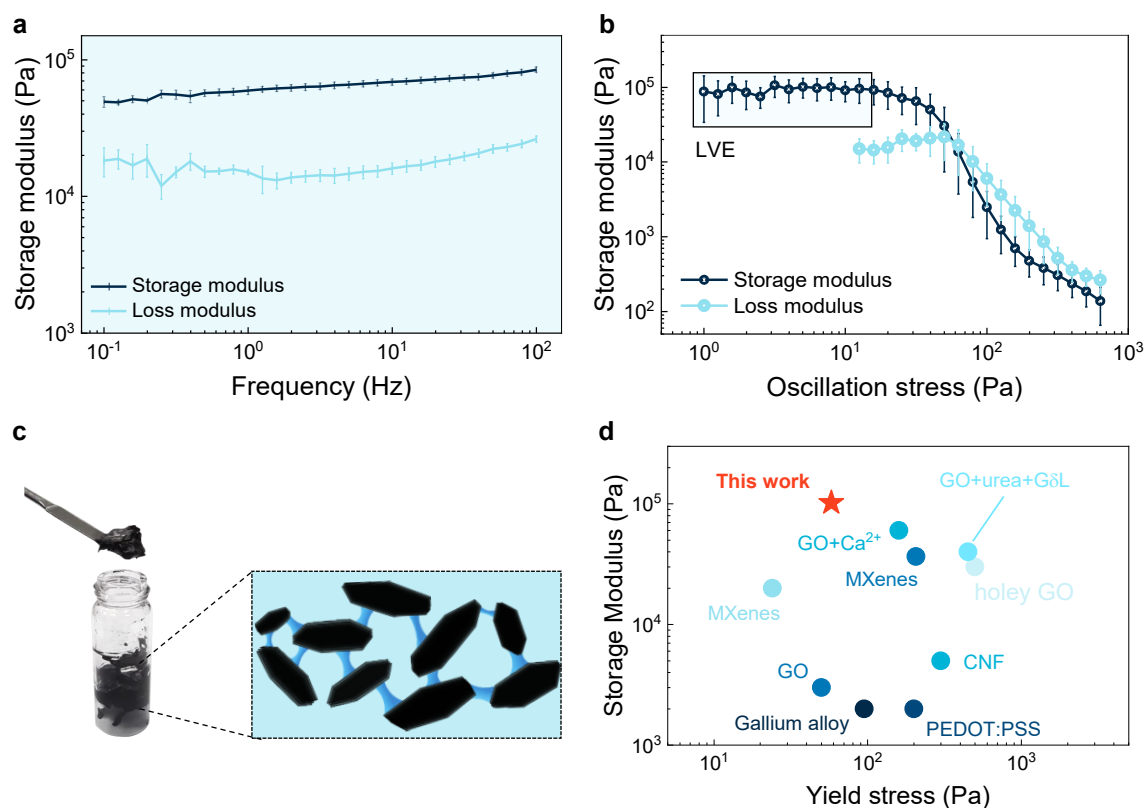


Figure 3.4: (a) Oscillatory frequency sweep in the LVE region of the graphene ink (oscillatory strain $\sim 0.1\%$); (b) Oscillatory amplitude sweep of the graphene ink displaying the region corresponding to the LVE (highlighted in light blue); (c) digital photograph of the graphene ink and schematic showing the pendular octanol bridges between graphene particles; (d) comparison of the yield stress and storage modulus of the graphene ink with previously reported inks for the DIW of energy storage devices (references for the comparison plot in Appendix A2).

The secondary bonds between the solid components of the ink must quickly recover after flow, in order to prevent the ink from spreading laterally on the substrate or collapsing during the extrusion of overhangs. The restructuring kinetic was assessed with three-interval thixotropy tests (3ITTs), monitoring the recovery of the storage modulus and viscosity after a high shear step. In oscillatory 3ITTs, a low oscillatory stress (10 Pa, within the LVE region) was applied during the first step to the ink to equilibrate its microstructure (Figure 3.5-a, step 1). In the following step, a high stress of 100 Pa was applied to break the capillary bonds and fluidize the material (step 2). This value of oscillatory stress was chosen to be higher than the yield stress (~ 60 Pa), so to ensure the complete destructuring of the ink. Finally, a small oscillatory stress of 10 Pa was applied again to non-destructively probe the recovery of the ink storage modulus (step 3). As shown in Figure 3.5-a, the storage modulus almost instantaneously recovers to its original value, indicating that the ink behaves as a simple yield-stress fluid with no thixotropic effects. A similar conclusion can be drawn from continuous flow tests, which present an almost instantaneous recovery of viscosity after a destructive shear of 100 s^{-1} (Figure 3.5-b).

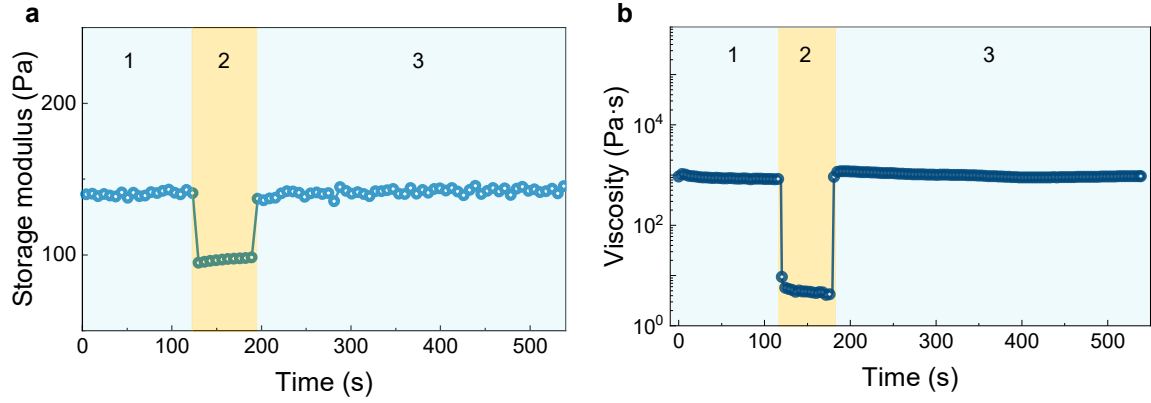


Figure 3.5: (a) Three-interval thixotropy test monitoring the time evolution of the storage modulus of the graphene ink, consisting of an equilibration step (step 1, oscillatory stress ~ 10 Pa), a fluidization step (step 2, oscillatory stress ~ 100 Pa) and a final recovery step (step 3, oscillatory stress ~ 100 Pa); (b) three-interval thixotropy test monitoring the time evolution of the viscosity of the graphene ink, consisting of an equilibration step (step 1, flow rate ~ 0.1 s $^{-1}$), a high-shear step (step 2, flow rate ~ 100 s $^{-1}$) and a final recovery step (step 3, flow rate ~ 0.1 s $^{-1}$).

1.2. Structural characterization

The rheological features of the graphene ink discussed in Section 1.1 are essential to print structures that do not undergo undesired shape change during extrusion and drying. The high storage modulus and fast thixotropic recovery prevent the lateral collapse of the filaments after deposition, enabling the fabrication of thick woodpile electrodes (~ 1.9 mm) with wide channels which facilitate the infiltration of the electrolyte (Figure 3.6-a,d). The shape retention of woodpile electrodes after printing can be quantified defining a printability index Pr as:¹⁶⁴

$$Pr = \frac{L^2}{16A} \quad , \quad (3.1)$$

where L is the perimeter of one of the woodpile grid holes and A its area. If the grid hole has a perfectly square shape, *i.e.* ideal shape retention with no lateral spread of the filaments, $Pr = 1$. The graphene structures have a high printability index of ~ 0.996 , demonstrating the possibility to deterministically control the geometry of the electrodes through the extrusion-printing process.

The graphene ink could be printed on a variety of different insulating substrates (silicon, glass and cellulose paper) and conductive current collectors (aluminium, copper and graphite foil), since

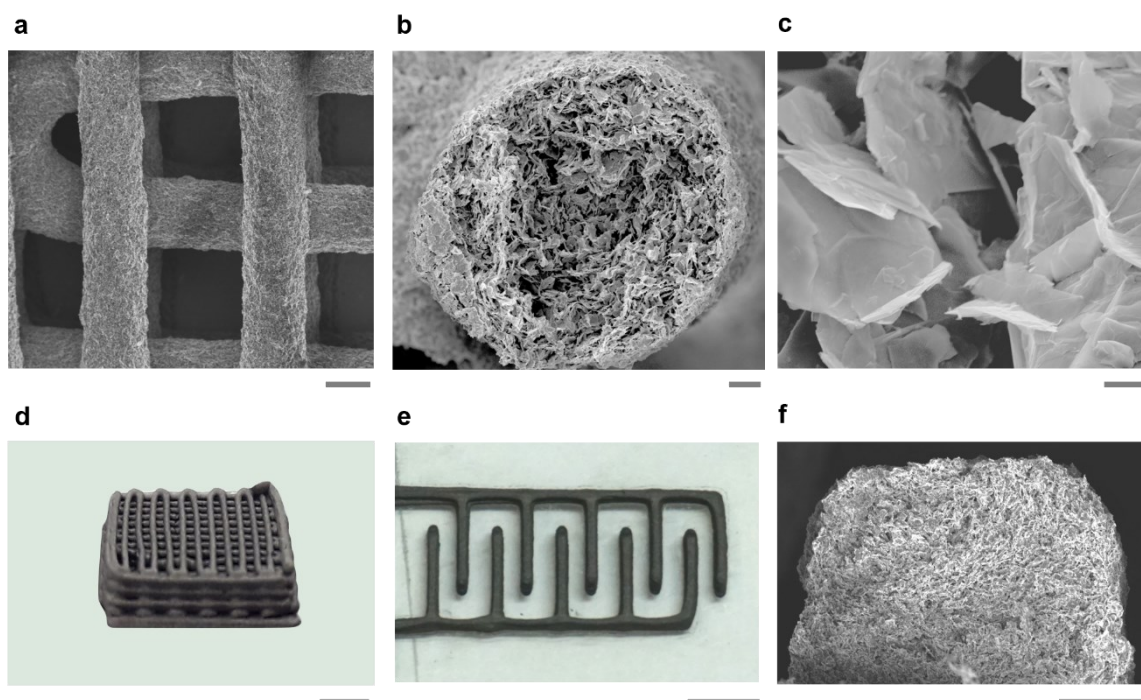


Figure 3.6: (a) SEM image showing a 3D printed woodpile electrode obtained from the graphene capillary ink (scalebar 200 μm); (b) cross-section of a woodpile electrode (scalebar 30 μm); (c) high magnification image of the electrode cross-section, showing large voids between the graphene platelets (scalebar 1 μm); (d) digital image of a 8-layer woodpile electrode (scalebar 25 mm); (e) digital image of an interdigitated electrode (scalebar 5 mm); (f) SEM image of the cross-section of an interdigitated electrode (scalebar 150 μm).

the equilibrium shape of the first printed layer is predominantly controlled by the high yield stress of the ink, rather than the capillary interactions with the substrate.²¹⁶ The printed woodpile electrodes are made of a network of graphene platelets with numerous interparticle connections, which provide conductive paths for the transport of charges to the current collector, as shown by cross-sectional SEM (Figure 3.6-b). Additionally, the filament cross-section is perfectly circular, as expected from the high printability index. In the inner region of the filaments, graphene nanoplatelets appear randomly oriented, forming large and irregular voids (Figure 3.6-c). The interdigitated structures (Figure 3.6-e) have a square cross-section, resulting from the deposition of two horizontally adjacent filaments at a slightly smaller distance than the filament diameter. The individual filaments merge seamlessly, forming a continuous network without any interruption or cracks between layers (Figure 3.6-f); this prevents the delamination of the electrode during operation, which would result in an increase in the internal resistance or in the loss of electroactive material. The mass loading of active material and the apparent density of the woodpile lattices can be easily controlled changing the number of printed layers and the diameter of the extrusion nozzle (Figure 3.7-a,b,c). Structures with filaments $\sim 200\ \mu\text{m}$ and ranging from 0.6 mm (2 layers) to 1.9 mm (8 layers) in thickness were printed (Figure 3.7-a,b). Although the ink experiences higher shear rates during extrusion through finer nozzles, the $200\ \mu\text{m}$ structure still exhibits excellent shape fidelity (Figure 3.7-d,e,f), as a result of the extremely fast thixotropic recovery demonstrated by 3ITTs. The dried printed filaments

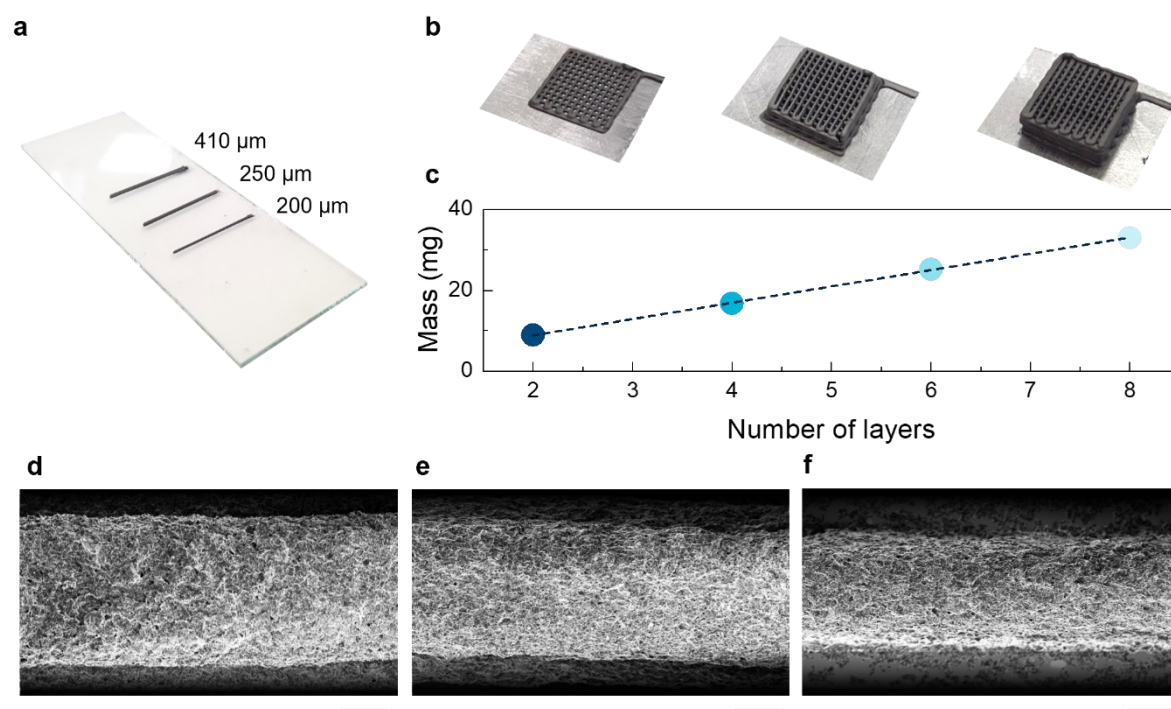


Figure 3.7: (a) Digital image of printed graphene lines using different nozzle diameters; (b) digital photographs of 3D printed graphene electrodes on a graphite foil current collector; (c) relationship between the mass of the graphene electrodes and the number of printed layers; (d-f) SEM imaging of printed lines using different printing nozzles (410 μm , 250 μm and 200 μm , respectively, scale bars are 100 μm).

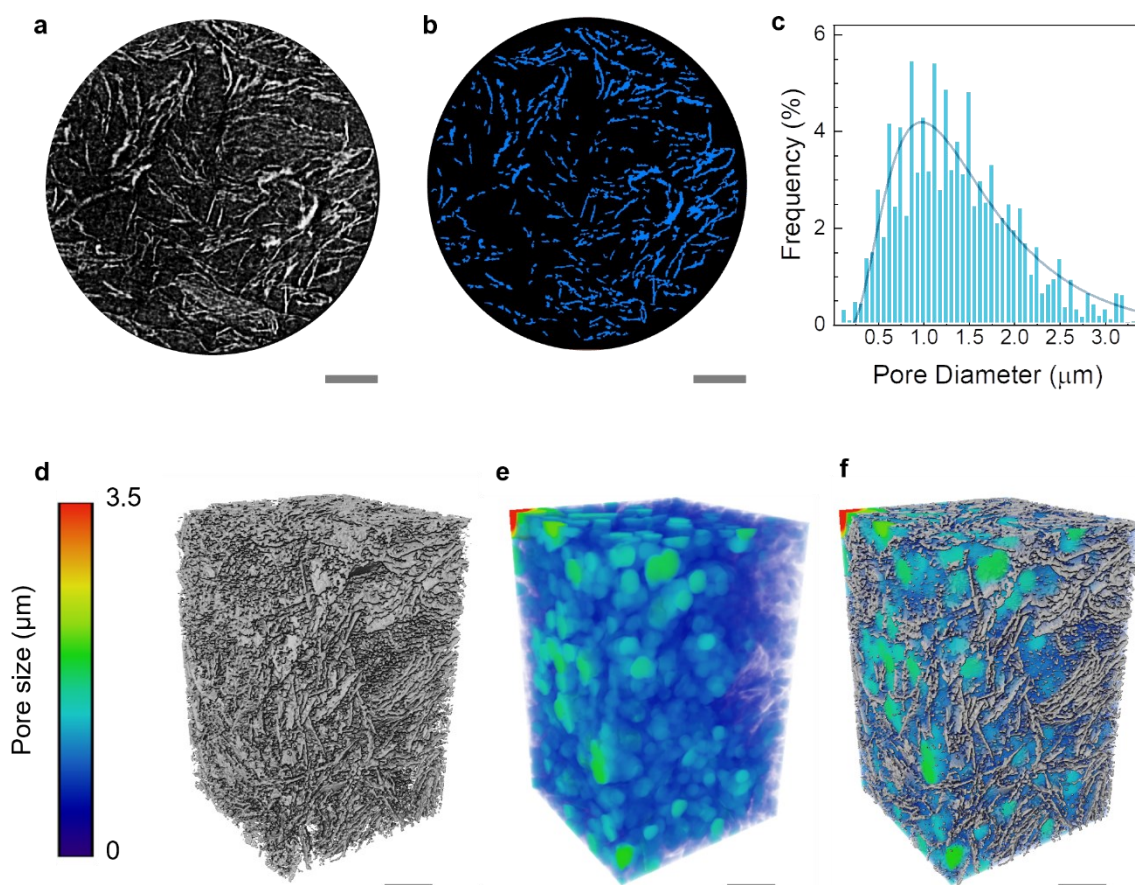


Figure 3.8: (a) Reconstructed tomogram slice showing bright graphene nanoplatelets; (b) tomogram slice after segmentation; (c) histogram showing the pore size distribution obtain from X-ray nanoCT; (d-f) three-dimensional visualization of the segmented tomogram (d), pores (e), and segmented tomogram and pores (f); all the scale bars are 10 μm .

present a diameter reduction $<10\%$ compared to the nozzle diameter, which can be attributed to the evaporation of water from the ink. No significant variation in the filament size was observed after annealing, although we did not perform a systematic study on the change of filament size during post-processing on a statistically relevant number of electrodes. The uncertainty on the filament diameter makes it difficult to measure the apparent density of the electrodes from the mass presented in Figure 3.7. Density measurements based on Archimedes' principle will be discussed in the next section.

In order to shed light on the three-dimensional organization of the graphene platelets inside the printed electrodes, phase-contrast X-ray Nano-Computed Tomography (X-ray nanoCT) was performed on the individual printed filaments. Two tomographic scans with a 65 μm field of view were carried out in the central and in the outer region of the filaments, respectively. The tomograms obtained from the X-ray nanoCT scans show bright aggregates of platelets with a thickness $\sim 1 \mu\text{m}$ on a dark background, resulting from the different refractive index of air and graphene (Figure 3.8-a). The two phases present in the tomograms were segmented by greyscale threshold (Figure 3.8-b) and the segmented tomogram was used to quantify the size of the macroscopic voids between

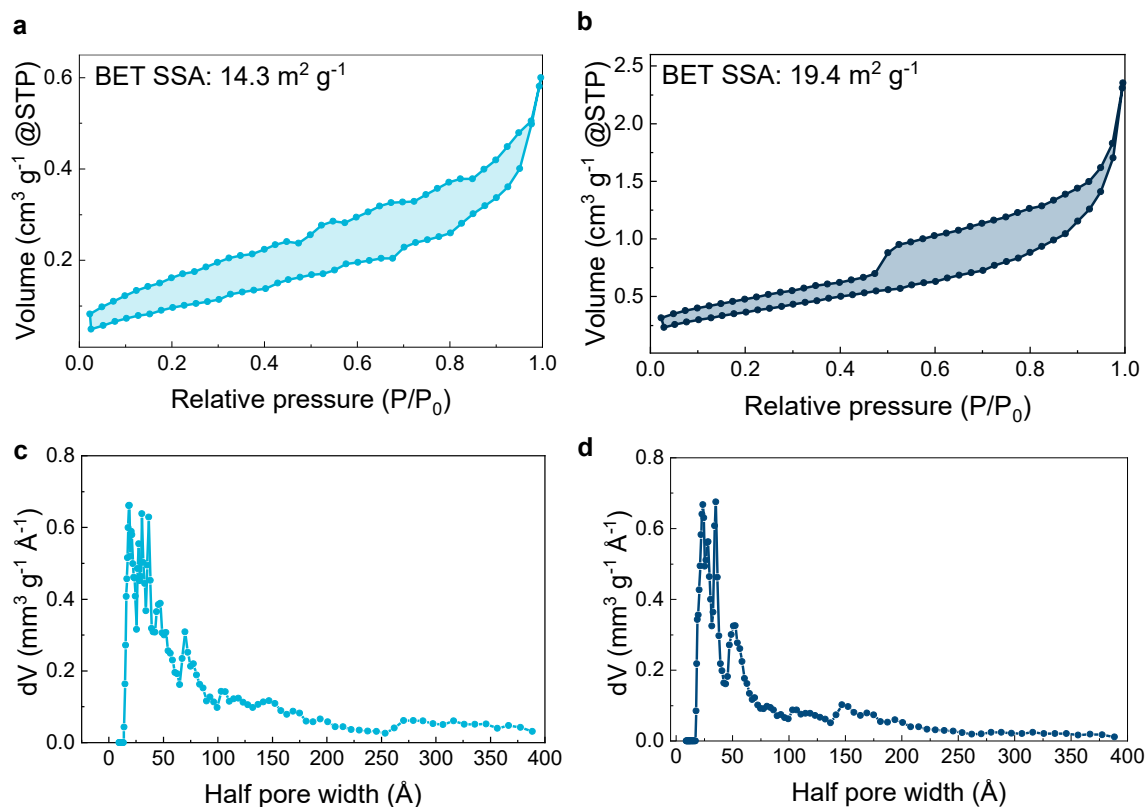


Figure 3.9 (a,b) Adsorption isotherms for the dried graphene ink before (a) and after (b) debinding; (c,d) pore size distribution for the dried graphene ink before (c) and after (d) debinding.

the interconnected platelets. The segmented tomogram (Figure 3.8-d) confirms the existence of a network of platelets spanning the entire field of view, forming large pores with an average diameter of $\sim 1.4 \mu\text{m}$ (Figure 3.8-c,e,f). However, the spatial resolution of the reconstructed tomogram was limited by the voxel size (63 nm), and could not provide information on the presence of pores smaller than 100 nm. To study pores in this dimensional range and to determine the specific surface area of the samples, the X-ray CT analysis was complemented with nitrogen adsorption tests, performed before and after the debinding treatment (Figure 3.9). The isotherms presented in Figure 3.9-a,b are characterized by a type H3 hysteresis loop, associated with slit-shaped pores between the aggregated graphene nanoplatelets.^{217,218} BET fittings of the isotherms provided a specific surface area $\sim 14.3 \text{ m}^2 \text{ g}^{-1}$ and $\sim 19.4 \text{ m}^2 \text{ g}^{-1}$ before and after debinding, respectively. This value are relatively low compared to typical carbon materials used in supercapacitors, *e.g.* activated carbons, with a BET specific surface area $> 10^3 \text{ m}^2 \text{ g}^{-1}$.¹⁸⁴ The low surface areas is probably a consequence of the high lateral size and multilayer nature the graphene nanoplatelets, which are essential to obtain mechanically stable 3D structures. The pore size of graphene platelet inks mainly falls in the 20-100 Å range (Figure 3.9-c,d), as determined from the adsorption isotherms by density-functional theory calculations.²¹⁹

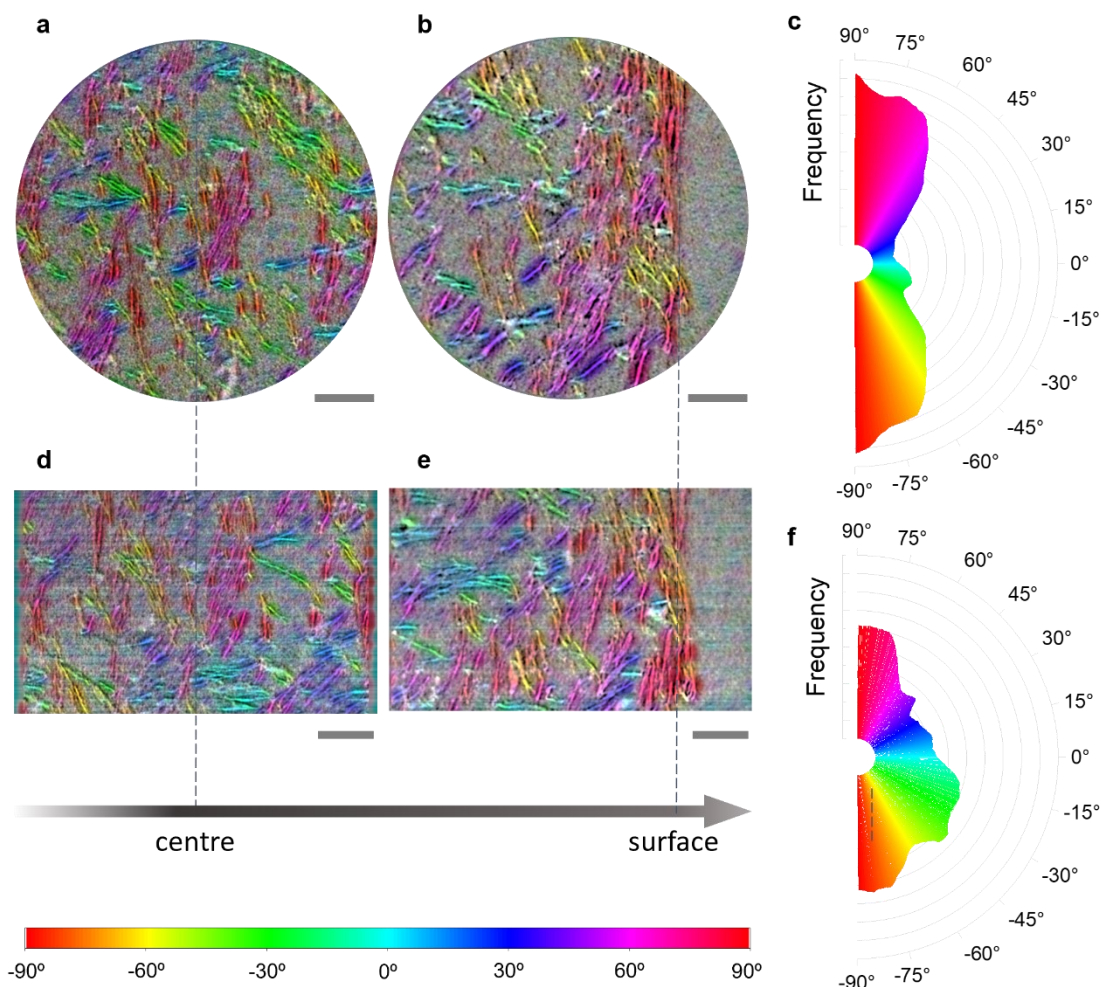


Figure 3.10: (a,b) Top (x-y) view of the printed filament in the central (a) and outer (b) region, as obtained from X-ray nanoCT (z is the filament axis), the different orientations of the platelets are marked with different colours; (c) histogram showing the preferential orientations of the platelets near the surface of the printed filament; (d,e) side (y-z) view of the printed filament in the central (d) and outer (e) region; (f) histogram showing the orientations of the platelets in the central region of the filament; all the scale bars are 10 μm .

X-ray nanoCT provided information on the orientation of the graphene platelets inside the three-dimensional electrodes (Figure 3.10). In the central region of the printed filaments, the nanoplatelets have a completely random orientation, as observed in the x-y and x-z tomographic slices in Figure 3.10-a,d. On the contrary, in the outer region of the filaments the nanoplatelets show a preferential orientation parallel to the filament surface (particles highlighted in red and orange in Figure 3.10-b,e). To better quantify the degree of orientation, the angle between each platelet and the horizontal y axis was determined with OrientationJ (Figure 3.10-c,f). The histogram corresponding to the outer region of the filament shows a strong preference for the 90°/-90° direction parallel to the filament surface (Figure 3.10-c), whereas the orientations of the platelets in the central region of the filament are more uniformly distributed (Figure 3.10-f). The different texture of the two regions is caused by the flow of the ink inside the nozzle during the extrusion process. Dispersions of anisotropic

particles can be oriented by extrusion flows as a consequence of the shear forces acting on the particles.^{220,221} However, during the extrusion of a yield-stress material, only the outer region of the fluid is subjected to a shear flow, whereas the inner region moves forward with a constant velocity profile (*plug flow*), since the shear stress acting on this region is smaller than the yield stress.^{220,222,223} Therefore, the central region of the extrudate is unyielded and the particles in this region cannot change their orientation, whereas the particles in the outer region tend to orient in the direction of the flow. A similar microstructure has been observed in the extrusion of cellulose nanocrystal and alumina platelets.^{220,221} The radius of the unyielded region depends on the ratio between the yield stress of the fluid and the maximum stress acting on the fluid (τ_Y/τ_W), becoming negligible when this ratio is sufficiently small.²²³

Computation-fluid dynamics (CFD) simulations were used to determine the velocity profile of the graphene inks during extrusion and the size of the unyielded region. The central region of the ink moves forward along the nozzle axis with a constant velocity $\sim 8.1 \text{ mm s}^{-1}$ (Figure 3.11-a,b).

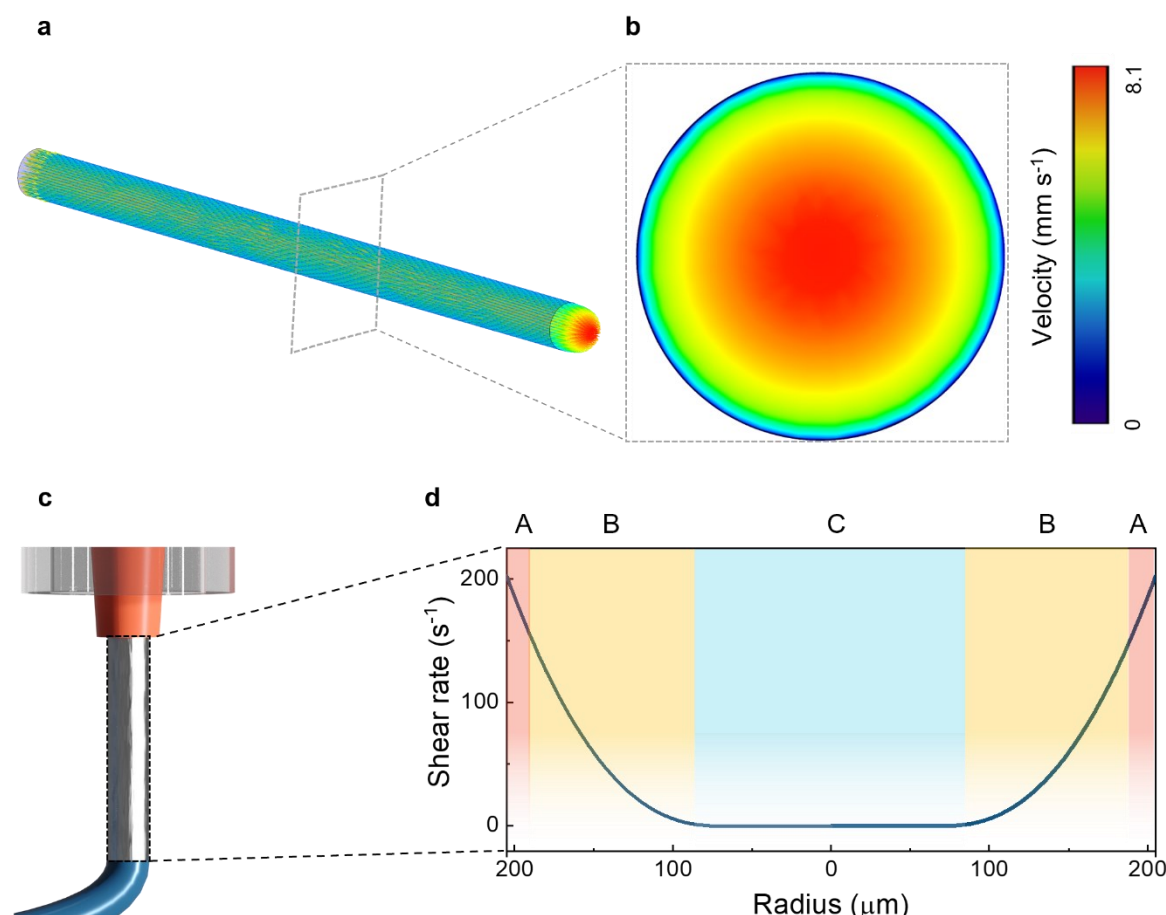


Figure 3.11: (a,b) Velocity profile of the graphene ink inside the printing nozzle (410 μm in diameter); (c,d) Schematic of the printing process and shear rate profile inside the printing nozzle, showing three different regions: region A, with aligned platelets as determined from X-ray nanoCT ($\sim 15 \mu\text{m}$ in size); region A+B, characterized by a shear flow; region C, characterized by a plug flow with a negligible shear rate.

The velocity profile gradually decreases in the outer region of the nozzle, becoming zero at the nozzle wall, coherently with the no-slip boundary conditions assumed for the simulation. The shear rate profile presents a central region characterized by a predominant plug flow and an outer region in which the shear rate gradually increases, reaching a maximum value of $\sim 200 \text{ s}^{-1}$. The plug flow region has a diameter of $\sim 150 \text{ }\mu\text{m}$, which is significantly smaller than the size of region with randomly-aligned platelets ($\sim 380 \text{ }\mu\text{m}$, as measured from X-ray nanoCT), as shown in Figure 3.11-c,d. This might be caused by the short residence time ($\sim 1 \text{ s}$) of the ink inside the nozzle during the extrusion process. The large graphene platelets require a finite amount of time to change their orientation during shear, thus only the platelets in the proximity of the nozzle wall, which experience the highest shear rate, can be aligned by the flow. In support of this explanation, it was recently demonstrated that the alignment time of cellulose nanocrystals during shear flow scales as the inverse of the shear rate.²²⁰ However, a direct correlation between the shear rate profile of the graphene inks and the degree of nanoplatelets orientation was here made difficult by the possible presence of wall slip in the extrusion nozzle. The CFD simulations could hence only provide a qualitative explanation of the morphological features observed in the printed graphene electrodes. In particular, wall slip during extrusion typically reduces the shear experienced by the particles and increases the volume of the region moving by plug flow, providing another explanation for the discrepancy between the size of the sheared region and the region presenting aligned platelets.¹¹⁸

In summary, this section shed light onto the physical properties of the 3D printed graphene structures that are relevant for their use in graphene supercapacitors. The macroscopic morphology and microstructure of the electrodes were here discussed. Section 1.3 will present the electrochemical characterization of the printed graphene electrodes and relate their microstructural properties to the electrochemical performance.

1.3. Half-cell electrochemistry

Three-dimensional electrodes must have high electrical conductivity to ensure fast transport of charges and uniform charge storage in different regions of the structure.²²⁴ The electrical conductivity of the graphene inks was evaluated with four-probe measurements, before and after the debinding treatment (Figure 3.12-a,b). After drying in air, the structures present a conductivity of $\sim 270 \text{ S m}^{-1}$, which is already higher than inks based on reduced graphene oxide reported in recent literature. The excellent electrical conductivity of the graphene inks arises from the presence of multilayer platelets with large lateral size and low defect density, as demonstrated by the physical characterization presented in the previous section. In addition to this, the graphene structures have higher density of active material compared to reduced graphene oxide electrodes owing to the high mass loading of the capillary paste. After the carbonization of the cellulose viscosifier during the debinding process, the conductivity of the structures reaches $\sim 1370 \text{ S m}^{-1}$, which is considerably higher than reduced graphene oxide electrodes (Figure 3.12-b). The debinding process for the

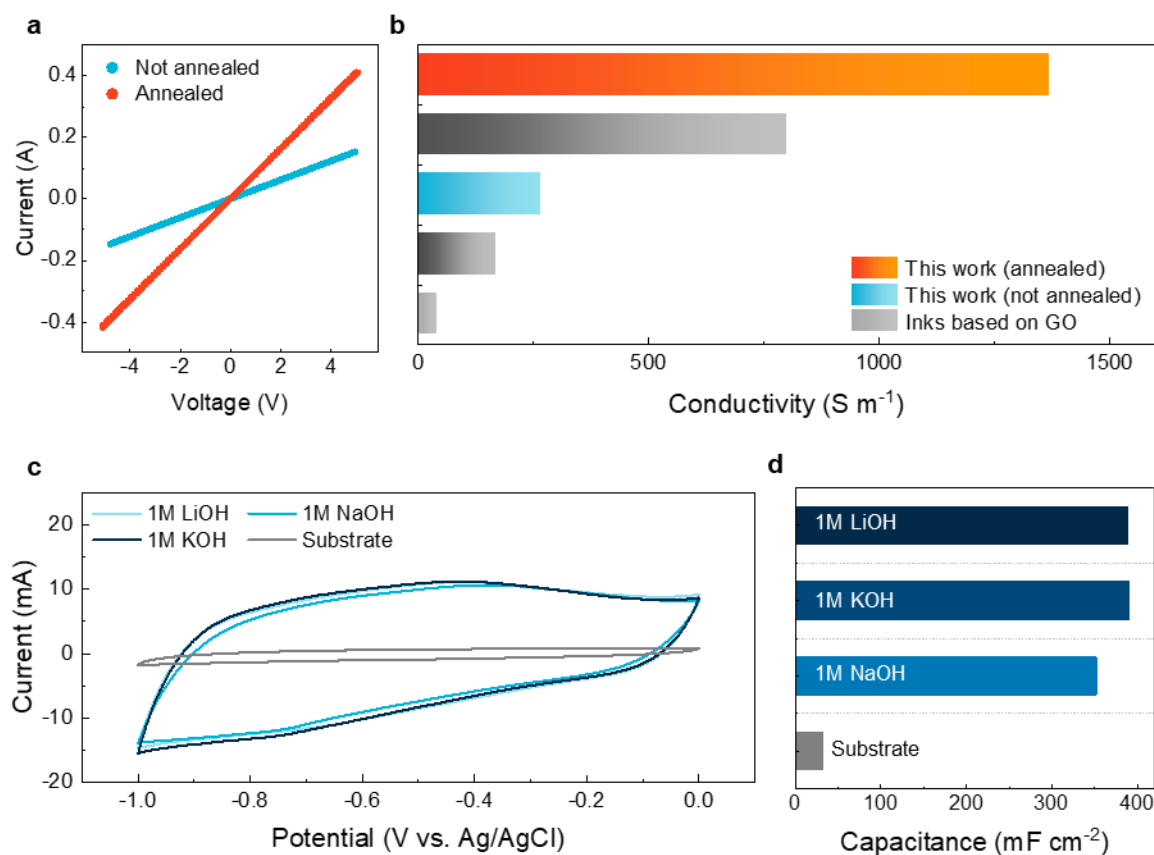


Figure 3.12: (a) Current-voltage curves for the graphene ink before and after debinding; (b) comparison of the electrical conductivity of the graphene ink with literature values for reduced graphene oxide inks (references for the comparison in Appendix A2); (c) cyclic voltammetry of the printed graphene electrodes in various aqueous electrolytes; (d) comparison of the specific capacitance of the 3D printed electrodes in different electrolytes.

capillary graphene structures only involves a thermal annealing at 350°C, and it is thus significantly more sustainable, energy-efficient and fast than the thermal reduction of graphene oxide at temperatures higher than 1000°C.

The capacitive properties of the graphene electrodes were investigated in conventional electrolytes for aqueous supercapacitors, *i.e.* solutions of alkali hydroxides, which present high charge mobility for the formation of an electrical double layer (Figure 3.12-c). In particular, 1 M LiOH electrolytes provided the highest capacitance, probably owing to the small radius and high charge density of Li^+ ions (Figure 3.12-d).²²⁵ The contribution of the graphite current collector to the charge storage processes in 1 M LiOH is negligible when compared to 3D printed electrodes (grey curve in Figure 3.12-c). The cyclic voltammogram for a 2-layer graphene electrode presents a quasi-rectangular shape in the 1 M LiOH electrolyte, in a potential range between -1 V and 0 V vs. Ag/AgCl (Figure 3.13-a), as expected from a supercapacitive material with a predominant EDL charge storage mechanism. However, a broad peak around -0.4 V vs. Ag/AgCl can also be observed, which

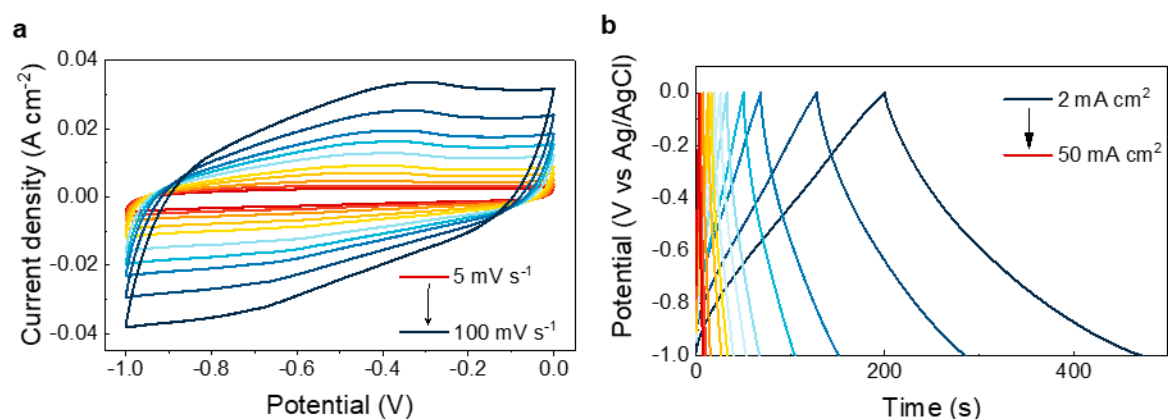


Figure 3.13: (a) Cyclic voltammetry for a 2-layer woodpile graphene electrode in 1 M LiOH at different scan rates (three-electrode configuration); (b) galvanostatic charge-discharge tests for a 2-layer woodpile graphene electrode in 1 M LiOH at different current densities (three-electrode configuration).

might arise from minor pseudocapacitive processes involving oxygen moieties on the surface of graphene platelets. The commercial graphene nanoplatelets used in this work were produced with a non-oxidative proprietary process (as stated by the manufacturer, XGSciences, in the technical datasheet); however naturally occurring groups (ether, carboxyl, hydroxyl) can be present on the surface of the platelets, as also stated in the technical datasheet. This can explain the pseudocapacitive response observed in Figure 3.13-a.

The electrodes retain a quasi-rectangular cyclic voltammogram even at high scan rates (100 mV s^{-1}), although a minor shape distortion is evident as a result of the IR drop in the electrolyte and other ohmic losses in the system. The corresponding charge-discharge curves are characterized by a quasi-triangular shape, again evidencing a capacitive charge storage process (Figure 3.13-b).

The effects of the geometry and mass loading of the electrodes on their electrochemical properties were studied by fabricating woodpile structures between 2 and 8 layers and testing them in a 3-electrode configuration, Figure 3.14. In addition, the capacitance of 4-layer woodpile electrodes was compared to a 4-layer compact structure to assess whether the electrolyte could infiltrate into the woodpile channels. The 4-layer woodpile electrode achieved a capacitance of $\sim 594 \text{ mF}$ (calculated from the CV scan), whereas the compact electrode only displayed a capacitance of $\sim 111 \text{ mF}$ despite its large loading of active material (58.3 mg vs. 16.7 mg for the woodpile electrode), indicating that the surface area in contact with the electrolyte was significant higher for the woodpile electrode (Figure 3.14-a). The 4-layer woodpile electrode presents a geometric surface area of $\sim 720 \text{ mm}^2$, with an envelope porosity (*i.e.* the relative volume of the empty channels between the printed filaments, calculated assuming the filaments are dense and non-porous) accounting for more than 55% of the total volume of a compact electrode with the same footprint area and thickness ($\sim 90.2 \text{ mm}^3$ out of a total volume of $\sim 164 \text{ mm}^3$). When the values of capacitance were normalized by the geometric surface area of the electrodes, the woodpile structure reached a specific

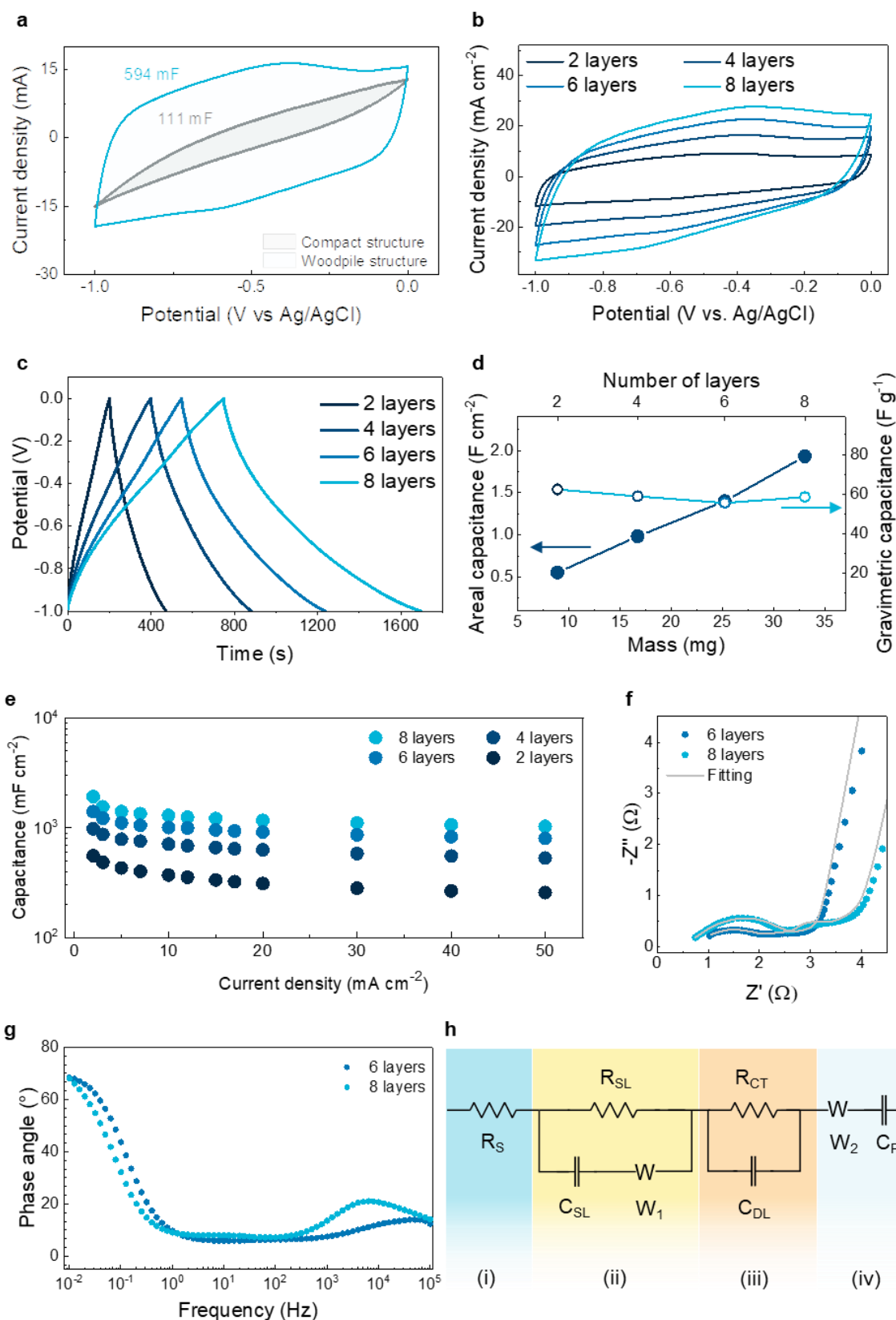


Figure 3.14: (a) CV of the 4-layer woodpile and compact structures; (b,c) CV and GCD of woodpile structures at different number of layers (at 20 mV s⁻¹ and 2 mA cm⁻², respectively); (d) comparison of the areal and gravimetric capacitance of woodpile structures with different number of layers; (e) capacitance retention at increasing current densities; (f, g) Nyquist and Bode plots for the 6- and 8- layer woodpile electrodes; (h) equivalent circuit used to fit the impedance spectra.

capacitance $\sim 0.82 \text{ mF mm}^{-2}$, still higher than the $\sim 0.68 \text{ mF mm}^{-2}$ of the compact structure. In addition, the cyclic voltammogram of the compact electrode shows a highly resistive behaviour, with a significant deviation from a rectangular shape. The lower specific capacitance and the distorted shape of the CV indicate the presence of irreversible ohmic loss in the compact structure, probably caused by incomplete binder removal from the central region of the thick electrode and the formation of internal cracks during the thermal treatment. Compact electrodes with high thickness are more prone to deformation and cracking, which can cause delamination or loss of electrical contact with the current collector.²²⁶ In contrast, when the number of printed layers of the woodpile electrode is increased, the CV retains a quasi-rectangular shape (Figure 3.14-b), and the charge-discharge curves remain approximately triangular, with a proportional increase in the charge and discharge time (Figure 3.14-c). The areal and gravimetric capacitance at increasing number of layers are compared in Figure 3.14-d, to assess whether thicker woodpile electrodes also exhibit higher charge transfer hindrance, similarly to what was observed for the compact electrode. Notably, the gravimetric capacitance remains approximately constant with the number of printed layers (around 58 F g^{-1} for the 8-layer electrode), whereas the areal capacitance increases linearly up to 1.93 F cm^{-2} ,^{††} demonstrating a direct proportionality between mass and areal capacitance. These results suggest that even in thicker woodpile structures, with higher mass of active material, electrons and ions can be transported quickly and efficiently owing to abundant and highly-conductive charge-transfer paths and the high envelope porosity ($\sim 55\%$) which promote electrolyte infiltration into the electrodes. The capability of the electrolyte to penetrate into the pores of the electrodes was further confirmed by density measurements based on the buoyancy method (*i.e.* Archimedes' principle). The density of the electrodes measured from weighing in air and deionized water is $\sim 2.2 \text{ g cm}^{-3}$, which corresponds to the density of graphite. The presence of closed pores or voids inaccessible to water would determine an apparent density value lower than the theoretical density of the active material making up the electrodes.

A further evidence of the fast transport of ions and electrons in the printed electrodes was provided by rate capability tests on the 6 and 8 layer electrodes, which retain more than 50% of the initial capacitance at a high current density of 50 mA cm^{-2} (Figure 3.14-e). Notably, the 8-layer electrode has a slighter smaller capacitance retention than the 6 layer (53% vs. 57%). To better investigate the lower capacitance retention of the 8 layer electrode, the charge transfer kinetic was further analysed with electrochemical impedance spectroscopy (EIS). The low frequency region of the Nyquist and Bode plots (Figure 3.14-f,g) represents the diffusion of the electroactive species between the bulk and the surface of the electrode, whereas the high frequency region accounts for the capacitive response and the ohmic drop in the electrolyte. The 3D electrode was modelled

^{††} This value of capacitance is normalized by the footprint area of the electrode (1 cm^2), consistently with the values of capacitance and capacity reported in the rest of the work. A discussion about this choice was presented in Chapter 2.

according to the electrochemical circuit in Figure 3.14-h, where the initial ohmic resistor R_S describes the resistance of the bulk electrolyte, the resistance of the bulk active material and the contact resistance between the current collector and the active material, Figure 3.14-h, (i).

The parallel connection between R_{SL} and C_{SL} represents the charge storage at the surface layer of the electrode, with a Warburg impedance to describe the diffusive transport of charges, Figure 3.14-h (ii).¹²⁵ The faradaic charge transfer at the electrode/electrolyte interface is described by R_{CT} , connected in parallel with the double-layer capacitance C_{DL} , Figure 3.14-h (iii). Finally at very low frequencies, a Warburg impedance W_2 and a capacitor C_P take into account the diffusion of the electrolyte inside the electrode structure, Figure 3.14-h (iv).¹²⁵ The 6-layer electrode presents a lower ohmic resistance and higher double-layer capacitive response compared to the 8-layer electrode (Table 3.2), possibly because some charge transport hindrance starts to be present in the thick 8-layer electrode, either connected to the slower and incomplete charge diffusion (as supported by the higher Warburg impedance), or because of the lower mechanical stability of the thicker electrode that might result in electrical disconnection with an increase of internal resistance. Graphene electrodes are mechanically stable, but unlike reduced graphene oxide they are rigid due to the lower aspect ratio of graphene nanoplatelets; therefore, thicker structures can be more easily disconnect from the flexible graphite current collector leading to higher internal resistance.

Table 3.2: EIS fitting parameters for the 8-layer and 6-layer electrodes.

	6 layers	8 layers		6 layers	8 layers
R_S (Ω)	0.53	0.58	R_{CT} (Ω)	0.39	0.51
R_{SL} (Ω)	1.5	1.9	C_{DL} (mF)	$35 \cdot 10^{-3}$	$19 \cdot 10^{-3}$
C_{SL} (mF)	$4.6 \cdot 10^{-4}$	$2.5 \cdot 10^{-4}$	W_2 (Ω)	1.4	2.8
W_1 (Ω)	0.18	0.24	C_P (mF)	5.7	4.4

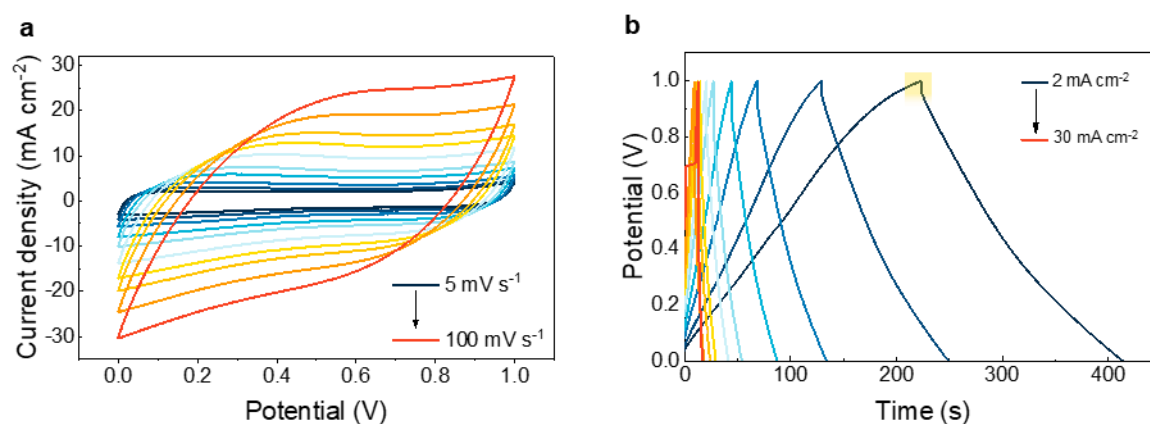


Figure 3.15: (a) Cyclic voltammetry on 6-layer symmetric supercapacitors in a 1 M LiOH liquid electrolyte; (b) Galvanostatic-charge discharge tests on 6-layer symmetric supercapacitors (IR drop highlighted in yellow).

1.4. Symmetric supercapacitors characterization

The practical use of the 3D printed graphene electrodes in full devices was investigated assembling symmetric supercapacitors in a 1 M LiOH electrolyte. Each supercapacitor consisted of two identical printed structures, *i.e.* same geometry and number of layers, acting respectively as the positive and negative electrode during charge and discharge. The cyclic voltammetry of the symmetric devices shows a quasi-rectangular shape in a potential window of 1 V (Figure 3.15-a), with no high-current tails at either side of the window which would be indicative of the decomposition of the electrolyte. Consistently with the CV tests, the galvanostatic-charge discharge curves present an approximately triangular shape similar to the one observed for single-electrode tests, with a small IR drop in the potential profile when the electrode starts to be discharged ($\sim 30 \text{ mV}$ at 2 mA cm^{-2} , Figure 3.15-b). From these results it is clear that the symmetric devices have a capacitive charge storage mechanism, as expected from the electrochemical response of the individual printed electrodes. More importantly, cyclic voltammetry and galvanostatic charge-discharge tests allowed for an accurate assessment of the main figure of merits describing the electrochemical performance of symmetric devices, namely areal capacitance, rate capability and energy and power density. Similarly to what was observed for single electrodes, the areal capacitance of symmetric devices increases gradually with the number of layers. However, the capacitance does not follow a direct proportionality, since the capacitance of the 8-layer device is only marginally better than the 6-layer device (1.64 F cm^{-2} vs. 1.57 F cm^{-2}), as indicated by GCD tests in Figure 3.16-a,c. Additionally, the gravimetric capacitance of the 8-layer device is the lowest compared to the other devices, probably a consequence of the electrical disconnection or incomplete charge diffusion already observed for the 8-layer electrode in three-electrode configuration (Figure 3.16-e). The symmetric devices show lower capacitance retention than the single electrodes (Figure 3.16-a), probably because of the higher transport resistance when two 3D printed electrodes are coupled to form a symmetric cell.

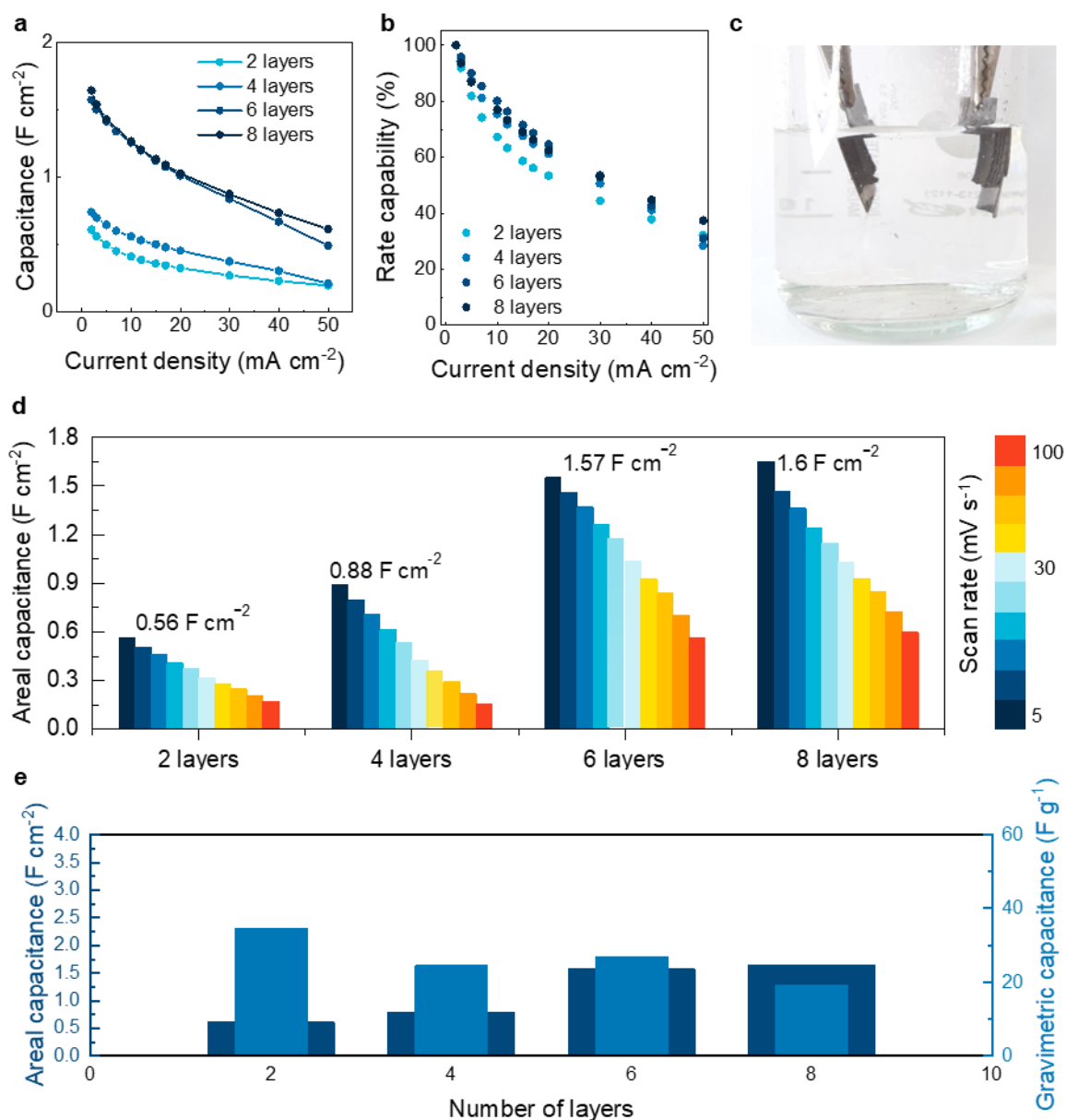


Figure 3.16: (a,b) Capacitance and rate capability of the 3D printed graphene supercapacitors as determined from galvanostatic charge-discharge tests at different current densities; (c) digital photograph showing the symmetric graphene electrodes in a beaker cell; (d) areal capacitance at different current densities for the symmetric graphene supercapacitors as determined from cyclic voltammetry; (e) comparison of the areal and gravimetric capacitance of the symmetric graphene supercapacitors as a function of the number of printed layers.

Nonetheless, the 6- and 8- layer devices still retain an areal capacitance of 0.61 F cm^{-2} and 0.49 F cm^{-2} at 50 mA cm^{-2} , respectively, as determined from GCD, and an areal capacitance of 0.60 F cm^{-2} and 0.56 F cm^{-2} at 100 mV s^{-1} , as determined from CV tests (Figure 3.16-a,b,d).

The 6-layer device exhibits the overall best performance for applications, considering the charge transfer limitations of the 8-layer systems evidenced by CV, GCD and EIS tests. Therefore, the electrochemical properties of the symmetric 6-layer devices were benchmarked against state-of-the-art supercapacitors based on carbon materials (Figure 3.17). The areal capacitance achieved by

the 6-layer device ($\sim 1.57 \text{ F cm}^{-2}$) outperforms supercapacitors obtained from reduced graphene oxide hydrogels, as a consequence of the better conductivity and higher density of the graphene structures (Figure 3.17-c). These features also ensure high power (0.968 mW cm^{-2}) and energy density ($51.2 \text{ } \mu\text{W cm}^{-2}$), which compare favourably with recently reported carbon supercapacitors (Ragone plot in Figure 3.17-b). The energy and power densities were here calculated according to Equations 2.32 and 2.33 (*i.e.* assuming a perfectly linear relationship between cell potential and discharge time in GCD tests). Although this choice might lead to a small overestimate of the energy density for our electrodes, since the GCD in Figure 3.15 are not perfectly linear, this method is used here for its simplicity. A better approach to calculate energy density is discussed by Arbizzani *et al.*²²⁷, leading to similar results as the one discussed here. It must also be noted that 3D printed EESDs are notoriously affected by low reproducibility, with uncontrollable differences in the electrochemical properties of electrodes printed using the same CAD file and ink composition. Accurate statistics on the power and energy density of the printed devices were not performed in this work owing to time limitations; nonetheless, such studies are fundamental for the commercialization of printed EESDs. In particular, a large variability in the key electrochemical parameters would require

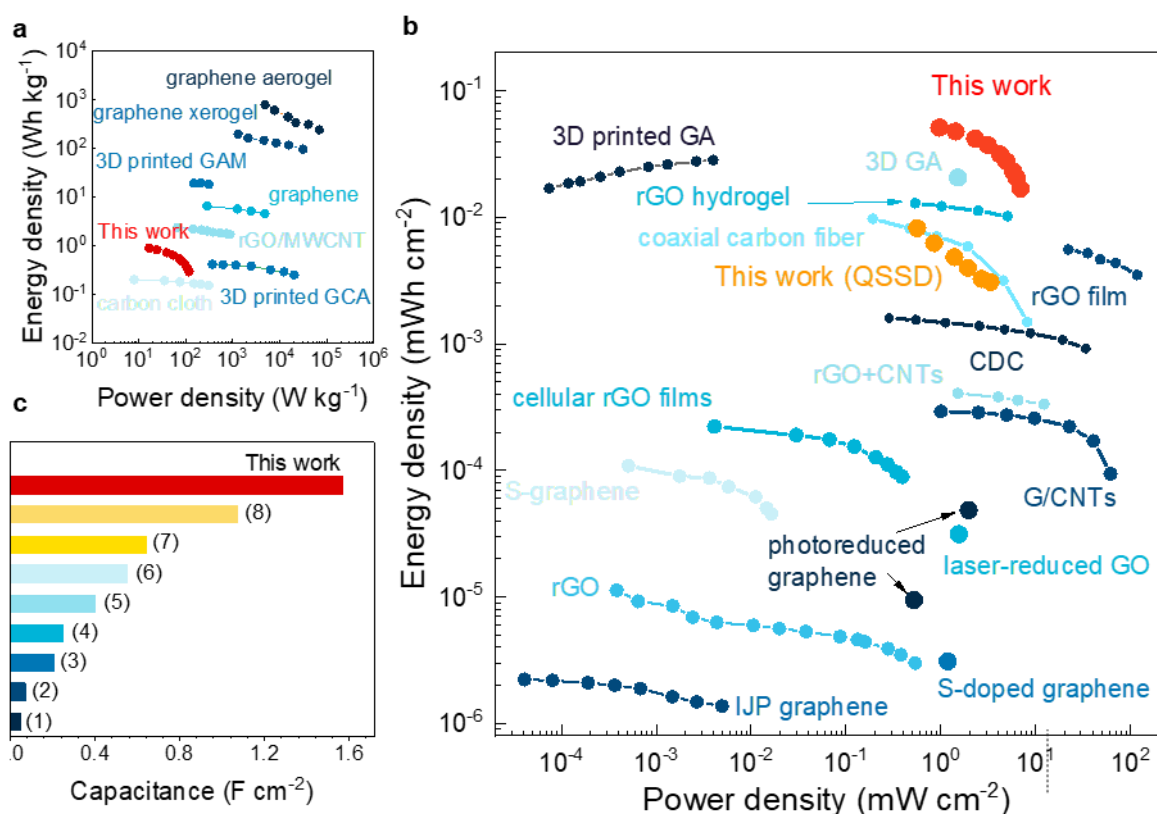


Figure 3.17: (a) Ragone plot comparing the gravimetric power and energy density of the 3D printed graphene supercapacitors with recent carbon-based devices (references in Appendix A2); (b) Ragone plot comparing the areal energy and power density of the 3D printed graphene supercapacitors with state-of-the-art carbon-based devices (references in Appendix A2); (c) comparison of the areal capacitance of the 3D printed graphene supercapacitors with recently reported carbon devices (references in Appendix A2).

extensive post-manufacturing quality control tests and would result in a large number of cells being rejected, thereby increasing the final cost of the printed devices.

When the gravimetric properties are considered, the 6-layer device is in line with carbon cloth and reduced graphene oxide/carbon nanotubes composites, but it shows significantly lower energy density than graphene aerogels because of the dense filaments and thick, multilayer nature of the platelets that constitute the electrodes. However, a large charge storage capability per unit area is

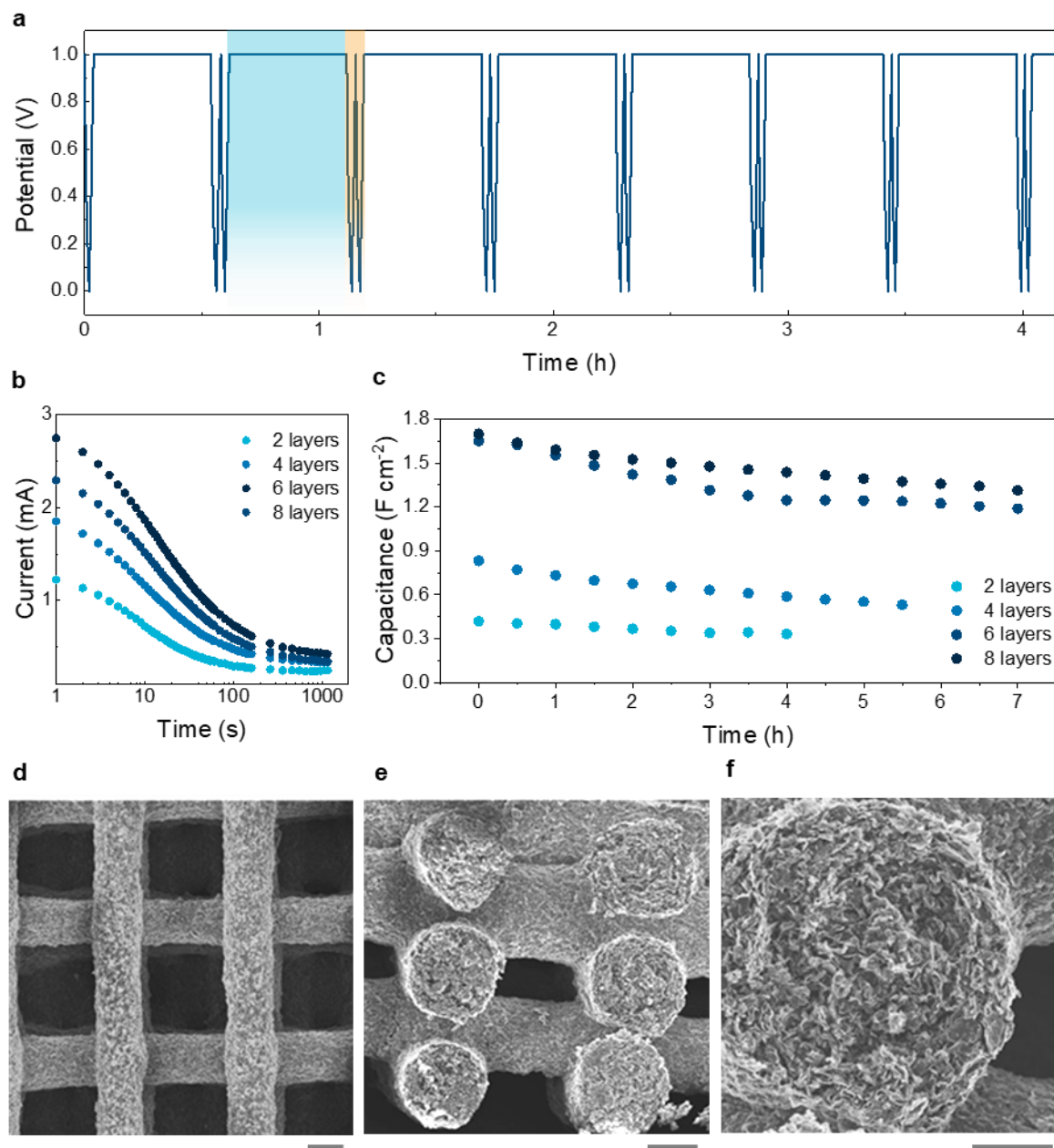


Figure 3.18: (a) Voltage holding test for an 8-layer symmetric device, the potential is kept constant at the maximum operating potential of the device (1V) for 30 min (blue region) and then it is charged and discharged to measure the capacitance; the test is then repeated; (b) leakage current of the symmetric graphene supercapacitors during voltage holding tests; (c) capacitance retention during voltage holding tests of symmetric graphene supercapacitors at different number of layers; (d-f) SEM imaging of the woodpile electrodes after cycling in a symmetric device (scale bars 200 μm , 200 μm and 100 μm , respectively).

more important than a low specific weight in miniaturized EESDs for portable or wearable electronics.

The stability of the symmetric supercapacitors during operation was studied with voltage-holding tests (VHTs), in which the devices are kept at the peak operating voltage for a prolonged time and the leakage current and capacitance fade are monitored over time. A typical voltage-holding test on the symmetric devices is presented in Figure 3.18-a. A constant potential of 1 V is applied to the supercapacitors for 30 min, and the devices are subsequently discharged to measure the capacitance and then recharged to start a new cycle. After more than 7 h of voltage holding, all the supercapacitors present a capacitance retention higher than 72% (Figure 3.18-c). The high initial leakage current (~ 1 -3 mA) is required to charge the thick electrodes when the voltage is first applied, but after a few minutes it decreases to a stable value of ~ 0.2 -0.5 mA. The structure of the electrodes appear unaltered after cycling, with no loss of material or cracks that might originate from unwanted side reaction with the evolution of gas, *e.g.* decomposition of the electrolyte and oxygen evolution inside the pores of the electrode (Figure 3.18-e,f).

Although the assembly of symmetric woodpile supercapacitors presented so far provides a more reliable characterization for real applications, it still requires the use of a flooded cell with a liquid

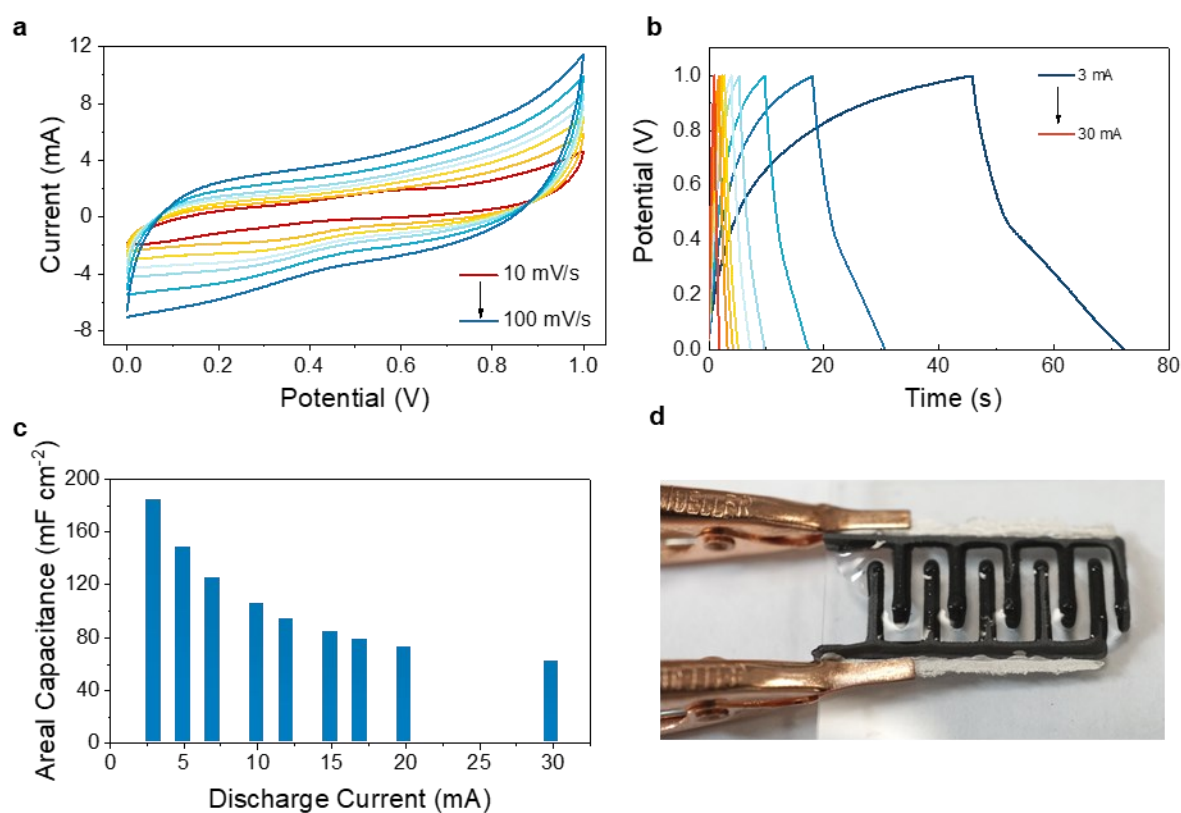


Figure 3.19: (a) Cyclic voltammetry on the interdigitated graphene supercapacitors; (b) galvanostatic charge-discharge on the interdigitated graphene supercapacitors; (c) rate capability of the interdigitated graphene supercapacitors; (d) digital photograph of an interdigitated device.

electrolyte and two stacked electrodes. For the direct integration into portable electronics, an interdigitated geometry with a solid-state or quasi-solid-state electrolyte is preferable. To fabricate an interdigitated supercapacitor, two interdigitated graphene electrodes were printed on an insulating glass substrate (Figure 3.19-c). A viscous polyvinyl alcohol electrolyte was poured between the fingers and the device was encapsulated with parafilm. The electrodes did not require a pre-patterned current collector owing to the good electrical conductivity of the graphene filaments, which could be directly contacted to the external circuit using silver paste. The interdigitated devices were tested with cyclic voltammetry (Figure 3.19-a) and galvanostatic charge-discharge (Figure 3.19-b), demonstrating a capacitance of 184 mF cm^{-2} , which is superior to similar devices based on reduced graphene-oxide (74.3 mF cm^{-2}) and activated carbon (104.4 mF cm^{-2}).^{88,121} At the discharge current of 30 mA the device still retained a capacitance of 62 mF cm^{-2} (Figure 3.19-c) and after an initial capacitance loss of $\sim 10\%$, the devices was stable over constant-current cycling for more than 4000 cycles (Figure 3.20-a). The interdigitated devices have a high equivalent series resistance ($\sim 5.18 \Omega$ as determined from GCD, Figure 3.20-b and $\sim 4.33 \Omega$, as determined from EIS, Figure 3.20-c), which can be explained considering the interface contact resistance resulting from the absence of a current collector and the long transport distances inside the electrodes and electrolyte. Additionally, the gel electrolyte has higher viscosity than water, resulting in lower charge mobility. After cycling, a further increase in the equivalent series resistance was observed (10Ω from GCD and 9Ω from EIS, Figure 3.20-b,c), which was probably caused by the gradual evaporation of water from the gel electrolyte, with a reduction in ionic mobility. In addition to this explanation, the electrochemical degradation of the polymer-based electrolyte might also occur during cycling, since the cyclic voltammogram presents a current spike in the high-voltage region that is notably higher than the devices in liquid electrolytes. This resulted in a relatively low coulombic efficiency ($\sim 60\%$ at a current density of 5 mA cm^{-2}) in the first cycles. The fast ageing of interdigitated devices might

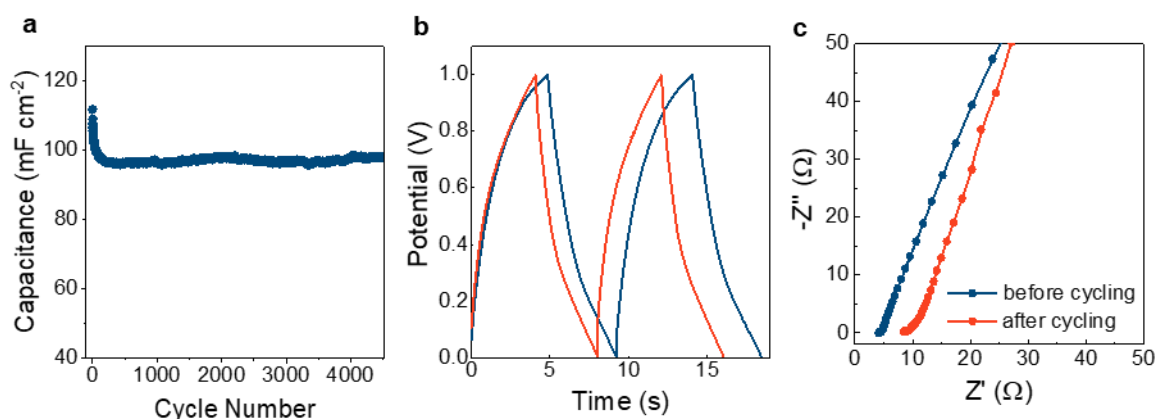


Figure 3.20: (a) Capacitance retention over repeated galvanostatic cycling (10 mA) for the interdigitated graphene supercapacitors; (b) initial and final charge discharge curves after repeated cycling; (c) EIS on the interdigitated supercapacitors before and after cycling.

be improved using water-in-salt or ionic liquid electrolytes, which are more electrochemically stable, and encapsulating the device in resin to prevent water evaporation.

1.5. Laser-annealed electrodes for paper supercapacitors

The 3D printing process for graphene supercapacitors presented in the previous sections is compatible with a wide range of substrates, ranging from metallic current collectors to insulating materials. Cellulose paper, in particular, is an appealing insulating substrate for interdigitated energy storage systems, for its natural abundance and flexibility. Cellulose paper is manufactured from renewable sources, and it is recyclable, biodegradable and chemically stable, providing ideal substrates for inkjet-printed supercapacitor electrodes.^{228,229} However, the use of extrusion-based 3D printing process to pattern three-dimensional electrodes on cellulose substrates has not been extensively investigated yet. This section presents the use of the capillary inks to manufacture graphene supercapacitors on cellulose paper *via* DIW. Considering the low cost and environmental safety of the materials employed, these paper supercapacitors can find application as disposable energy storage devices, which can be directly discarded in landfills and fragment into inert particles without releasing harmful chemicals.²³⁰ Cellulose paper thermally decomposes around $\sim 250^{\circ}\text{C}$,²³¹ which is lower than the decomposition temperature of most of the polymeric binders and viscosifiers used in DIW inks. A debinding process based on a CO_2 laser annealing was thus investigated to increase the

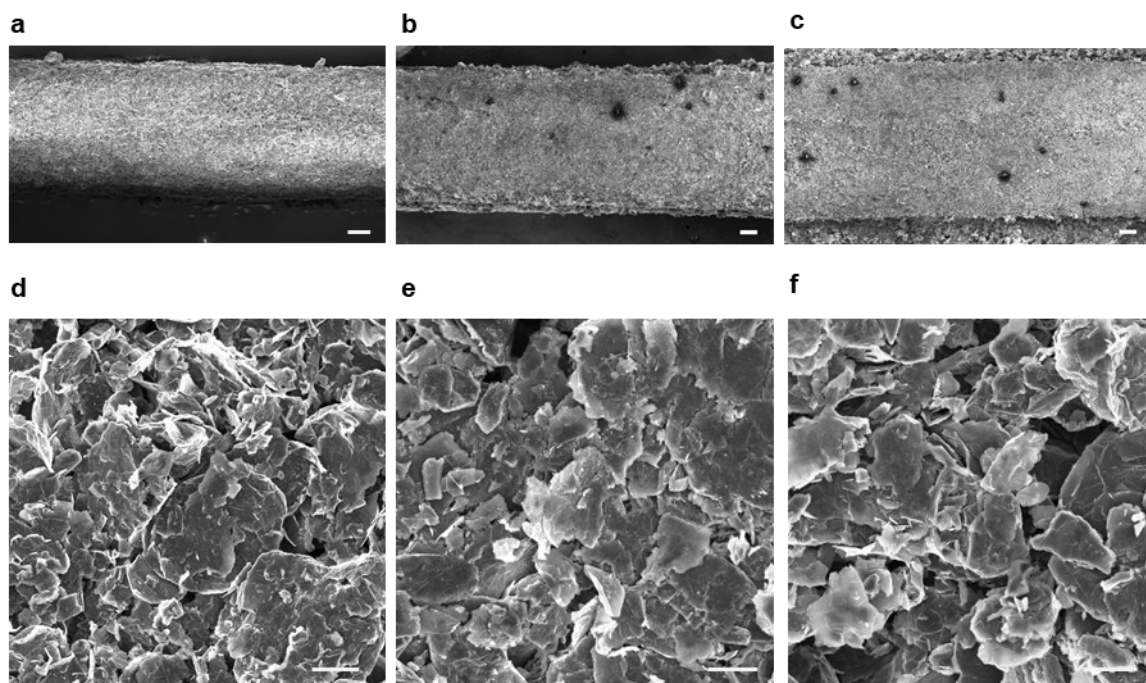


Figure 3.21: (a-c) Low magnification SEM images of printed lines after thermal annealing (a), laser annealing on a glass substrate (b) and laser annealing on a paper substrate (c), scale bars are 100 μm ; (d-f) high magnification SEM images of the electrode surface, after thermal annealing (d) (scale bar 10 μm), laser annealing on a glass substrate (e) (scale bar 5 μm), and laser annealing on a paper substrate (f) (scale bar 5 μm).

electrical conductivity and mechanical stability of the electrodes without damaging the cellulose substrates.

Interdigitated graphene electrodes were at first printed on cellulose paper and glass substrates. After drying in air, the electrodes were annealed with a CO₂ laser process, and the morphology and chemical nature of the laser-annealed electrodes were compared to thermally-annealed structures on glass. From SEM imaging (Figure 3.21) it is evident that the surface topology of the electrodes, consisting of a layer of graphene platelets parallel to the electrode surface, is not significantly affected by the laser-treatment (Figure 3.21-d,e,f). Importantly, the high temperatures reached on the surface of the electrodes and the decomposition of the binder do not induce cracks that might compromise the mechanical stability of the structures. Additionally, the laser-annealed filaments do not present uncontrolled shrinkage, warping or buckling when compared to the thermally annealed electrode (Figure 3.21-a,b,c).

The chemical nature of the graphene platelets after the annealing process was assessed with Raman spectroscopy (Figure 3.22-b). All the electrodes still present the characteristic features of pristine graphitic carbon, with a strong G-band ($\sim 1581\text{ cm}^{-1}$), and two weaker peaks corresponding to the D-band (1348 cm^{-1}) and 2D-band (2705 cm^{-1}). Notably, the ratio between the intensity of the D- and G-band for the laser-annealed and thermal-annealed structures is similar (~ 0.13 for thermal annealing vs. ~ 0.17 for laser annealing on paper), indicating that the laser process did not significantly increase the defect density or alter the chemical nature of graphene platelets in the proximity of the surface. Nonetheless, the laser treatment resulted in a reduction of the electrode resistance, as displayed in Figure 3.22-a, as a consequence of the removal of the cellulose binder hindering electron transport between the platelets.

The electrochemical properties of the interdigitated supercapacitors with a neutral sodium-chloride gel electrolyte are presented in Figure 3.23. The supercapacitors on paper achieved the highest

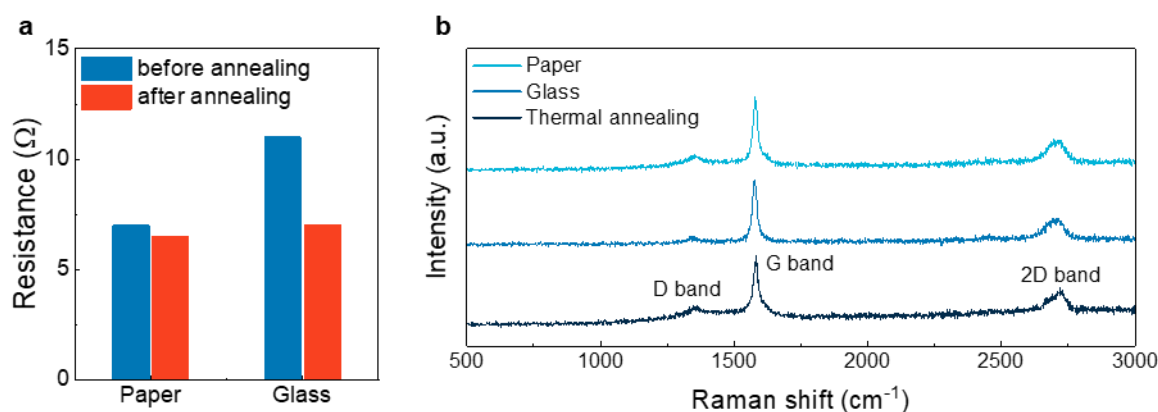


Figure 3.22: (a) Comparison of the electrical resistance of the printed graphene structures before and after annealing; (b) Raman spectra of the annealed electrodes.

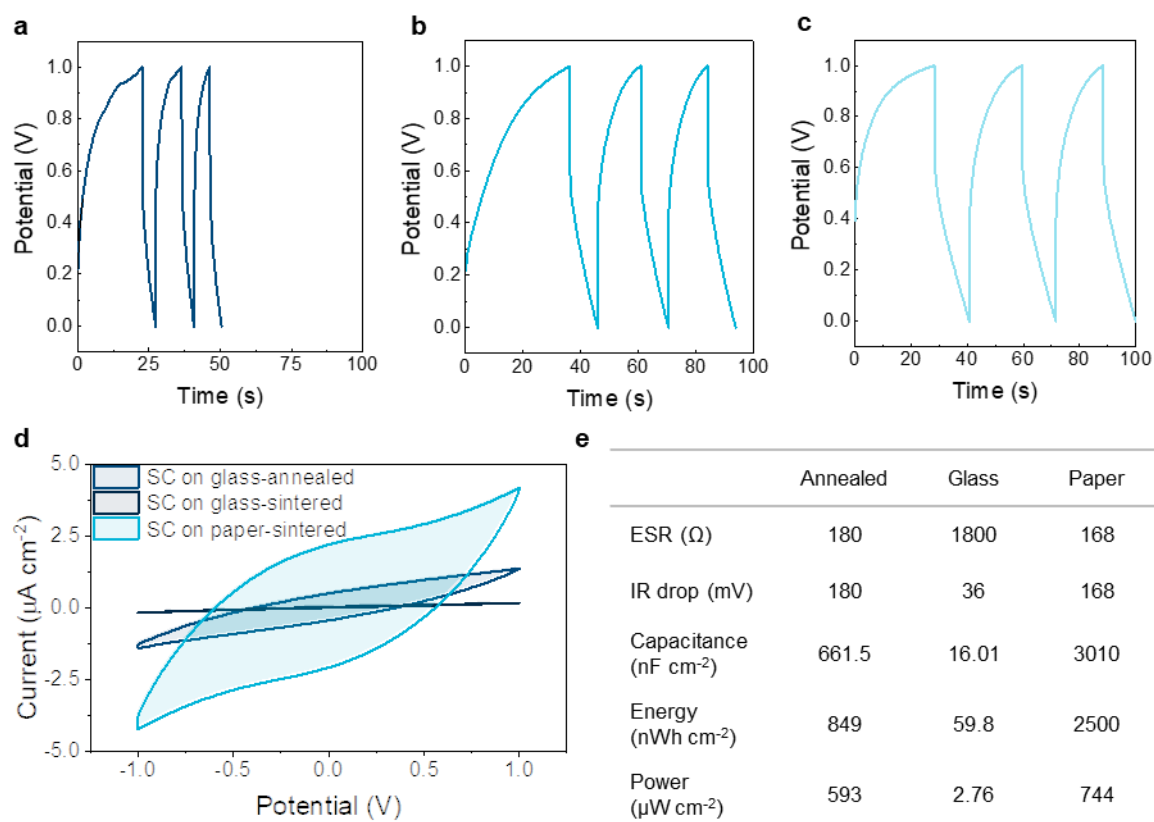


Figure 3.23: (a-c) Galvanostatic charge-discharge tests on the interdigitate devices: thermally-annealed devices on glass (a), laser-annealed devices on glass (b) and laser-annealed devices on paper (c); (d) cyclic voltammetry of the printed graphene devices after laser and thermal annealing; (e) comparison of the electrochemical properties of the printed graphene devices as determined from galvanostatic charge-discharge and cyclic voltammetry.

specific capacitance ($\sim 3 \mu\text{F cm}^{-2}$), significantly higher than the devices on glass (Figure 3.23-e). Notably, the capacitance of the devices on glass is limited by the high equivalent series resistance of these systems (Figure 3.23-e), determining irreversible energy dissipation during the charge-discharge process. The lower equivalent series resistance of the devices on paper might be explained taking into account the high porosity of cellulose paper, which promotes better adhesion of the electrodes and reduces the risk of detachment from the substrate and cracks. Additionally, cellulose presents a lower volume variation during annealing (thermal expansion coefficient $\sim 0.1 \text{ ppm K}^{-1}$),²³² whereas the larger thermal expansion of soda lime glass substrates can induce mechanical strain and cracks in the printed structures, increasing their internal resistance. The overall capacitance of the interdigitated devices is probably still limited by the incomplete annealing of the cellulose binder in the core of the printed electrodes, as the laser annealing process is mainly expected to affect the surface of the structure. This can explain the relatively low areal capacitance ($\sim 3 \mu\text{F cm}^{-2}$) observed for relatively thick electrodes (6 layers, corresponding to $\sim 2 \text{ mm}$).

2. Graphene electrodes for zinc hybrid capacitors

The 3D printed graphene devices presented in Section 1 are characterized by a capacitive charge-storage mechanism, reaching an energy density of $\sim 51.2 \mu\text{Wh cm}^{-2}$. Although this value is comparable with the best-performing carbon devices in the field, it is significantly lower than the energy densities achieved by aqueous batteries ($> 1 \text{ mWh cm}^{-2}$ for zinc ion batteries), presenting a faradaic charge storage mechanism.^{233,234} In order to increase the energy that the printed devices can store per footprint area, and at the same time retain a fast discharge kinetic, zinc hybrid capacitors (ZHCs) were fabricated using 3D printed graphene electrodes. The capacitive graphene structures were coupled with a negative zinc electrode, capable of storing charges by the reversible oxidation and reduction of zinc ions. A zinc-battery material was selected for the negative electrode because of its compatibility with aqueous electrolytes. On the contrary, sodium- and lithium-battery materials are often unstable in aqueous environment and call for organic electrolytes, such as organic carbonates.²³⁵

In addition to the introduction of a zinc negative electrode, the composition of the graphene ink was modified to overcome the charge transport hindrance observed in 8-layer structures (as detailed in Section 1). Carbon nanotubes (CNTs) were added to the graphene ink to enhance the mechanical stability of the final electrodes, by bridging different nanoplatelets and increasing the connectivity of the 3D network. CNTs also provided highly conductive paths which helped retain satisfactory charge-storage capability at fast charge and discharge rates. For these reasons, the addition of the carbon nanotubes made it possible to increase the electrode thickness to 12 layers and still retain excellent mechanical stability.

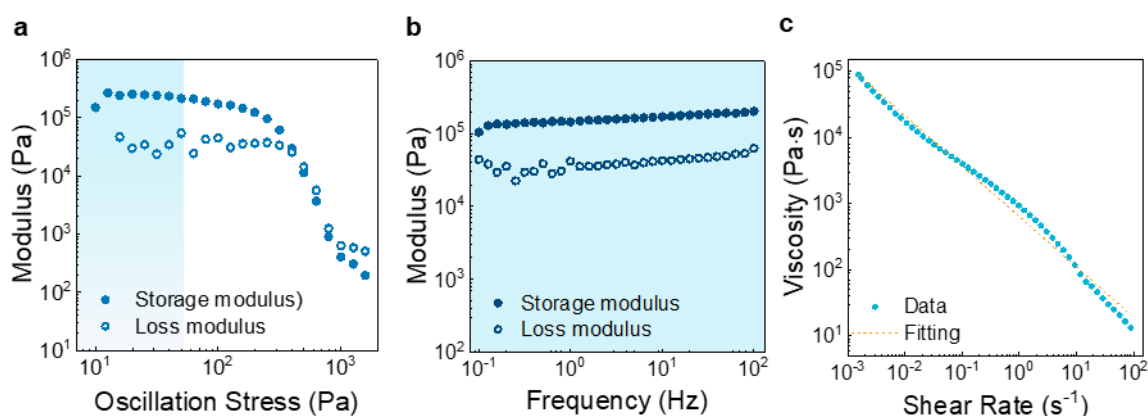


Figure 3.24: (a) Oscillatory amplitude sweep of the graphene-carbon nanotube inks (linear viscoelastic region highlighted in blue); (b) oscillatory frequency sweep of the graphene-carbon nanotube inks within the linear viscoelastic region; (c) flow ramp showing the viscosity of the graphene-carbon nanotube inks as a function of the shear rate; the experimental data were fitted using a power law.

2.1. Rheology and structural characterization

The rheology of the CNT-graphene ink was investigated with oscillatory and flow tests (Figure 3.24). In oscillatory amplitude sweeps (Figure 3.24-a), the ink exhibits a transition from a linear viscoelastic response to a non-linear behaviour at an oscillatory stress of ~ 50 Pa, marked by the gradual deviation of the storage modulus from a constant plateau. In the linear viscoelastic region, *i.e.* below ~ 50 Pa, the ink predominantly responds to the oscillatory stress as an elastic material, with a high storage modulus of $\sim 1.5 \times 10^5$ Pa (Figure 3.24-b). The high value of the storage modulus in the LVE region, which can be interpreted as the modulus of the ink at rest, ensures minimal bending of overhangs and buckling of stacked filaments, enabling the retention of the electrode structure during drying. At stress values higher than 50 Pa, the storage modulus progressively decreases, as a consequence of the destruction of the secondary interactions between the graphene nanoplatelets and carbon nanotubes (Figure 3.24-a). When the yield stress (~ 435 Pa) is reached, the storage modulus falls below the loss modulus indicating the fluidization of the gel structure, resulting from the complete destruction of the ink microstructure by the oscillatory shear.

The continuous flow tests evidence a shear-thinning behaviour, with a significant reduction of viscosity (from 10^5 Pa s to 10 Pa s) in the range of shear rate studied, 10^{-3} - 10^2 s $^{-1}$ (Figure 3.24-c). The flow index of the inks based on graphene-carbon nanotubes ($n = 0.24$) is smaller than the flow index of graphene inks ($n = 0.43$), probably because of the higher connectivity of the graphene-CNT microstructure and the greater degree of structural breakdown that the ink experiences during

Table 3.3: Comparison of the flow properties of the graphene and graphene-carbon nanotube inks.

	K (Pa s ^{n})	n	τ_Y (Pa)
Graphene ink	94	0.43	60
Graphene-CNT ins	641	0.24	435

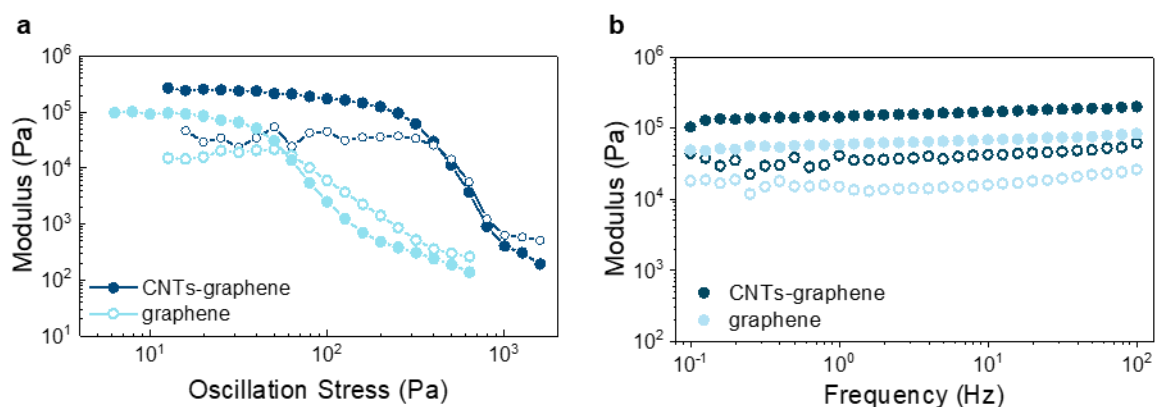


Figure 3.25: (a,b) Comparison of the oscillatory properties of the graphene ink (light blue) and the CNT-graphene ink (dark blue) determined from amplitude sweep (a) and frequency sweep tests (b), closed circles represent G' , open circles G'' .

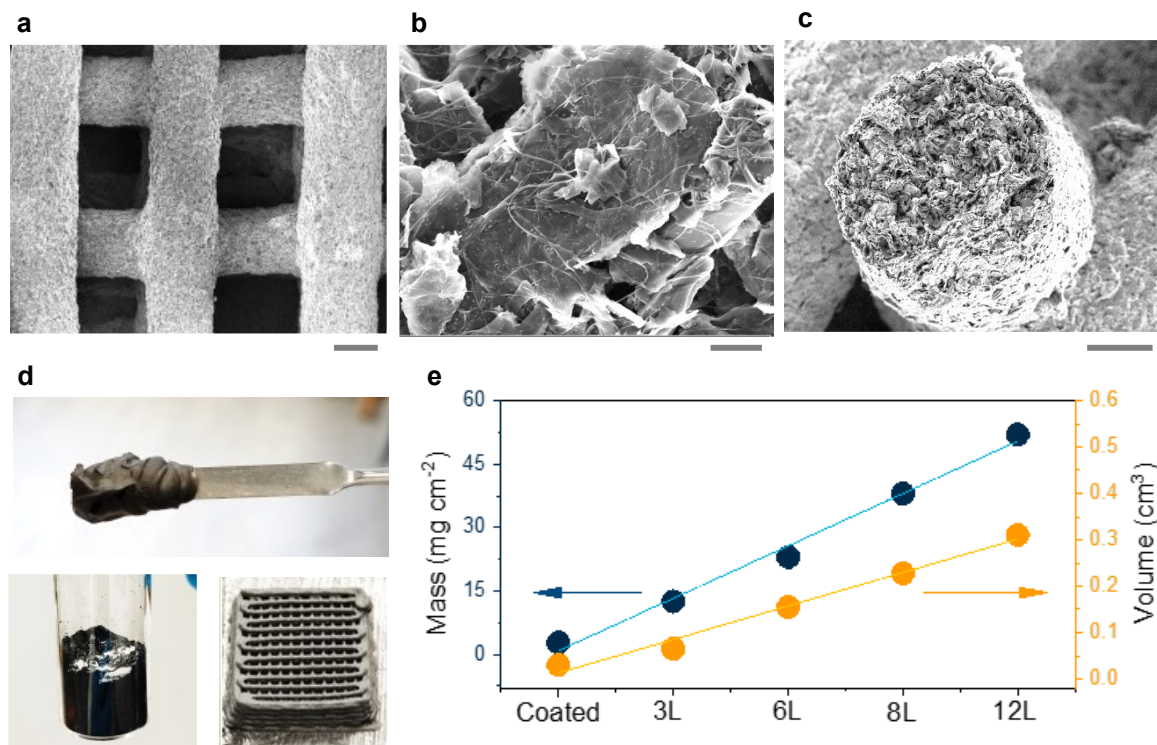


Figure 3.26: (a-c) SEM imaging of the graphene-carbon nanotubes electrodes (scale bars 200 μm , 2 μm and 100 μm , respectively); (d) digital photographs of the graphene-carbon nanotube inks and of a 3D printed woodpile structure on a graphite foil current collector (lateral size 1 cm); (e) areal mass loading and volume of the printed electrodes as a function of the number of printed layers.

flow (Table 3.3). When the oscillatory properties of the graphene and graphene-CNT inks are compared, the former presents a slightly smaller storage modulus at rest (Figure 3.25-b). More importantly, the yield stress of the graphene-CNT ink is significantly higher (~ 60 Pa vs. ~ 435 Pa, Figure 3.25-a), owing to the higher mass content of the ink and the presence of long carbon nanotubes, that can interact with multiple platelets delaying the yielding of the structure.

The morphology of the graphene-CNT composite structures are presented in Figure 3.26-a,b,c. The highly shear thinning behaviour enabled the extrusion of inks containing high concentrations of active materials, with no clogs or flow instabilities. Structures up to 12 layers in thickness (~ 3.1 mm), with a mass loading ~ 12 times higher than conventional slurry-coated electrodes, could be printed owing to the high storage modulus at rest and yield stress of the composite inks (Figure 3.26-a,d). The mass and volume of the electrodes could be accurately controlled with the layer-by-layer printing process, as shown in Figure 3.26-e. Despite the large volume of the electrodes (> 0.5 cm^3 for the 12 layer one), the woodpile architecture ensures large electroactive surface area in contact with the electrolyte, presenting periodic channels between the printed filaments. Each filament has an almost perfectly circular cross-section, and is made of a continuous and mechanically strong network of platelets and nanotubes. As evidenced by SEM images in Figure 3.26-b, the carbon

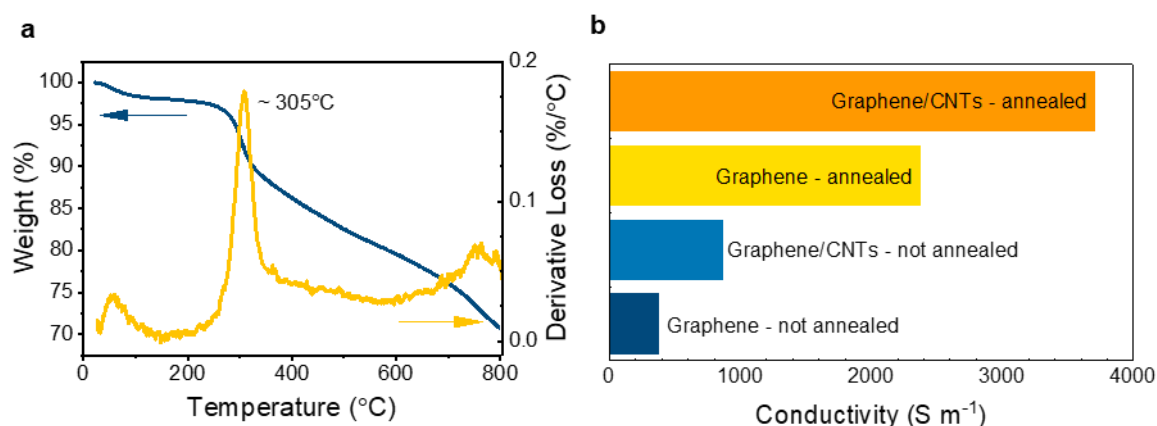


Figure 3.27: (a) Thermogravimetric analysis on the graphene-carbon nanotube inks in inert nitrogen atmosphere; (b) comparison of the electrical conductivity of the graphene and graphene-carbon nanotube inks before and after annealing.

nanotubes sit on the surface of the graphene platelets, forming a net that extends to the neighbouring platelets. This conductive net promotes the transport of electrons between platelets, providing a highly conductive structure. The conductivity of the graphene-CNTs ink was already > 2 times higher than the graphene ink before debinding, and it reached a final conductivity of $\sim 3700 \text{ S m}^{-1}$ after thermal annealing at 350°C (Figure 3.27-b). At this temperature, cellulose pyrolyzes as demonstrated by the thermogravimetric analysis in Figure 3.27-a, which presents a significant mass loss at $\sim 305^\circ\text{C}$, compatible with the decomposition temperature of cellulose reported in literature. The carbonization of cellulose leaves a highly interconnected structure of conductive platelets and nanotubes, which can promote fast charge transfer during discharge.

2.2. Electrochemical characterization

The 3D printed graphene-carbon nanotube electrodes were coupled with zinc foil anodes to assemble zinc hybrid capacitors (ZHCs). The devices were tested in a pouch cell configuration, with an aqueous electrolyte containing 2 M ZnSO_4 and 2 M NaCl (Figure 3.28-a). The presence of sodium chloride reduces the pH of the electrolyte by inductive effect, increasing the polarization of the O-H bonds inside the water molecules coordinated to Zn^{2+} , and it stabilizes the deprotonated complexes $[\text{Zn}(\text{OH})_2]_x\text{OH}^+$.^{236–238} The lower pH is thermodynamically unfavourable to the formation of inert by-products associated with the corrosion of zinc, in particular zinc hydroxysulfides. Additionally, the de-passivating effect of chloride ions hinders the growth of an insulating layer on the zinc anode, which would prevent the efficient transfer of charges between the electrode and the electrolyte.^{236,239}

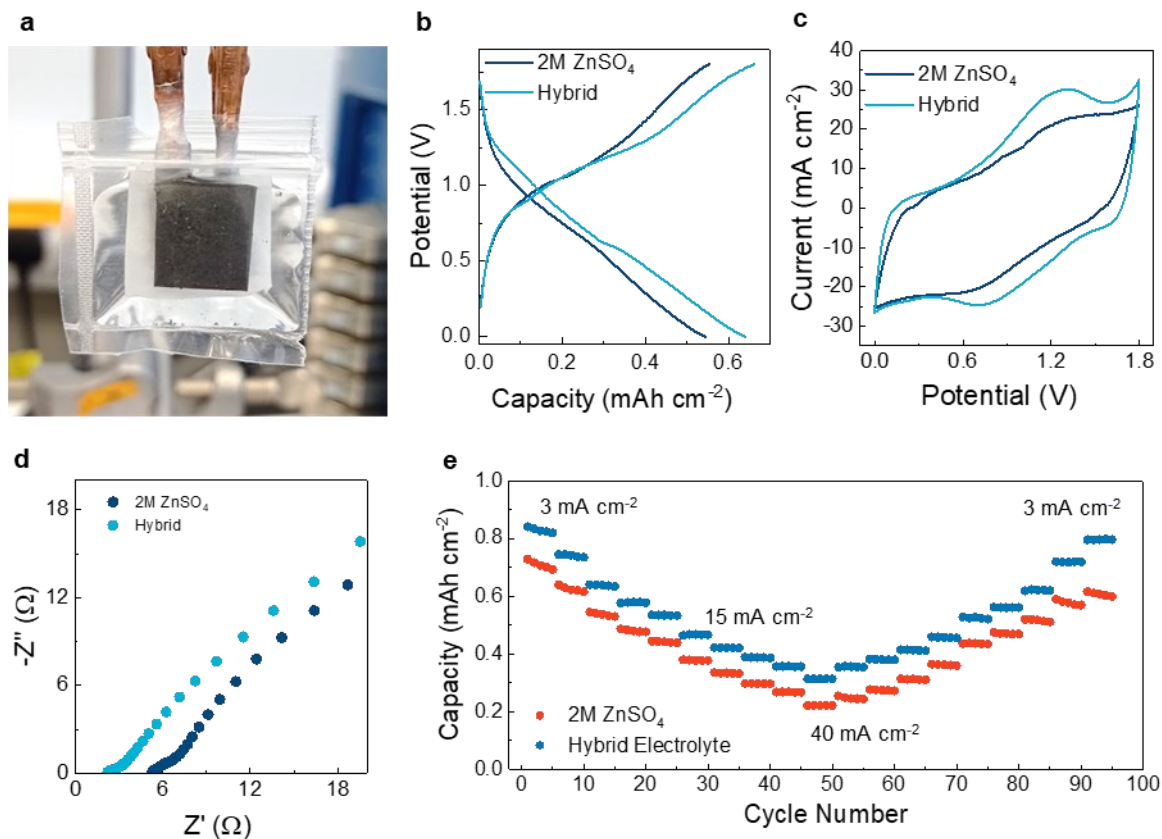


Figure 3.28: (a) Digital photograph of the ZHC pouch cell; (b) galvanostatic charge discharge on 6-layer ZHCs at a current density of 6 mA cm^{-2} in different electrolytes; (c) cyclic voltammetry of a 6-layer ZHC at a scan rate of 20 mV s^{-1} in different electrolytes; (d) electrochemical impedance spectroscopy on 6-layer ZHCs in different electrolytes; (e) rate capability of 6-layer ZHCs as determined from galvanostatic charge discharge tests between 3 and 40 mA cm^{-2} .

The CV curves of the ZHCs deviate from a rectangular shape (Figure 3.28-c), since the charge storage mechanism is not purely capacitive but it involves faradaic processes.^{††} Owing to the use of asymmetric electrodes and the high overpotential for hydrogen evolution of zinc, the operating potential window can be extended to 1.8 V in 2 M ZnSO₄ (vs. 1 V of the symmetric graphene devices), increasing the energy density without causing the decomposition of the electrolyte.²⁴⁰ The small oxidative peak that is visible in the high-potential region for the sodium chloride electrolyte can be ascribed to the more favourable hydrogen evolution reaction on the zinc electrode in a more acidic pH, but this contribution to the charge current is negligible as demonstrated by coulombic efficiencies studies. As evidenced by galvanostatic charge-discharge tests (Figure 3.28-b), the 3D printed electrodes achieve a higher capacity in the sodium chloride electrolyte than the conventional 2 M ZnSO₄ electrolyte (0.64 mAh cm^{-2} vs. 0.54 mAh cm^{-2} at a current density of 6 mA cm^{-2}). The

^{††} Since there is not a direct proportionality between the charge stored and the voltage of the device, capacitance is ill-defined for hybrid capacitors and it does not provide a reliable metric to assess their performance (as discussed in Chapter 2). Capacity, *i.e.* the charge that can be extracted when the devices are discharged, is considered instead.

improved charge storage in the presence of sodium chloride can be ascribed to the higher mobility of sodium ions and the enhanced ionic conductivity of the solution, as demonstrated by EIS (Figure 3.28-d). The impedance curve for the sodium electrolyte is shifted to the left by $\sim 3 \Omega$, indicating a lower equivalent series resistance in the sodium chloride system. In addition to this, sodium ions can be non-specifically adsorbed on the graphene electrodes, contributing to the charge storage process.^{241,242} The rate capability of the printed electrodes was studied measuring the capacity of the devices at different discharge currents. The ZHCs with sodium chloride electrolytes achieved an excellent rate capability of 30.3% at 40 mA cm^{-2} , owing to the high electronic conductivity of the electrodes and electrolyte and reduced charge transfer resistance.

Cyclic voltammetry at different scan rates provided information on the nature of the charge storage mechanism, consisting of a faradaic contribution, originating from the reversible oxidation and reduction of zinc on the surface of the anode, and a capacitive contribution, associated with the EDL formation and adsorption of positive ions on the printed carbon electrode. The oxidation and reduction currents exhibit a power-law relationship to the scan rate (Figure 3.29-a,b). The b exponent value of ~ 0.8 indicates that there is a significant diffusive contribution to the charge storage

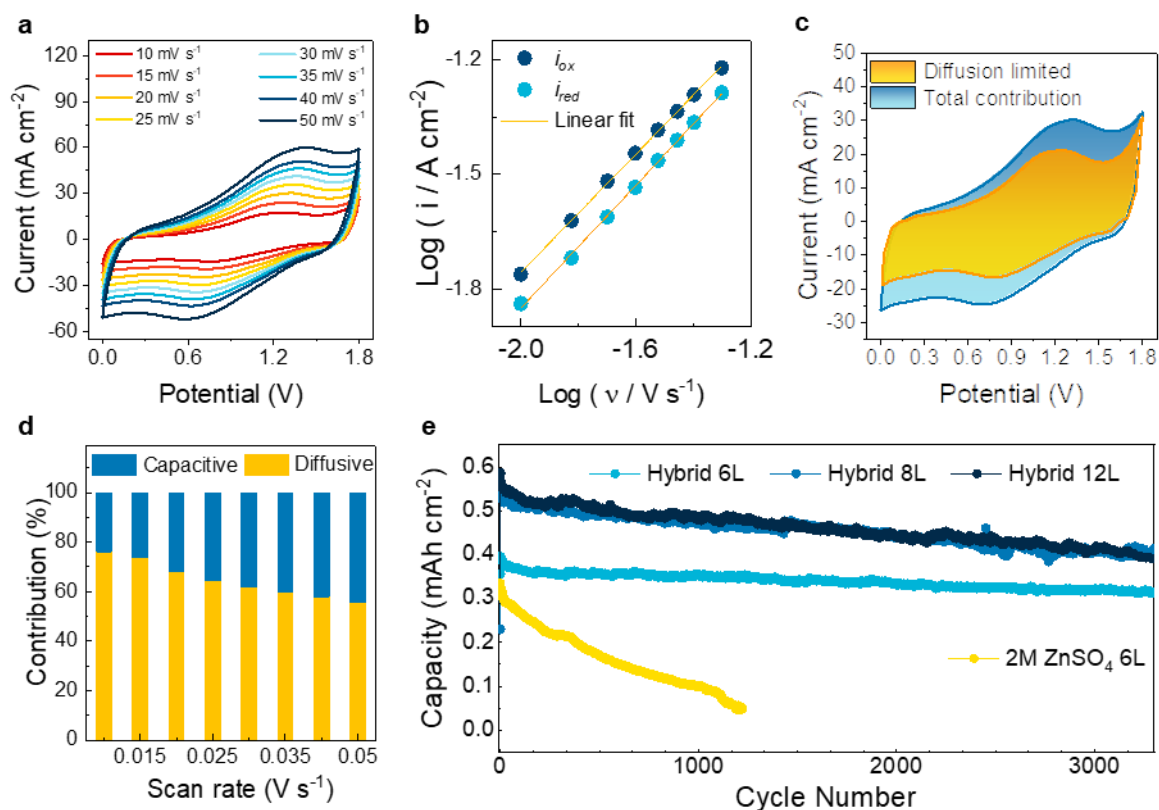


Figure 3.29: (a) Cyclic voltammetry on a 6-layer ZHC at different scan rates (10-50 mV s^{-1}); (b) power-law fitting of the CV current as a function of the scan rate for a 6-layer ZHC; (c) diffusion-limited current for the CV of a 6-layer ZHC at 20 mV s^{-1} ; (d) capacitive and diffusive contributions to the total current at different scan rates as measured for a 6-layer ZHC with the Trasatti method; (e) cycling stability of the ZHCs in different electrolytes

process (as discussed in Chapter 2, Equation 2.23). The ratio between the slow diffusion-controlled response and the fast capacitive response was evaluated with the Trasatti method (Equation 2.22), as shown in Figure 3.29-c,d. The diffusive current is predominant at slow scan rates ($\sim 76\%$ of the total current), falling to $\sim 55\%$ at a scan rate of 50 mV s^{-1} . At lower scan rates the ions have longer time to diffuse and react with the battery-type anode, whereas at high scan rates only fast, capacitive charge storage processes can take place, such as the charging of the electrical double layer at the interface of the electrodes. The durability and the protective effect of the sodium chloride electrolyte were evaluated by repeated GCD tests, Figure 3.29-e. The 12 layer electrode had a capacity retention of $> 0.39 \text{ mAh cm}^{-2}$ after 3300 cycles, whereas the device based on the zinc-sulfate electrolyte died shortly after 1000 charge-discharge cycles ($< 0.05 \text{ mAh cm}^{-2}$ residual capacity) owing to the irregular plating of zinc onto the anode and to the formation of insulating corrosion products. Sodium ions have a significantly lower reduction potential than zinc, therefore they do not contribute to the redox processes on the anode side. Nonetheless, Na^+ ions can adsorb on the regions of the

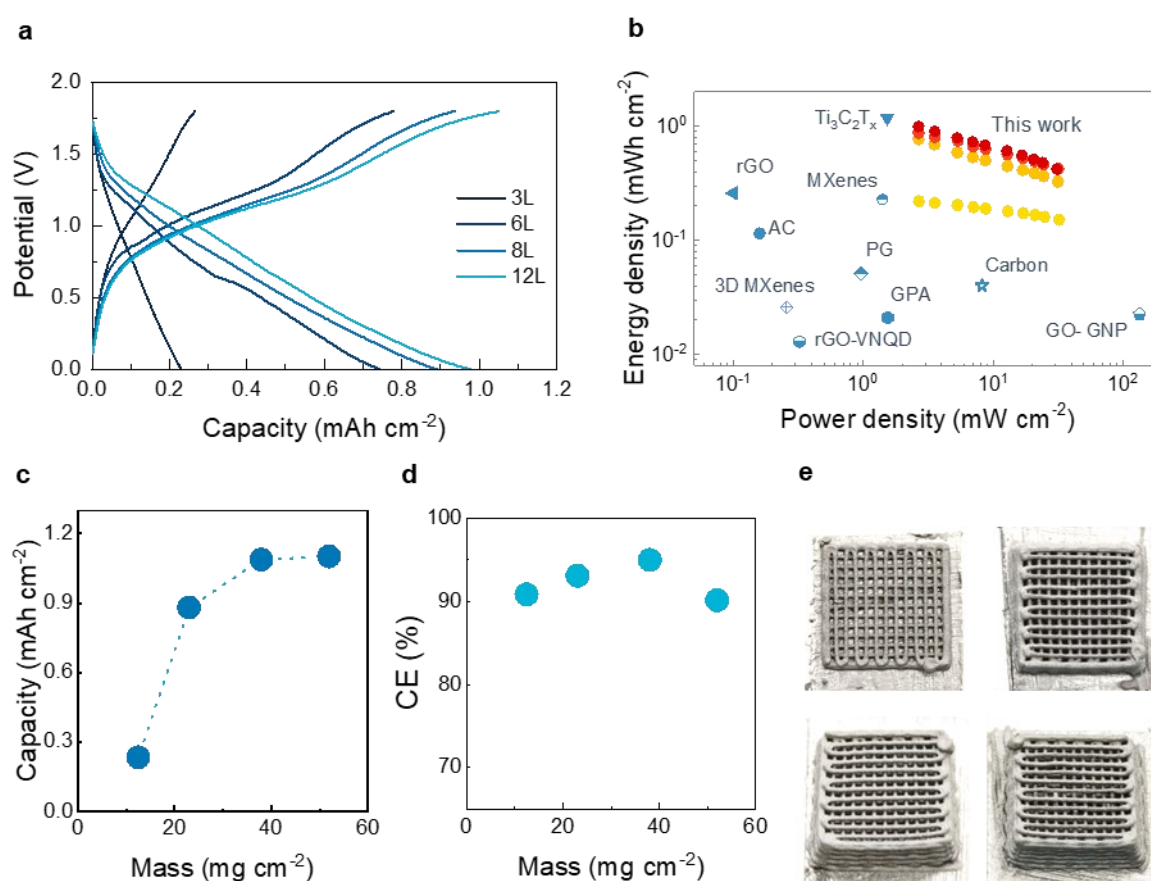


Figure 3.30: (a) Galvanostatic charge-discharge tests at 3 mA cm^{-2} for different ZHCs; (b) Ragone plot comparing the performance of the ZHCs with state-of-the-art devices (references for the comparison in Appendix A2); (c) areal capacity of the ZHCs as a function of the mass of the printed cathode; (d) Coulombic efficiency of the ZHCs as a function of the mass of the printed cathodes; (e) digital photographs of printed graphene-carbon nanotube cathodes at increasing number of layers.

electrode surface where the electric field is higher because of morphological irregularities, providing an electrostatic shield that hinders the growth of dendrites and enhances the cycle life.²³⁸

The number of layers of the printed positive electrodes was gradually increased to investigate the effect of the electrode thickness on the charge storage capability (Figure 3.30-e). The specific capacity increases with the areal mass loading of the electrodes (Figure 3.30-a,c), but it reaches a saturation value $\sim 1.1 \text{ mAh cm}^{-2}$ at mass loadings $> 40 \text{ mg cm}^{-2}$. Considering the high viscosity of concentrated zinc sulfate solutions compared to alkali metal hydroxides, this can be ascribed to the difficult infiltration of the electrolyte into the channels of the electrodes, rather than to mechanical instabilities and cracks. The incomplete wetting of larger electrodes results in higher local current densities and a more irregular electric field in the proximity of the surface, which can contribute to irreversible electrochemical processes reducing the coulombic efficiency (Figure 3.30-d). The 12-layer device thus achieves an efficiency of $\sim 90\%$, smaller than the 95% efficiency of the 8-layer device. Despite this limitations, the 8-layer ZHC presents an energy density of 0.87 mWh cm^{-2} at a power density of 31.72 mW cm^{-2} . This value is superior to the zinc hybrid capacitors previously reported in the field and based on reduced graphene oxide, MXenes and activated carbon cathodes (Figure 3.30-b).

Conventional rate capability tests, based on the charge-discharge of the device at increasing current densities, are impractical for electrodes with high mass loading of active material because of their large capacity and long discharge time. The time required by a 12-layer ZHC for a single charge-discharge cycle at 0.2 mA cm^{-2} is $> 15 \text{ h}$. For this reason, the use a chronoamperometric technique to monitor the rate capability of 3D printed electrodes was also investigated. The devices were discharged at a constant potential, and the discharge current was monitored over time. From the integration of the discharge curve, it was possible to calculate the capacity as a function of the discharge rate, as detailed in Chapter 2 (Equations 2.38 and 2.39). The discharge current for the ZHCs quickly falls from 350 mA cm^{-2} to 0.1 mA cm^{-2} (Figure 3.31-a) in $\sim 3600 \text{ s}$, providing a dense set of data points in a wide range of discharge rates. The chronoamperometric tests for the ZHCs with different number of printed layers are presented in Figure 3.31. The chronoamperometric data follow the same trend of the charge-discharge tests for all the devices, with the exception of the 12-layer ZHC, where the CA data consistently overestimate the value of capacity retention (Figure 3.31-e). This might be related to the lower coulombic efficiency of the 12-layer devices, which undergo irreversible side-reactions during charge and discharge for prolonged times. For the other electrodes the ageing processes that occur during the repeated galvanostatic tests are negligible, leading to a good agreement between the two techniques (Figure 3.31-b,c,d). In particular, the 8-layer ZHC still retains a capacity of $\sim 0.24 \text{ mAh cm}^{-2}$ at an extremely fast rate of 1000 h^{-1} , owing to the fast capacitive mechanism that accompany the faradaic charge storage in the hybrid devices.

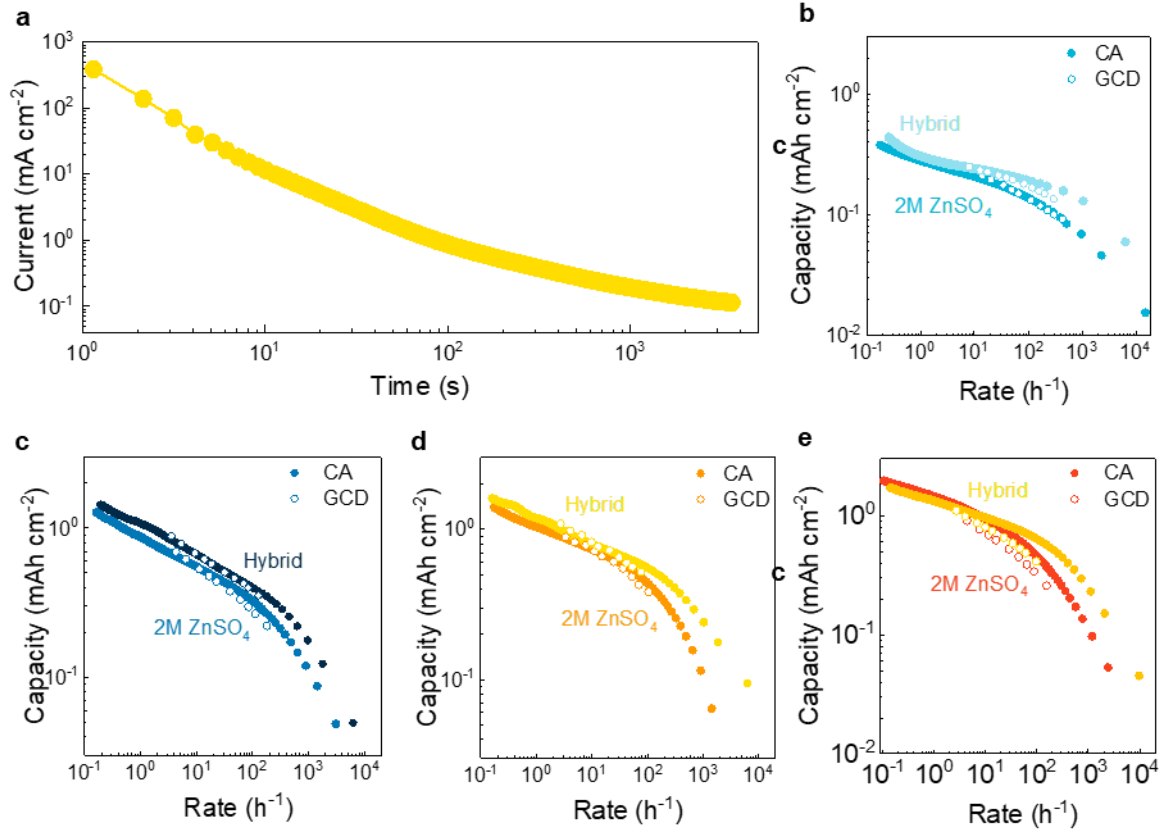


Figure 3.31: (a) Current transient for a 6-layer ZHC when discharged at a constant potential; (b-e) comparison of the rate performance obtained with conventional charge-discharge tests and chronoamperometric tests for 3-layer ZHCs (b), 6-layer ZHCs (c), 8-layer ZHCs (d) and 12-layer ZHCs (e).

3. Conclusions

The development of water-based carbon inks that do not require harsh postprocessing is needed for the DIW of sustainable and safe energy storage systems presenting fast supercapacitive charge storage processes. This chapter proposed two water-based ink formulations for the 3D printing of graphene and graphene-CNT electrodes *via* DIW. The flow behaviour of the inks and the correlation between the rheological properties of the inks and the macroscopic and microscopic structure of the electrodes was discussed. Additionally, the feasibility of the 3D printed structures for aqueous energy storage systems, namely symmetric supercapacitors and zinc hybrid capacitors, was demonstrated assembling full cells and benchmarking their performance with state-of-the-art devices. The 3D printed supercapacitors and zinc hybrid capacitors reported here achieved excellent areal energy and power densities, owing to the high areal mass loading of active material and high conductivity and electrochemically active surface area of the structures. Nonetheless, the gravimetric properties of the printed electrodes fall short of the benchmark, owing to the thick and dense nature of graphene nanoplatelets. This limits the use of the printed electrodes in devices where low specific weight is a more crucial figure of merit than high areal performance, for example electric vehicles or medium-size portable electronics, *e.g.* smartphones and laptops. In small-size and miniaturized portable and wearable electronics it is expected that small variation in the device mass can be better tolerated with the prospect of higher areal energy and power densities and customizable geometry.

The electrochemical characterization also highlighted charge-transfer limitations in the thicker electrodes which could not be resolved increasing the electrical conductivity of the electrodes. This investigation suggests that simply increasing the mass of the printed electrodes to control the energy density might not be a viable option in real applications, unless the mass increase is accompanied by the optimization of the electrode architecture, *e.g.* to aid electrolyte infiltration and complete wetting of thick structures.

Importantly, this chapter also assessed the use of a chronoamperometric method to test the rate capability of 3D electrodes. The advantage of CA over conventional GCD tests lies in the possibility to obtain more data point in a shorter time and in a wider rate window, which is essential for 3D electrodes with long charge-discharge times. This investigation evidences how conventional characterization methods might be practically unfeasible for 3D structures, indicating that the development of 3D printed energy systems must be accompanied by the development of efficient and reliable characterization techniques to assess the performance of such devices.

Chapter 4

Printed Zinc Anodes

Chapter 3 presented the fabrication of 3D printed carbon electrodes for zinc hybrid capacitors using DIW. Printed carbon electrodes have high mass loading of active material ($\sim 50 \text{ mg cm}^{-2}$), which enhances the charge storage capability and energy density of ZHCs. However, as a result of the higher capacity of the printed cathodes, the zinc foil anodes are subjected to high local current densities for longer charge and discharge times. Such conditions are detrimental to the cycling stability of the electrochemical device, since they promote the growth of dendrites and the formation of inert reaction by-products on the surface of the zinc electrodes. In the absence of electrolyte additives, which shield the intense electric field near the dendritic seeds on the zinc surface and prevent the formation of dead zinc (*e.g.* zinc hydroxysulfates), the ZHCs with 3D printed carbon cathodes die after ~ 1200 cycles (as shown in Chapter 3). These cyclability issues are even more crucial in zinc batteries, which are characterized by higher energy densities than hybrid capacitors resulting in longer charge-discharge times. The use of metal-foil anodes also limits the design flexibility of the electrochemical devices, hindering direct integration into electronic systems with complex shapes.

The fabrication of 3D-structured anodes presenting a rationally designed geometry can mitigate the stability issues of zinc-foil electrodes. In particular, the high surface area of 3D anodes can inhibit the formation of zinc dendrites, owing to the lower local current density at the electrode surface and a more uniform electric field in the proximity of the surface.²⁴³ Several strategies have been recently reported to fabricate 3D zinc electrodes, including the thermal sintering of zinc particles to obtain porous zinc foams and the electrodeposition of zinc onto three-dimensional scaffolds.^{232,243,244} However, only few works have investigated the direct fabrication of zinc electrodes with 3D printing processes.^{245,246} In these reports, a printable slurry is usually obtained by dispersing zinc powder in N-Methylpyrrolidone (NMP) with a polyvinylidene difluoride (PVDF) binder, following a similar approach as the commercial manufacturing of lithium-ion battery electrodes. Nonetheless, the manufacturing of zinc anodes should not rely on large volumes of organic solvents such as NMP, which overshadows the advantages of aqueous batteries in terms of toxicity and environmental sustainability. Therefore, this chapter will present the formulation of inks based on aqueous dispersions of zinc, enabling the fabrication of 3D electrodes with enhanced electrochemical properties.

The formulation of aqueous zinc inks is complicated by the chemical instability of sub-micrometric zinc particles in water, as a result of their high specific surface area and of the low standard reduction potential of zinc (~ -0.76 V vs. SHE).²⁴⁷ Larger zinc particles (~ 1 - 10 μm in diameter) are more chemically stable in aqueous environment, because of their lower surface area and the presence of a thin surface layer of zinc oxide that is stable in neutral and slightly acidic pH.²⁴⁷ However, these particles are unsuitable to formulate colloidal inks (as described in Chapter 2), since they are too large to form homogeneous colloids and they easily sediment. Polymeric additives can stabilize the zinc particles in aqueous dispersions at high mass concentration, forming a paste with adequate rheological properties for the manufacturing of 3D electrodes *via* DIW. However, the polymeric binders used for DIW are typically not electroactive and they inhibit electronic transport inside three-dimensional structures. In order to improve the electrical conductivity and prevent the dissolution of the structure in aqueous electrolytes, the electrodes are often thermally annealed in inert atmosphere to decompose or carbonize the polymeric binder. Nonetheless, a thermal post-processing at temperatures higher than 450 $^{\circ}\text{C}$ is incompatible with the low melting point of zinc (~ 420 $^{\circ}\text{C}$).

This chapter will present two ink formulation strategies for zinc anodes that do not require thermal annealing. The former relies on poly(3,4-ethylenedioxythiophene) - polystyrene sulfonate (PEDOT:PSS) as the conductive and electrochemically active binder and rheology modifier. The latter is based on a conductive mixture of high molecular weight polyvinyl alcohol and carbon black to form mechanically stable and electrically conductive zinc electrodes.

1. PEDOT:PSS inks

This section will discuss the use of PEDOT:PSS as a binder and gelating agent for aqueous zinc inks. PEDOT is an intrinsically conductive polymer presenting a backbone made of thiophene rings, which form a conjugated π system with p-doping.²⁴⁸ A thiophene ring every three to four in the polymer backbone carries a net positive charge, which makes PEDOT a polycation (Figure 4.1-d). Aqueous suspensions of PEDOT are typically stabilized by polyanions, *e.g.* polystyrene sulfonate (PSS, Figure 4.1-e), which do not contribute directly to charge transport but aid the dispersion of PEDOT molecules, forming polyelectrolyte complexes (Figure 4.1-c). PEDOT:PSS complexes are characterized by an excess of PSS ($> 1:2$ molar ratio between the thiophene and sulfonic acid moieties), therefore not all the negative sulfonic groups are electrostatically screened by the positive thiophene groups, which improves the dispersibility in polar solvents.²⁴⁸ PEDOT molecules connect the negatively charged groups of the PSS chains forming microgel particles, that are stable in water. The inner core of the particles is richer in PEDOT and has a more hydrophobic character due to the partial charge neutralization. In contrast, the outer region of the particles is richer in PSS, forming

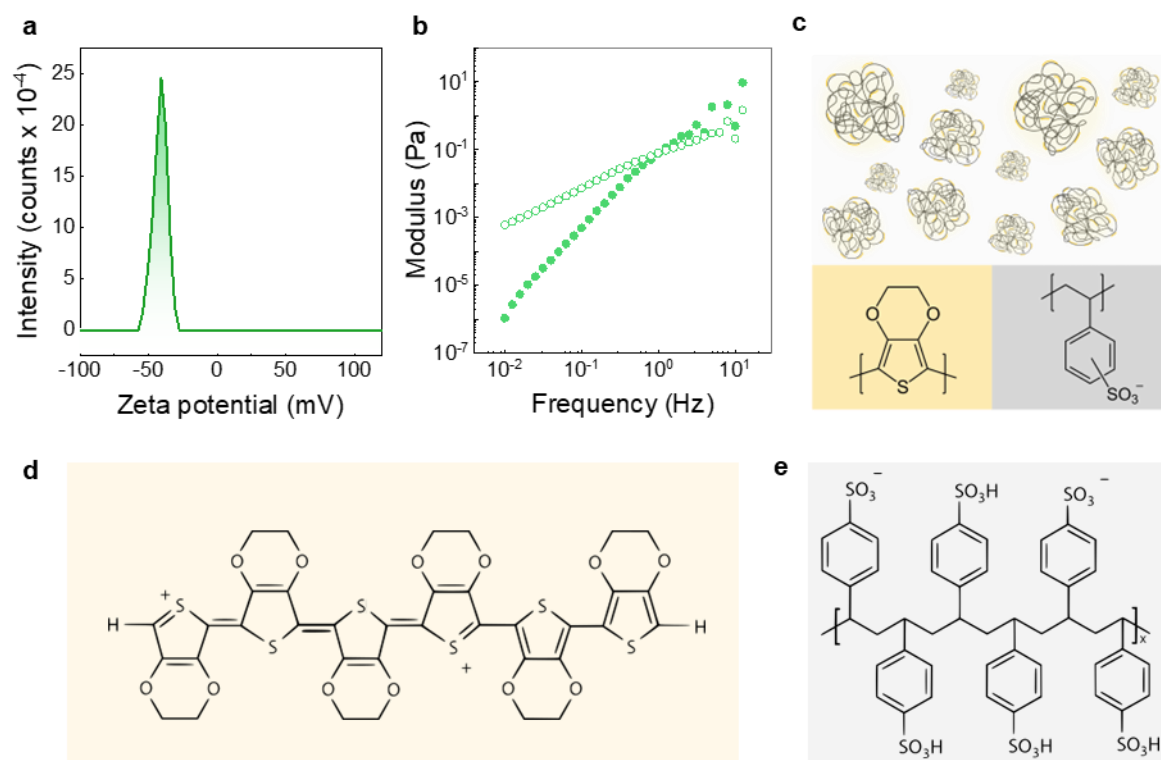


Figure 4.1: (a) Zeta potential distribution for the PEDOT:PSS dispersion; (b) oscillatory frequency sweep for the pure PEDOT:PSS suspension, closed circles represent G' , open circles G'' ; (c) schematic showing the structure of the PEDOT:PSS suspension, presenting microgel particles dispersed in water; (d,e) chemical structure of PEDOT (d) and PSS (e).

a negatively charged shell around the microgel. The colloidal dispersion of PEDOT:PSS is stabilized by the repulsive interactions between the charged microparticles. As a consequence, it is possible to control the state of aggregation of the suspension by screening these interactions, in order to obtain a colloidal gel that can act as a binder for zinc inks. The main advantage of this ink formulation approach lies in the conductivity and redox-active nature of the PEDOT:PSS binder, which would not require carbonization in inert atmosphere after printing.

1.1. Ionotropic gelation of PEDOT:PSS

The electrostatic forces stabilizing the particles in a colloidal suspension can be adjusted by altering the pH of the solution or its ionic strength. When PEDOT:PSS solutions are acidified with sulfuric acid, the PSS chains become partially protonated resulting in a weaker electrostatic repulsion between PEDOT:PSS microparticles.²⁴⁹ This lowers the critical coagulation concentration to 0.78 wt%, enabling the formation of a hydrogel with high conductivity of $\sim 46 \text{ S m}^{-1}$ despite the low polymer content, as shown by Yao *et alii*.²⁴⁹ Similarly, the introduction of ions in the dispersion can screen the negative charge of PSS chains, reducing the inter-particle repulsion and causing the coagulation of the system, as demonstrated adding NaCl to aqueous PEDOT:PSS dispersions.²⁵⁰

The critical coagulation concentration of PEDOT:PSS colloids rapidly decreases with increasing valence of the counterions, therefore multivalent counterions such as Fe^{3+} and Sn^{4+} are more effective coagulants than monovalent or bivalent ions.²⁵¹ However, the direct addition of multivalent cations to PEDOT:PSS dispersions can lead to the immediate precipitation of a polymeric coacervate, rather than the formation of a uniform gel, as demonstrated by studies on the ionotropic gelation of PEDOT:PSS with Fe^{3+} salts.²⁵² Zn^{2+} ions have smaller charge density than Fe^{3+} and they are already present in the electrolyte of zinc ion batteries. Therefore, the gelation of PEDOT:PSS with zinc ions would not introduce other redox-active soluble species into the electrochemical device, which might cause undesirable redox reactions. The possibility to gelate PEDOT:PSS using zinc sulfate, a common electrolyte salt for aqueous ZIBs, was here investigated.

The PEDOT:PSS gel was formulated starting from a commercial dispersion of PEDOT:PSS in water, at a concentration of 1.1 wt%. The PEDOT:PSS microgel particles have a zeta potential of -40 ± 2 mV, as demonstrated by dynamic light scattering experiments (Figure 4.1-a). The negative zeta potential is coherent with the presence of a negatively charged outer shell around the microgel particles; additionally, the high absolute value of zeta potential is indicative of the colloidal stability of the dispersion. At room temperature the PEDOT:PSS dispersion behaves as a viscoelastic liquid, with a low-frequency storage and loss modulus that scale as ω^2 and ω , respectively (Figure 4.1-b). The pure PEDOT:PSS suspension has a shear thinning behaviour (Figure 4.2-c), likely arising from the deformation and alignment of the microgel particles in the shear direction rather than from the rupture of the microgel, as observed for dispersions of soft colloidal particles.²⁵³

The ionotropic gelation of PEDOT:PSS was investigated by direct addition of zinc sulfate to the suspension, which was then let to equilibrate for ~ 30 min. After the addition of zinc sulfate, the PEDOT:PSS dispersion turns into a soft hydrogel, as demonstrated by vial inversion tests in Figure 4.2-d. The formation of a gel was confirmed by oscillatory rheology tests, carried out on samples at different concentrations of zinc sulfate (50 mM and 500 mM, respectively). Both samples present a gel-like response in a regime of linear deformation (Figure 4.2-a), with a storage modulus around one order of magnitude higher than the loss modulus and almost independent of the oscillation frequency. The storage modulus of the sample with higher zinc sulfate concentration is significantly lower than the sample with less coagulant (~ 165 Pa vs ~ 54 Pa at 0.1 Hz). This is in agreement with previous reports on polyelectrolyte complexes at different ionic strength, which show that the complexes behave as soft solids at lower salt concentrations, whereas they have a marked liquid-like character at higher salt concentrations.²⁵⁴ This behaviour can be attributed to an effective screening of the microgel particle charges at lower salt concentrations, whereas at higher concentrations the salt ions start screening the charges of the individual polyelectrolyte molecules causing the rupture of the microparticles.^{255,256} The strength of the bonds in the gel network was investigated with amplitude sweep tests (Figure 4.2-b), which demonstrate a typical yield-stress behaviour.

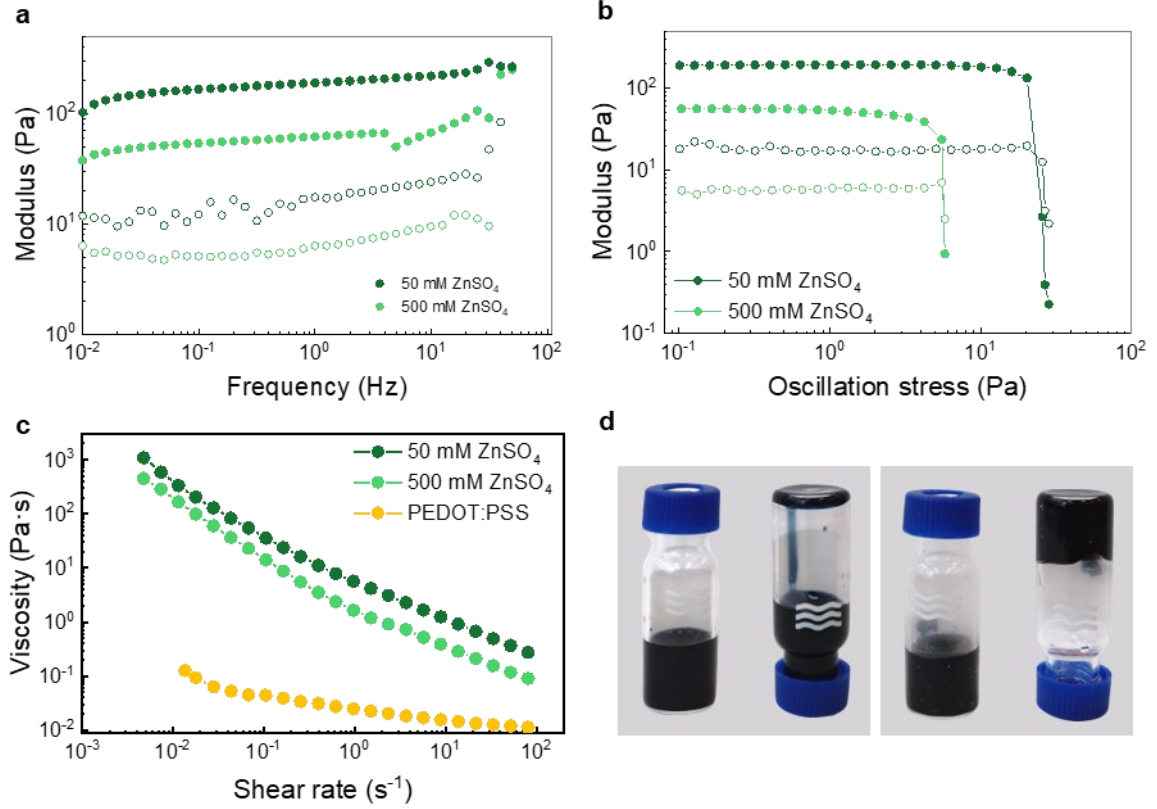


Figure 4.2: (a) Oscillatory frequency sweep in the linear viscoelastic region of PEDOT:PSS suspensions coagulated with different concentrations of zinc sulfate, closed circles represent G' , open circles G'' ; (b) oscillatory amplitude sweep of PEDOT:PSS suspensions coagulated with different concentrations of zinc sulfate, closed circles represent G' , open circles G'' ; (c) flow curves of PEDOT:PSS suspensions with and without the zinc sulfate coagulant; (d) vial inversion tests on the pure PEDOT:PSS suspension (left) and on the suspension gelled with 500 mM zinc sulfate (right).

Coherently with the trend observed for the storage modulus, the limit of the linear viscoelastic region and the value of yield stress are also lower at higher ZnSO_4 concentration (~ 23 Pa vs. ~ 6 Pa), indicating the formation of a weaker gel at higher salt content. The PEDOT:PSS gels are significantly more shear thinning than the pure PEDOT:PSS dispersion (Figure 4.2-c), as a consequence of the breakdown of the attractive interactions between microparticles during flow. Overall, the coagulated PEDOT:PSS suspensions present the expected qualitative response of a DIW ink; nonetheless, the storage modulus at rest and the yield stress are significantly lower than typical inks ($G' > 10^3$ Pa and $\tau_Y > 50$ Pa). The PEDOT:PSS gels are too soft to be printed on their own, forming irregular structures that sag laterally after extrusion. Lower concentrations of zinc sulfate would enhance the storage modulus and yield stress of the gels, as observed in other polyelectrolyte complexes;^{255,256} however, dissolving such low amounts of salt without further diluting the PEDOT:PSS suspension is challenging. A viable alternative is to take advantage of the low pH (< 2.5) of the PEDOT:PSS suspension, and directly add metallic zinc particles to the suspension without a preliminary gelation process. The spontaneous oxidation of zinc from the surface of the particles would

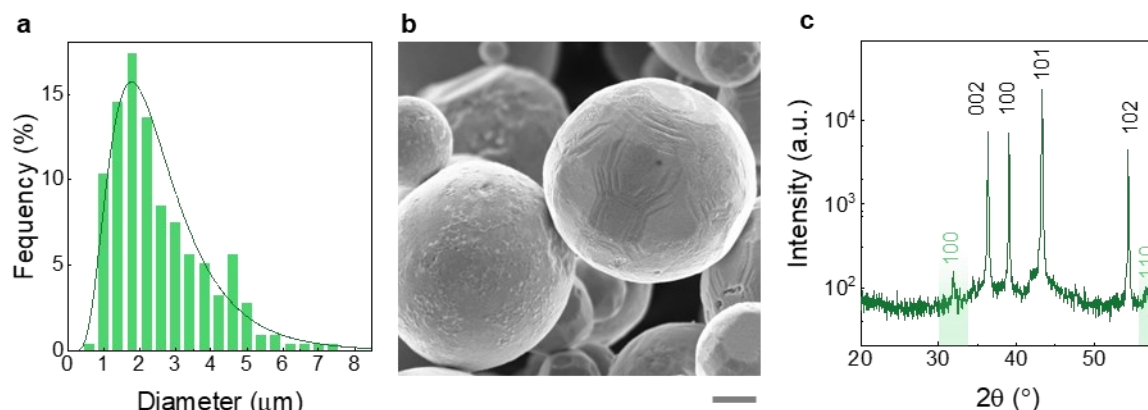


Figure 4.3: (a) Particle size distribution for the zinc particles used to formulate the PEDOT:PSS inks following a log-normal trend; (b) SEM imaging of the zinc particles (scale bar 1 μm); (c) powder XRD on the zinc particles used to formulate the PEDOT:PSS inks, with the peaks corresponding to zinc oxide highlighted in green.

determine the release of Zn^{2+} ions, that can coagulate the PEDOT:PSS colloid. This approach will be discussed in the next section.

1.2. PEDOT:PSS zinc inks

The PEDOT:PSS zinc inks were formulated using commercial zinc particles, with an average diameter of $\sim 2.6 \mu\text{m}$ (Figure 4.3-a). The particles have uniform spherical shape, presenting a disperse diameter distribution in the dimensional range 1-10 μm . The absence of particles larger than 10 μm is essential to prevent clogging during the extrusion through dispensing nozzles $\sim 100 \mu\text{m}$ in diameter, since spherical particles $> 10 \mu\text{m}$ can easily aggregate and form a load-bearing arch which obstructs the flow of the ink.²⁵⁷ The zinc spheres are covered by a layer of oxide, as indicated by powder XRD (Figure 4.3-c), showing two small peaks, corresponding to the 100 and 110 reflections of hexagonal zinc oxide, together with the intense and sharp reflections of zinc. The layer of native oxide is unstable at low pH (< 5), and it dissolves when the particles are dispersed in the acidic PEDOT:PSS suspension, which is beneficial for the conductivity of the printed electrodes.²⁴⁷

The PEDOT:PSS ink was prepared by directly dispersing the spherical zinc particles in the PEDOT:PSS suspension and mixing it at high shear for 10 min. During mixing, the acidic pH of the suspension promotes the dissolution of zinc, releasing Zn^{2+} ions that can be coordinated by the sulfonate moieties of PSS and destabilize the PEDOT:PSS colloid. The oxidation of Zn^0 to Zn^{2+} might cause a partial reduction of the PEDOT chains, which would be detrimental to charge transfer along the polymer backbone. However, a recent study on the gelation of PEDOT:PSS in the presence of metallic iron has shown that PEDOT:PSS remains significantly more conductive than conventional binders ($\sim 20 \text{ S m}^{-1}$), even though some reduction occurs during the coagulation process.²⁵² The reduction of PEDOT is associated with a change of the suspension colour, from blue

to green, which can be measured with UV-vis spectroscopy.²⁵² The UV-vis absorption spectra of the PEDOT:PSS formulated here are unchanged after the addition of zinc particles (Figure 4.4-f), which suggests that there is no noticeable reduction of PEDOT during the coagulation process. The oxidation of zinc can be mainly associated to the reduction of water (protons), with the evolution of hydrogen, rather than to the reduction of the conductive polymer. After mixing, the coagulated dispersion appears as a dark-blue gel (inset in Figure 4.4-b), that disperses the zinc particles and is stable against sedimentation.

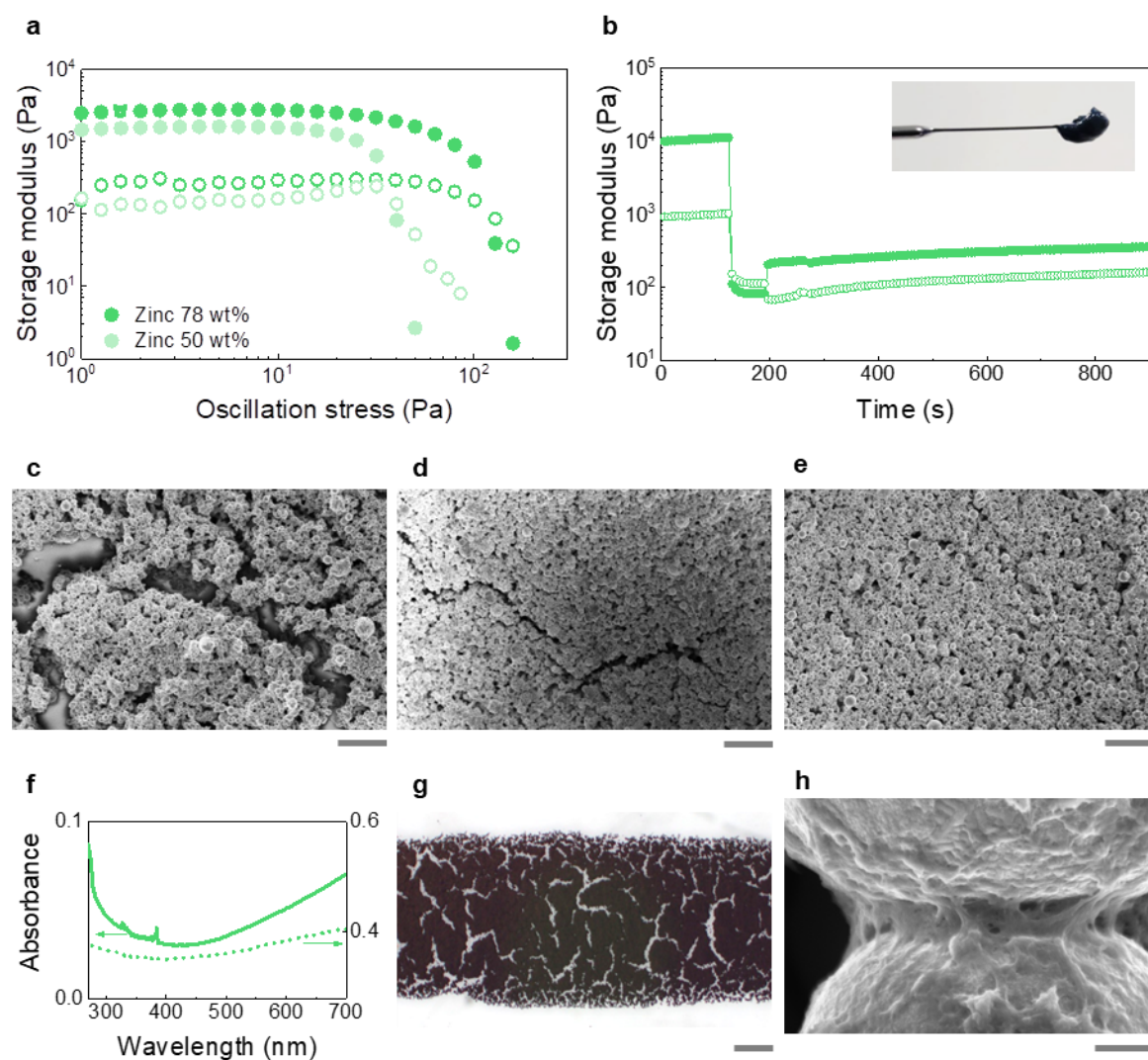


Figure 4.4: (a) Oscillatory frequency sweep of the zinc – PEDOT:PSS gels at different zinc content, closed circles represent G' , open circles G'' ; (b) recovery tests on the 78 wt% zinc – PEDOT:PSS ink, using an initial and final low-amplitude step at an oscillation amplitude of 10 Pa and an intermediate step at 50 Pa, closed circles represent G' , open circles G'' ; (c-e) SEM imaging of 1-layer PEDOT:PSS electrodes at increasing zinc content, from 50 wt% to 78 wt% (left to right, scale bars are 50 μm); (f) UV-vis spectrum of the PEDOT:PSS suspension before (continuous line) and after (dotted line) the addition of zinc particles; (g) optical microscopy on the 1-layer 50wt% zinc electrode (scale bar 200 μm); (h) high-magnification SEM imaging showing the PEDOT:PSS binder connecting the zinc particles in the dried ink (scale bar 500 nm).

The rheological properties of the PEDOT:PSS ink were studied at different concentrations of zinc, as shown in Figure 4.4-a. The storage modulus is not significantly affected by the concentration of zinc particles, whereas the yield stress increases from ~ 37 Pa to ~ 120 Pa, as a result of the higher hindrance to yielding in the dispersion with a higher concentration of solid particles. Lines printed using the 50 wt% ink tend to form large cracks after drying (hundreds of microns in length, Figure 4.4-g), while a progressive increase in the zinc particle concentration leads to more uniform and continuous lines (Figure 4.4-c,d,e). The printed lines are made of a network of contacting zinc particles, linked together by the polymeric binder. The polymer forms a continuous layer at the boundary between neighbouring particles, as shown by SEM imaging (Figure 4.4-h). The polymeric necks connecting the particles can act as a conductive path that promotes the transfer of electrons in the structure. Nonetheless, the high concentration of solid particles in the 78 wt% ink causes a discontinuous extrusion flow, with the intermittent clogging of the nozzle. Additionally, immediately after extrusion the ink appears notably less viscous and spreads laterally on the substrate; as a consequence, the printed lines are twice as large as the diameter of the extrusion nozzle. Single-layer electrodes are mechanically brittle and they are easily cracked, which hinders the accurate evaluation of the film conductivity.

The deposition of more than one printed layer is limited by the lateral sagging of the structure, despite the high storage modulus and yield stress of the ink. The causes of this behaviour were investigated with three-interval thixotropy tests (Figure 4.4-b). At a low oscillatory stress (10 Pa) the ink has a stable solid-like response, with a storage modulus around an order of magnitude higher than the loss modulus and constant over time. In the high-shear step the ink transitions to a fluid state presenting a loss modulus higher than the storage modulus, as expected from amplitude sweep tests. Nonetheless, after the cessation of the high shear the original storage modulus is not recovered, and the ink exhibits an irreversible storage modulus loss of $\sim 97\%$. The storage modulus is stable over time, indicating that the disruption of the ink microstructure cannot be recovered, unlike thixotropic inks for which the storage modulus gradually increases over time, approaching a constant plateau value.¹⁵⁰

The microstructure of the ink before water evaporation was investigated using cryo-SEM, which shed light on the causes of the irreversible breakdown of the ink structure after shear and of the cracks observed in the printed films. The cryo-SEM samples were prepared in two different ways: for the first sample the ink was directly loaded onto the cryo-stage and vitrified; whereas for the second sample a cylindrical metal rivet mounted on the cryo-stage was filled with the ink, and the ink in the rivet was then vitrified. The first sample shows a continuous network, probably originating from the PEDOT:PSS gel, joining the zinc particles together (Figure 4.5-a,b). The zinc particles

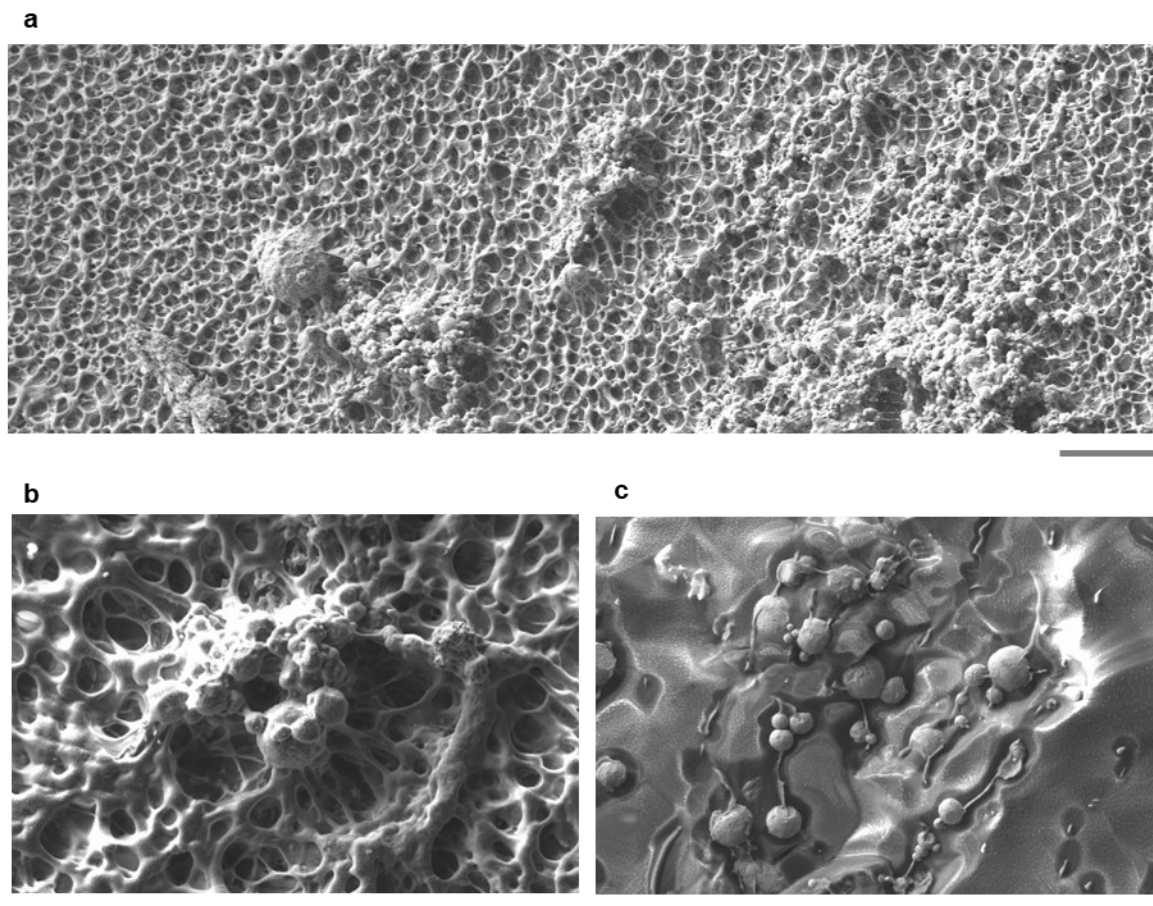


Figure 4.5: (a, b) Cryo-SEM imaging on the 78 wt% zinc-PEDOT:PSS ink directly loaded onto the cryo-stage and vitrified; (c) cryo-SEM on the 78% zinc-PEDOT:PSS ink loaded in a cylindrical rivet and then vitrified.

are not uniformly distributed inside the ink, but tend to form separate clusters. On the other hand, in the second sample the polymer network is filled with a vitrified phase (Figure 4.5-c), even after the sublimation of the surface layer of water to expose the inner structure of the sample. The different morphologies of the two samples are compatible with the hypothesis that the liquid component of the ink is not a homogeneous phase, but a biphasic mixture made of a water-rich phase and a polymer-rich coacervate deriving from the coagulation of the PEDOT:PSS microgel. A similar associative phase separation of polyelectrolyte complexes, induced by variations in ionic strength, has been widely studied in the literature for non-conductive natural polyelectrolytes.²⁵⁸ When the ink is directly loaded onto the stage, the water-rich phase can escape the ink structure, leaving the hydrated coacervate and zinc particles. This is not possible in the second sample, where the rivet walls prevent water from draining out of the ink. In support of this hypothesis, a clear liquid phase is often observed around the printed filaments immediately after the extrusion process. The application of a high shear stress breaks the stiff coacervate and destroys the particle aggregates, causing

the irreversible loss of the network elasticity. Additionally, as observed from cryo-SEM, the PEDOT:PSS binder is not able to disperse the solid particles uniformly, causing large agglomerates. The presence of agglomerated particles hinders the printing process, causing a discontinuous extrusion and the formation of obstructions in the dispensing nozzle. After printing, the coacervate phase starts drying, shrinking significantly in the regions between the particle agglomerates because of the low concentration of solid material, causing the formation of cracks.

In summary, this section demonstrated the possibility to gelate PEDOT:PSS using zinc ions, either by direct addition of a zinc salt, or taking advantage of the dissolution of metallic zinc particles in the acidic pH of the PEDOT:PSS suspension. However, the PEDOT:PSS coagulate does not form a continuous phase that uniformly disperses the metallic particles. As a consequence, irreversible changes in the ink microstructure are observed during shear, which are detrimental to the shape fidelity and mechanical stability of the printed electrodes.

2. PVA inks

Dense dispersions of non-colloidal zinc particles can form yield stress fluids at sufficiently high volume fractions; however, an adequate binder is needed to stabilize the suspension and disperse the solid uniformly.²⁵⁹ At the high volume fraction needed to obtain a yield-stress response, the larger zinc particles can easily form dense clusters or segregate from the dispersion and settle, causing blockages during extrusion. A binder with good adhesion to the zinc particles can improve the homogeneity of the dispersion and hold the three-dimensional structure after printing. In particular, the polymeric binder should be able to convey charges, *i.e.* ions and electrons, from the external circuit to the electroactive material inside the three-dimensional structure. Nanostructured carbon additives, such as carbon black, can be added to polymeric binders to form electrically conductive paths in the printed electrodes and ensure electron transport to the zinc particles. The polymeric binder must, additionally, be highly hydrophilic and absorb the aqueous electrolyte to promote ionic transport.

Polyvinylidene fluoride (PVDF) is an established binder for tape-casted battery electrodes, and it has been recently used to print zinc anodes.^{245,246} However, PVDF is highly hydrophobic and it is unable to swell in aqueous electrolytes, presenting an electrolyte uptake < 30% (Figure 4.6-a). Additionally, it lacks specific interactions with the surface of zinc particles, which can strengthen the surface adhesion and preserve the integrity of the printed electrodes. Carboxymethyl cellulose (CMC) has also been recently studied as a binder for sodium-ion battery electrodes, owing to the abundance of carboxylic groups along its polymeric backbone, which can physically or covalently interact with the surface functionalities of the active material.¹⁰⁹ However, CMC is highly soluble in water, and it readily dissolves in aqueous zinc electrolytes leading to the collapse of the electrode. Similarly to carboxymethyl cellulose, polyvinyl alcohol (PVA) is rich in hydroxy moieties that can specifically interact with the surface oxide functionalities of the zinc particles, but it has lower water solubility than CMC. The highly hydrophilic moieties of PVA ensure a swelling ratio > 300% in aqueous electrolytes (Figure 4.6-a), more than ten times higher than PVDF.

To further investigate the effect of a polymeric binder on the electrochemical properties of zinc, polymer-coated zinc electrodes were tested in a symmetric cell configuration in 2 M ZnSO₄. EIS data were fitted with the equivalent circuit in Figure 4.6-c, which has been proposed to study the charge transfer kinetic of coated metal electrodes.^{194,260} The impedance spectra of the PVDF-coated electrodes show a higher charge transfer resistance at the interface with the zinc metal (R_{CT}) and through the polymeric layer (R_p), as shown in Figure 4.6-b,c and Table 4.1. The equivalent series resistance is also higher for the PVDF system, possibly because of the incomplete wetting of the PVDF-coated electrodes.²⁶¹ In plating-stripping tests the PVDF coated electrodes have an unstable plating overpotential with spikes > 100 mV, as a result of the hydrophobicity and higher charge transfer resistance (Figure 4.6-d). Conversely, the PVA coated electrodes retain a uniform plating

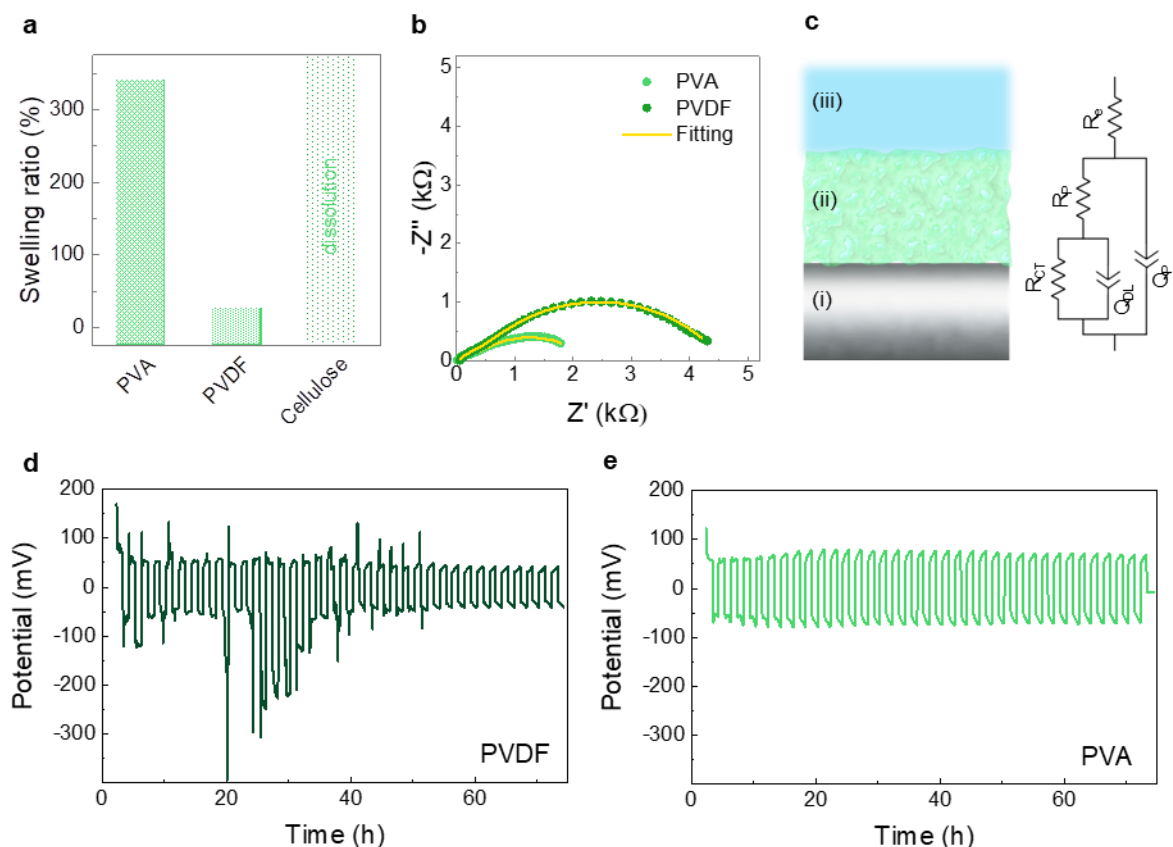


Figure 4.6: (a) Swelling ratio for different polymeric binders; (b) Nyquist plot for the symmetric polymer-coated zinc cell, with a PVA and PVDF coating, respectively; (c) schematic showing the polymer coated electrode and the equivalent circuit used to model the electrode; the resistive element R_E describes the high-frequency resistance of the electrolyte (iii), the $R_P - Q_P$ parallel describes the resistance to transport and the capacitance of the polymeric coating (ii), whereas the parallel $R_{CT} - Q_{DL}$ describes the capacitance and charge transfer resistance at the interface with the zinc electrode (i); (d, e) plating-stripping curves at a constant current of 1 mA cm^{-2} for the PVDF-coated electrodes (d) and the PVA-coated electrodes (e).

potential $\sim 65 \text{ mV}$ over repeated charge and discharge (Figure 4.6-e). Overall, the PVA coating displays better electrochemical properties than PVDF for aqueous zinc batteries, and is better suited as a binder for water-based dispersions. The formulation of PVA-based printable zinc ink to fabricate ZIB anodes is discussed in the next section; this research is currently under consideration for intellectual property protection.

Table 4.1: EIS fitting parameters for the polymer coated electrodes.

	PVDF coated	PVA coated		PVDF coated	PVA coated
$R_E (\Omega)$	56.8	12.9	$R_{CT} (\text{k}\Omega)$	4.13	1.9
$R_P (\Omega)$	422.2	385.5	$Q_{DL} (\text{F s}^{n-1})$	1.4×10^{-4}	6.8×10^{-4}
$Q_P (\text{F s}^{n-1})$	20.8×10^{-6}	63.2×10^{-6}	n_{DL}	0.54	0.47
n_P	0.65	0.59			

2.1. Ink formulation and rheology

The zinc inks were formulated using a mixture of high molecular weight PVA as the hydrophilic binder and carbon black as the conductive additive, as detailed in Chapter 2. To obtain a printable paste, the ratio between carbon black and zinc particles was maintained constant, while the total concentration of solid materials in the dispersion (zinc particles and carbon black powder) was gradually increased. The change in the flow behaviour of the dispersion at different solid contents was monitored with oscillatory and flow rheology (Figure 4.7-a,b,c). At low concentrations of solid particles, the dispersion has a liquid-like response to a small-amplitude oscillatory stress (Figure

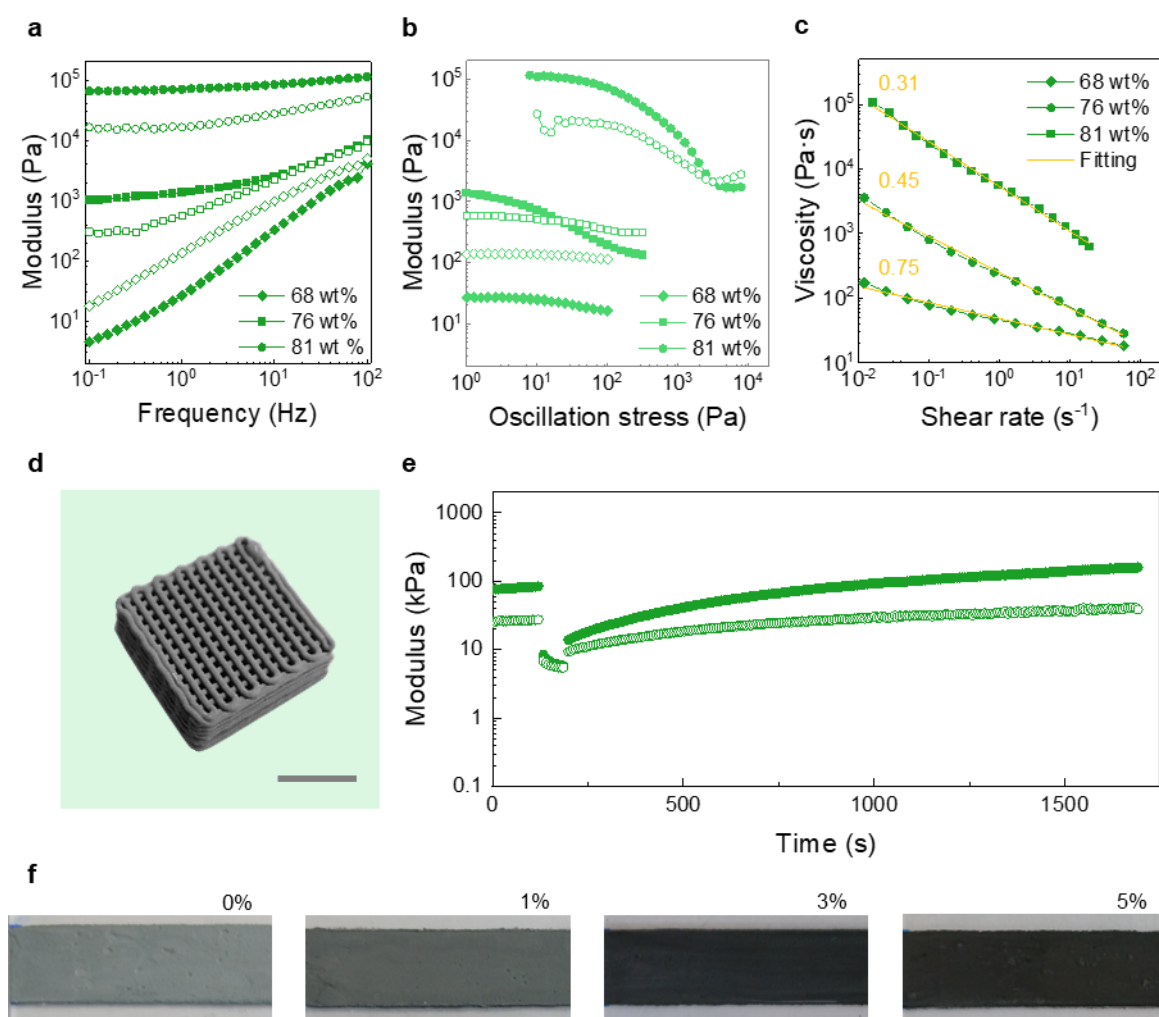


Figure 4.7: (a) Oscillatory frequency sweep tests for the zinc ink with 5% carbon black at increasing total weight fraction of solid material (closed circles represent G' , open circles G''); (b) oscillatory amplitude sweep tests at a fixed frequency of 1 Hz for the zinc ink with 5% carbon black at increasing total weight fraction of solid material (closed circles represent G' , open circles G''); (c) flow ramp tests on the zinc ink (5% carbon black) at increasing total weight fraction of solid material and corresponding power law fitting, the flow index n is reported near each curve; (d) digital photograph of a woodpile zinc electrode, showing excellent shape fidelity and stability (scale bar 5 mm); (e) three-interval thixotropy tests on the zinc ink (3% carbon black) at an oscillatory frequency of 10 Hz (closed circles represent G' , open circles G''); (f) blade casted zinc inks on glass substrates at increasing content of carbon black.

4.7-a), with a loss modulus higher than the storage modulus in the whole range of frequencies investigated. Increasing the solid content, a solid-like response starts to appear at low frequencies (76 wt% in Figure 4.7-a), but the viscoelastic moduli show a significant variation with the frequency. When a total solid content ~ 81 wt% is reached (Figure 4.7-a, top curves), the viscoelastic response becomes almost independent of frequency and it presents the features of a predominantly elastic material ($G' \gg G''$). At this concentration of solid particles, the microstructure of the suspension is in a kinetically-arrested state, behaving as a solid material at rest. The slow decline of storage modulus at an oscillatory stress higher than 100 Pa (Figure 4.7-b) indicates that the yielding process is more gradual than in capillary suspensions (Chapter 3, Figure 3.4-b), for which a sudden drop of the storage modulus near the yield stress is associated with the avalanche breakdown of the particle network. Below the yield stress, the 81 wt% zinc ink appears more stretchable and cohesive than the stiff and brittle capillary pastes, probably owing to the abundant hydroxy functionalities and high molecular weight of the PVA chains, which form strong links between the solid particles. Accordingly, the ink also presents strong adhesion to glass and graphite substrates, and can be blade-coated to form continuous and tough films ~ 100 μm in thickness (Figure 4.7-f). The yield stress of the ink, defined as the crossover point between G' and G'' , is ~ 2800 Pa, significantly higher than the capillary inks presented in Chapter 3 ($\tau_y \sim 60$ Pa), as a result of the more gradual decay in the storage modulus and the stronger bonds between the particles. All the zinc dispersions behave as shear thinning fluids during flow, as a consequence of the rupture of the particle network under a shear force (Figure 4.7-c). The flow index n decreases with the content of particles, reaching a value ~ 0.31 for the suspension with the highest particle concentration (81 wt%). These rheological features indicate that the 81 wt% dispersion is a promising ink for DIW, owing to its solid-like behaviour at rest, high yield stress and marked shear thinning.

Inks with different concentrations of carbon black were formulated to study the effect of the conductive additive on the electrochemical properties of the printed electrodes. In detail, the mass fraction of carbon black was varied between 0% and 5% (Figure 4.7-f), gradually increasing the total content of solid particles in the PVA suspension until a jammed paste was obtained. The rheological properties of the different PVA inks are summarized in Table 4.2. They all present a storage modulus higher than 10^5 Pa and a yield stress between 1.7×10^2 and 3.5×10^3 Pa, which fall in the

Table 4.2: Rheological properties of the final zinc inks at different content of carbon black.

Carbon content	Storage modulus (Pa)	Yield stress (Pa)
0%	2×10^5	170
1%	2×10^5	920
3%	5×10^5	3500
5%	1×10^5	2000

printability range for typical DIW inks. Notably, the yield stress of the zinc inks is much higher than the capillary graphene inks presented in Chapter 3 ($\tau_Y \sim 60$ Pa), which suggests that the extrusion throughout the nozzle might be dominated by plug flow. This would explain the excellent shape fidelity of the printed structures (Figure 4.7-d), even though all the inks present a certain degree of thixotropy, with a slow recovery of the viscoelastic properties after shear. As an example, the 3% ink exhibits a slow storage modulus increase after being sheared at an oscillatory stress near the yield stress (Figure 4.7-e). The storage modulus returns to the equilibrium value after ~ 1000 s, with no irreversible loss comparable to the one observed for PEDOT:PSS. Despite the long recovery time, the ink immediately recovers a solid-like response after the high shear step, with a storage modulus $\sim 10^4$ Pa. This value is already sufficiently high to prevent the lateral instability of the printed filament, considering that the inner core of the extrudate is not sheared and retains its structure. The shape fidelity of the electrodes is also aided by the fast drying of the ink, determined by the low water content and high concentration of solid particles.

2.2. Morphological and physical characterization

The zinc inks were used to print structures with complex geometry and excellent stability, as shown in Figure 4.8-a. The serpentine electrodes do not show any lateral buckling, despite consisting of unsupported walls made of stacked filaments with high aspect ratio (~ 400 μm in lateral width and > 3 mm in height). SEM imaging confirmed the cylindrical shape of the extruded filament, with a small diameter increase where the filaments of the upper layer cross the lower layer (Figure 4.8-b). The consecutive layers were printed at a vertical distance smaller than the nozzle diameter in order to promote adhesion between the layers, which determined a deformation of the solid-like filament where the layers were pressed against each other. The cross-section of the structure appears perfectly circular and it is made of a network of zinc particles, with large pores and cavities between them (Figure 4.8-c,d). At higher concentrations of carbon black (Figure 4.8-e,f), the particles are not in direct contact with each other anymore, but they are linked by a conductive layer made of carbon black and polymeric binder. In the structures with a 5% carbon black content (Figure 4.8-f), the carbon particles start to fill the voids in the network, forming a continuous phase that surrounds the zinc particles. X-ray tomography was used to non-destructively characterize the inner structure of the filaments (Figure 4.8-g,h). The tomogram in Figure 4.8-h confirms the existence of a network of zinc particles, which appear as bright circular regions because of the high X-ray absorption coefficient of zinc. Interestingly, the tomograms of the 5% carbon black structures also present large dark areas (several microns in extension) with no zinc particles, which are not visible

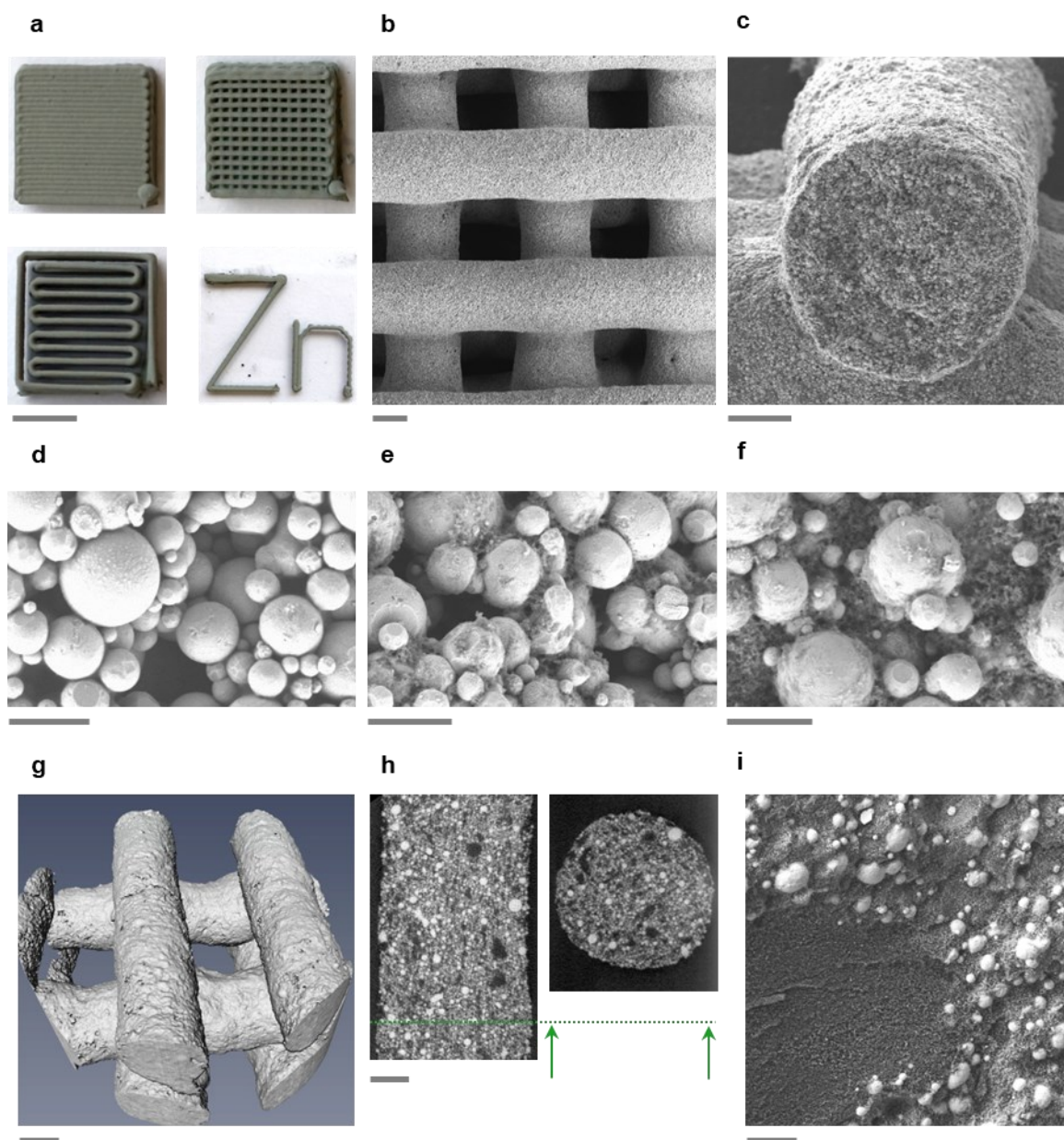


Figure 4.8: (a) Digital photograph of the 3D printed structures fabricated using the zinc inks (scale bar 500 μm); (b) SEM image showing a woodpile electrode printed using the 5% carbon black zinc ink (scale bar 200 μm); (c) cross-sectional SEM view of a printed struct of a woodpile electrode (scale bar 100 μm); (d-f) SEM imaging of the surface of the printed structures at increasing content of carbon black: 0% carbon black (d), 1% carbon black (e) and 5% carbon black (f), all the scale bars are 5 μm ; (g) visualization of the X-ray tomogram on the 5% carbon black woodpile electrode after segmentation (scale bar 200 μm); (h) tomographic slice of the 5% carbon black electrode (scale bar 100 μm); cryo-SEM on the 5% carbon black ink, showing an area with uniformly dispersed zinc particles (upper-right) and a cluster of carbon black particles with no zinc (lower-left area).

in cross-sectional SEM. These areas are probably made of a low-density mixture of carbon black and polymer with lower absorption coefficient than zinc, originating from unbroken clusters of carbon black particles present in the initial ink. To confirm this hypothesis, cryo-SEM was performed on the 5% carbon black ink (Figure 4.8-i), showing areas with a uniform distribution of zinc particles in a homogeneous carbon black matrix, and areas made solely of large clusters of carbon

black particles. The fact that these aggregates are still present after the extrusion process is a further confirmation that the ink is not subjected to high shear when it flows through the extrusion nozzle. The shear flow could easily break the carbon black aggregates promoting a more uniform distribution of zinc particles in the extrudate.

The presence of low-density areas rich in carbon black particles might be detrimental to the mechanical stability of the printed filaments. Compression tests were performed on electrodes with different geometries to assess their mechanical properties (Figure 4.9-a,b). After an initial elastic deformation, the electrodes with serpentine geometry start yielding plastically, and then fracture at a stress ~ 2.7 MPa. The catastrophic failure of the electrode is probably associated with the buckle of the thin walls of the serpentine structure under the compression load. Compact and woodpile structures present a different compression behaviour, with an elastic deformation followed by an apparent increase in the stiffness of the structure at growing compression stress. The apparent stiffening is caused by the progressive densification of the structure, which does not lead to catastrophic

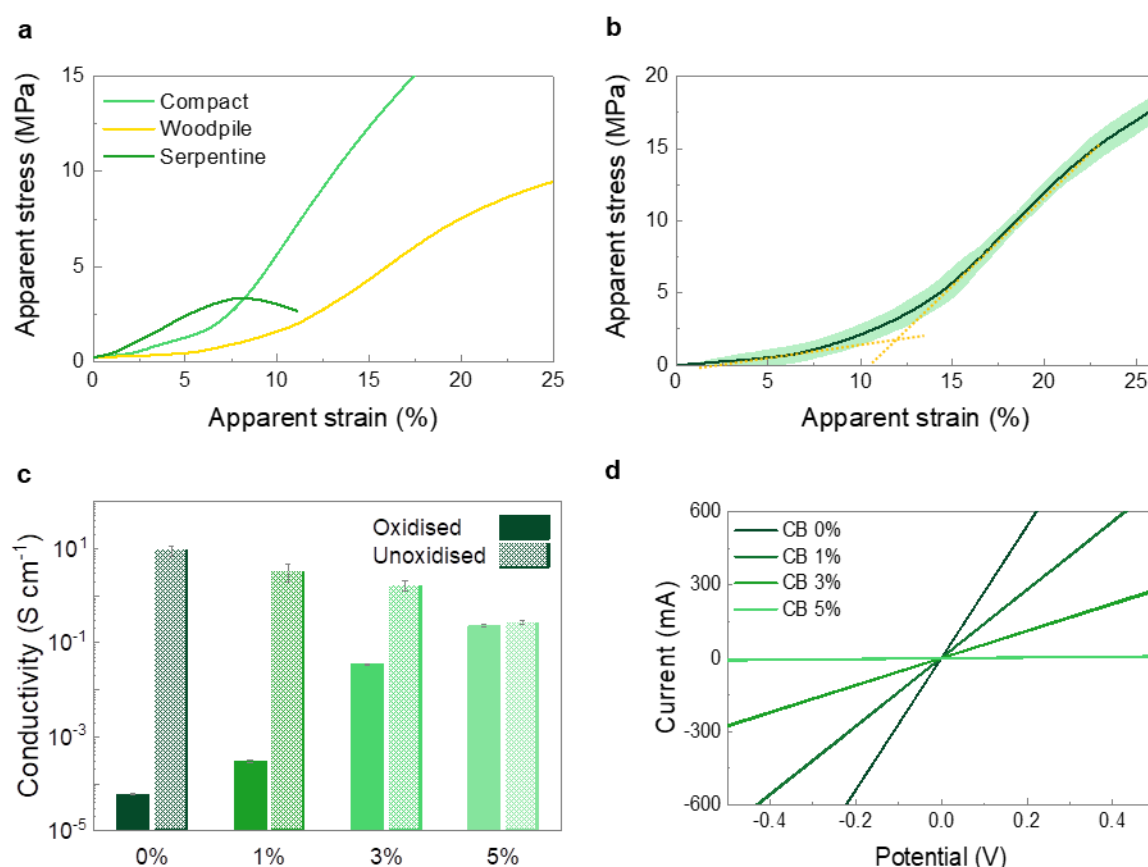


Figure 4.9: (a) Comparison of compression stress-strain curves for 3D printed zinc electrodes with different geometries; (b) Compression stress-strain curve on a cylindrical woodpile zinc electrode (5% carbon black), showing a progressive increase in the sample stiffness caused by densification (marked with orange dotted lines); (c) comparison of the electrical conductivity of zinc structures at different concentrations of carbon black before and after acid treatment; (d) current-potential curves for the zinc structures with different concentrations of carbon black.

failure. When compared to printed graphene electrodes, the zinc structures are significantly stiffer, owing to the denser and more compact filaments. In particular, the densification starts at high values of apparent stress for the woodpile structure (> 8 MPa), much higher than graphene electrodes reported in literature (~ 10 kPa) and closer to polymer-based 3D printed woodpile structure made of polylactic acid.^{127,262} Although the zinc structures can sustain a higher mechanical stress than graphene oxide electrodes before densification, the deformation is not reversible owing to the plastic yield of the filaments, thus the electrodes are not mechanically flexible.

The printed electrodes with no carbon black additive have a conductivity $\sim 6 \times 10^{-3} \text{ S m}^{-1}$, significantly lower than the bulk conductivity of zinc ($1.6 \times 10^5 \text{ S m}^{-1}$),²⁶³ despite the abundant contact points between the zinc particles in the structure (Figure 4.9-c,d). The reason for the low electronic conductivity of the pure zinc electrodes lies in the presence of a layer of zinc oxide on the particle surface, together with the formation of insulating PVA bridges between the particles. To confirm this hypothesis, the surface layer of oxide was etched in an acidic solution ($\text{pH} \sim 2$), which lead to an increase of conductivity to $\sim 900 \text{ S m}^{-1}$. When the carbon black content is increased, the difference between the conductivity of the oxidized and unoxidized electrode decreases, until the two conductivities become almost equal ($\sim 270 \text{ S cm}^{-1}$) at a carbon black content of 5% (Figure 4.9-c). This indicates that the carbon black particles form a percolative conductive network in the 5% structure, which is able to transport charges irrespective of the surface oxidation of the zinc particles. The presence of a conductive network able to convey electrons to the active material inside the electrodes is fundamental to limit the ohmic loss during charge and discharge and avoid the formation of electrically-disconnected zinc particles.

2.3. Half-cell electrochemistry

The 3D printed zinc structures were electrochemically characterized as zinc anodes for aqueous batteries. Zinc anodes notoriously suffer from continuous corrosion in mildly-acidic electrolytes, which is associated with the formation of inert and insulating species, *e.g.* zinc hydroxysulfates and hydroxychlorides, and with the evolution of hydrogen gas.^{34,264} In addition to this, three-dimensional electrodes can undergo mechanical instabilities over prolonged discharge, caused by the progressive dissolution of zinc and the destruction of the electrode structure.

The stability of the printed zinc electrodes in aqueous electrolytes was investigated in symmetric cells in a 2 M ZnSO_4 electrolyte. The 3D printed zinc electrodes with no conductive additives (CB 0%) present high deposition overpotential in plating-stripping tests (Figure 4.10-a,c), with voltage spikes higher than 500 mV at a current density of 10 mA cm^{-2} . This unstable plating behaviour is probably caused by the progressive passivation of the surface of the zinc particles during cycling, which disrupts electronic transport in the thick structures and causes a non-uniform electric field near the surface, with irregular zinc deposition. As a consequence, these electrodes cannot be used as anodes for rechargeable zinc batteries with aqueous electrolytes. Conversely, the electrodes with

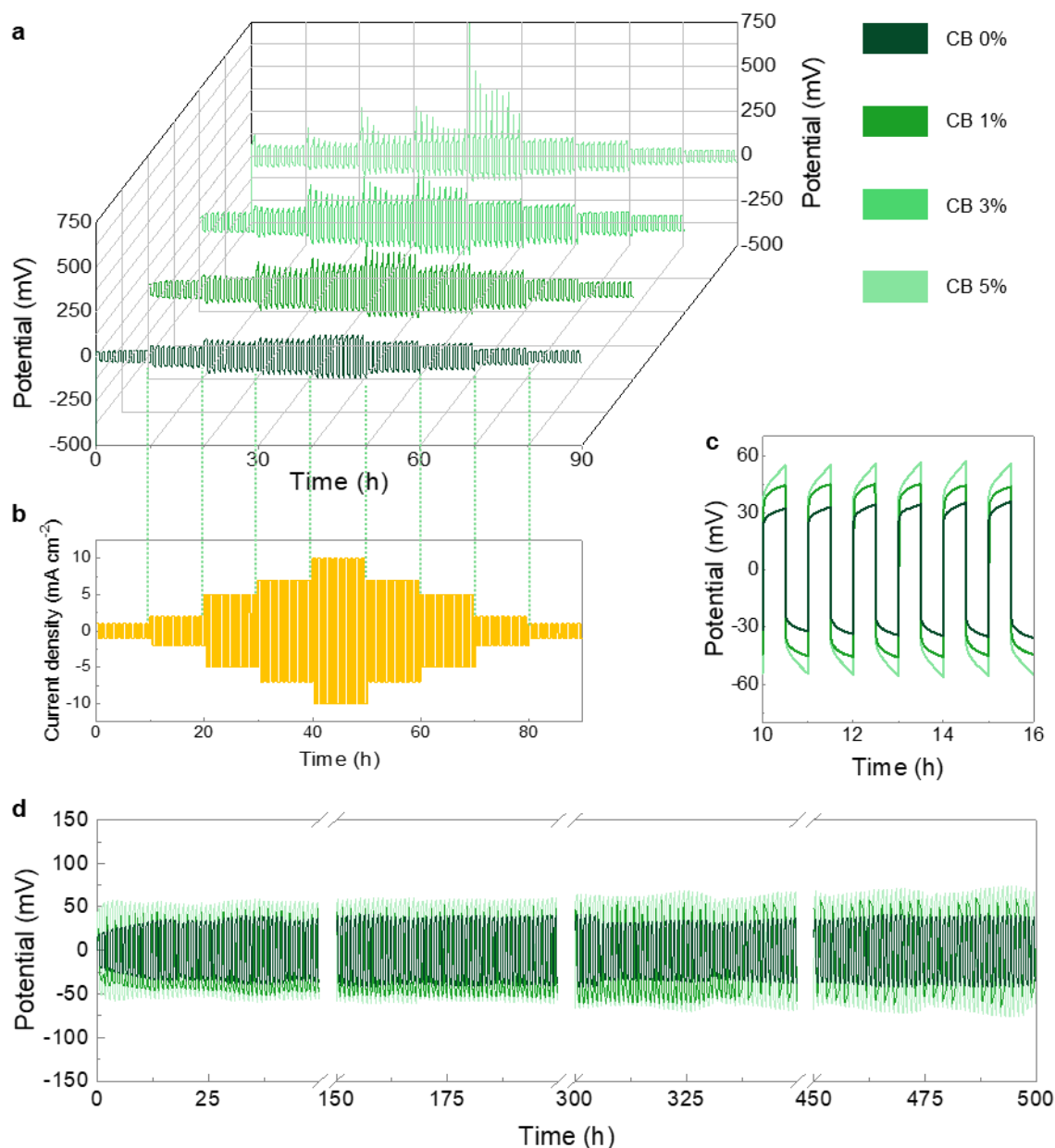


Figure 4.10: (a,b) Comparison of the plating-stripping overpotential of the 3D printed symmetric cells at increasing current density values (b); (c,d) cycling stability of the symmetric cells during plating-stripping tests at 1 mA cm⁻² for 500 h, (c) is a zoomed-in section of (d).

a higher content of conductive carbon present a smaller deposition overpotential (~ 100 mV for the 5% carbon black electrode at a current density of 10 mA cm⁻²), attributable to the improved conductivity of these structures, which ensures faster electron transport and larger electrochemically active regions. Notably, the overpotential of the 3D printed electrodes with the carbon black additive remains stable for over 500 h of continuous cycling (Figure 4.10-c,d), which indicates that the plating and stripping process has good reversibility. The plating and stripping overpotential at low current densities is smaller than recently reported anodes, which require surface modifications to achieve stable cycling, such as coating with MXenes or reduced graphene oxide (Figure 4.11-a).

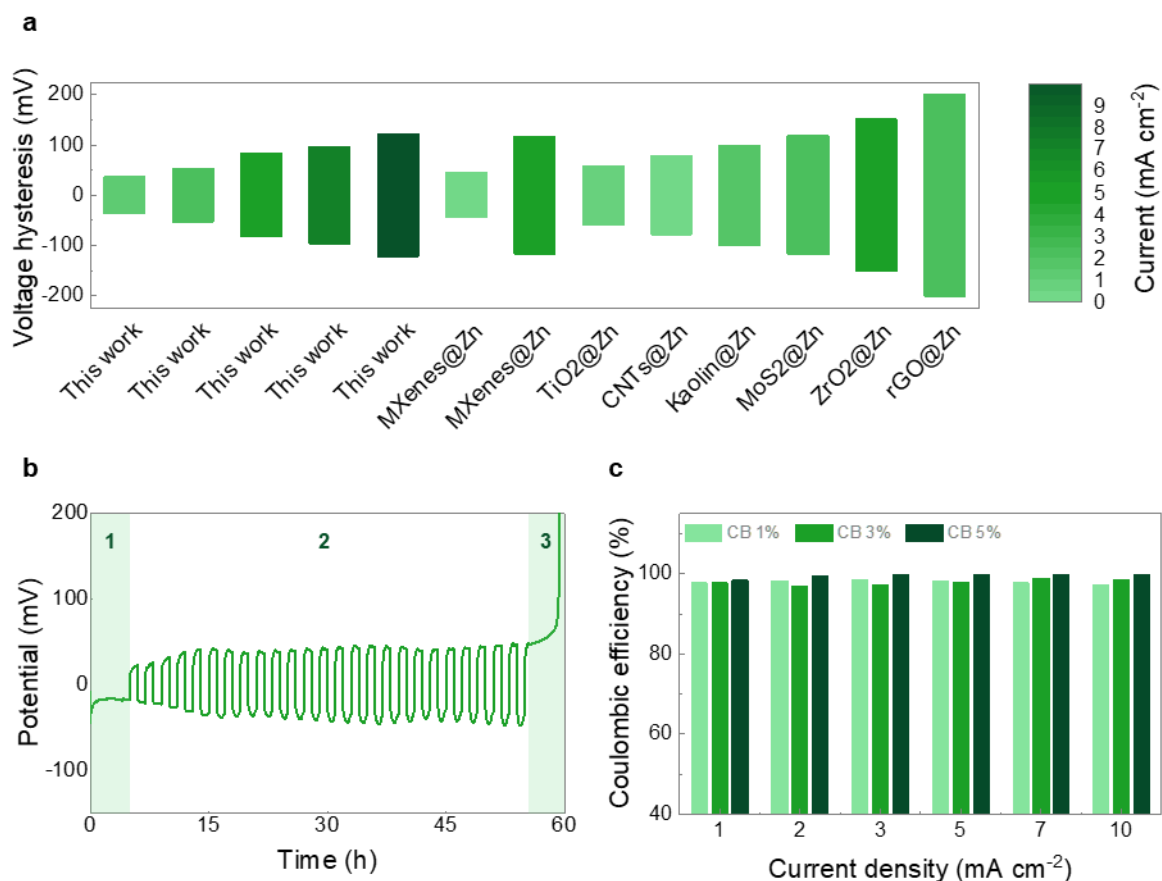


Figure 4.11: (a) Comparison of the voltage hysteresis for the plating and stripping of zinc-CB 5% electrodes with other zinc anodes recently reported in the literature (references in Appendix A2); (b) potential profile for the coulombic efficiency tests with the reservoir method, presenting three regions: formation of the zinc reservoir on the copper counter electrode (1), cycling between the reservoir and the 3D printed electrode (2), stripping of the residual zinc in the reservoir (3); (c) comparison of the Coulombic efficiency of the 3D printed electrodes with different carbon black content.

The reversibility of the oxidation and reduction processes in the 2 M zinc sulfate electrolyte was further characterized by measuring the coulombic efficiency with a half-cell reservoir method, using a copper counter electrode (as described in Chapter 2). A zinc reservoir was plated on the copper counter electrode at a constant current (1-10 mA cm⁻² to a plated capacity of 2.5 mAh cm⁻², Figure 4.11-b). A fraction of the zinc plated on the copper reservoir (0.5 mAh cm⁻²) was then cycled between the reservoir and the 3D electrode for 25 galvanostatic plating-stripping cycles. Finally the residual zinc in the reservoir was stripped away at a constant current until a cut-off potential of 500 mV was reached. Any irreversible reactions during cycling would determine the formation of dead zinc, with a reduction of the capacity that than can be stripped from the reservoir in the last step. The 5% carbon black electrodes achieve the highest coulombic efficiency, reaching 99.7% at the high current density of 10 mA cm⁻² (Figure 4.11-c). Although this value is higher than previously reported zinc systems without additives or protective coatings (coulombic efficiency lower than 95%),^{196,265} it is still far from the coulombic efficiency achieved by lithium-metal batteries in

organic electrolytes (> 99.9%).²⁶⁶ This is indicative of secondary reactions happening in the cell alongside the plating-stripping of zinc, probably associated with the spontaneous corrosion of zinc in the aqueous electrolyte and the consequent increase in the electrolyte pH.

Linear sweep voltammetry is a standard electrochemical method to assess the corrosion rate of metallic electrodes, typically carried out through Tafel analysis of the current response in the proximity of the open circuit potential (Chapter 2).¹⁹⁴ This procedure has also been used in literature to measure the rate of hydrogen evolution deriving from zinc corrosion and the irreversible formation of corrosion by-products on ZIB anodes.^{267–269} However, the Tafel method is based on the hypothesis that the predominant cathodic process near the open circuit potential is hydrogen evolution (as discussed in Chapter 2). If the electrolyte contains Zn^{2+} or $\text{Zn}(\text{OH})_4^{2-}$ ions, there is an additional contribution to the cathodic current arising from the deposition of zinc.²⁷⁰ Even though in these conditions hydrogen evolution is thermodynamically more favourable (higher reversible potential), the deposition of zinc becomes kinetically predominant at a concentration of zinc ions higher than $10^{-4} \text{ mol L}^{-1}$.²⁴⁷ For these reasons, Tafel analysis does not provide a reliable measurement of zinc

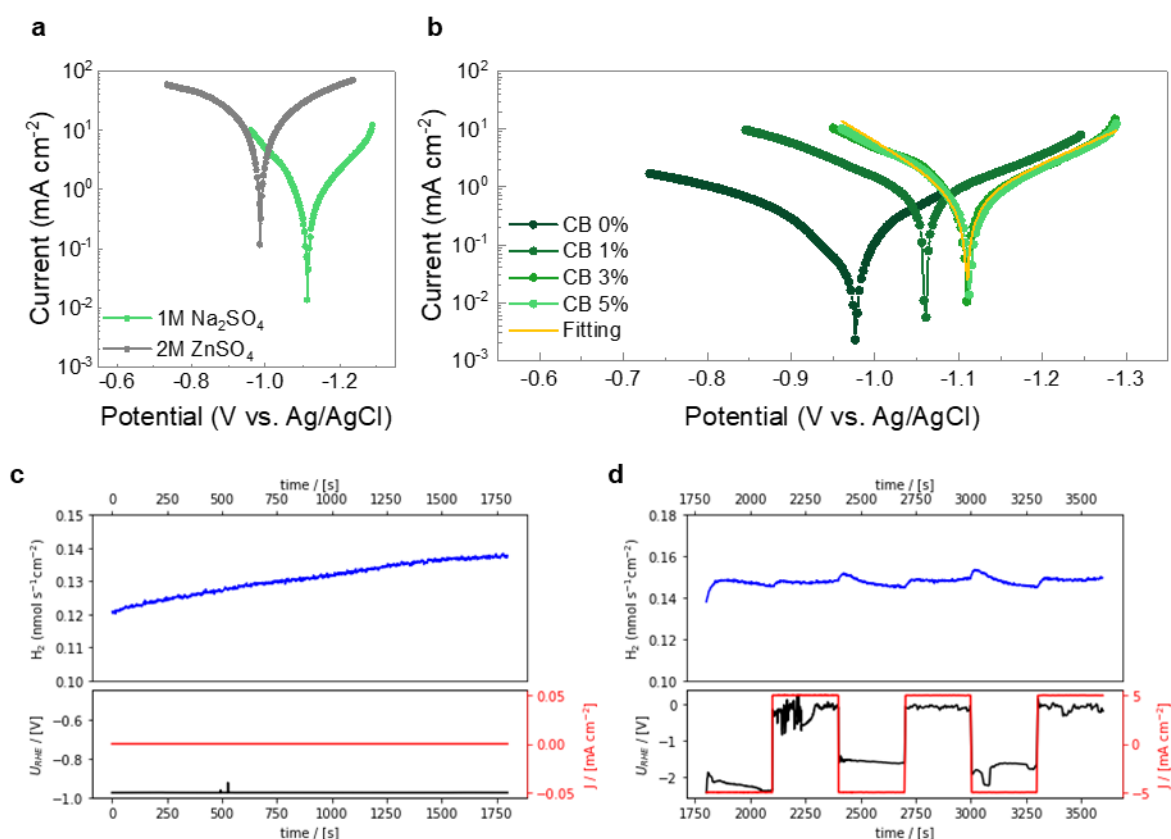


Figure 4.12: (a) Linear sweep voltammetry on the 5% carbon black ink in different electrolytes (scan rate 5 mV s^{-1}); (b) comparison of the linear sweep voltammograms of the zinc inks with different content of carbon black in a $1 \text{ M Na}_2\text{SO}_4$ electrolyte (acidified to pH 5) and Tafel fitting; (c,d) *in-situ* mass spectrometry experiments on the 5% carbon black ink, measuring the rate of hydrogen evolution at the open circuit potential (c) and during galvanostatic charge discharge (d).

corrosion in real ZIB electrolytes (such as 2 M ZnSO_4).

The corrosion of the zinc inks at different carbon black contents was studied in a 1 M Na_2SO_4 electrolyte, acidified to pH 5 to emulate the acidic condition of aqueous zinc sulfate employed in real cells (Figure 4.12-a,b). Compared to linear sweep voltammograms in a zinc sulfate electrolyte, the curve in sodium sulfate shifts to lower currents and a higher corrosion potential (Figure 4.12-a), as a consequence of the different redox processes being probed in the two electrolytes. The higher current density observed in concentrated zinc sulfate is associated with the deposition of the abundant zinc ions in the proximity of the electrode, and does not provide information on the rate of hydrogen evolution. In the sodium sulfate electrolyte, the corrosion current progressively increases with the amount of carbon black in the ink (Figure 4.12-b and Table 4.3), even though the recent literature has reported that a carbon coating can have a protective action against corrosion.^{271,272} The increase in the corrosion current with carbon black content can be attributed to two factors: (1) as observed from SEM imaging, carbon black does not form a continuous layer protecting the zinc particles, but it mainly concentrates at the junction between particles and in the voids of the network; (2) the presence of a conductive network of carbon black enhances the number of zinc particles that are electrically connected to the current collector, increasing the electrochemically active surface area of the sample. As a consequence, the 5% carbon black electrode presents the highest corrosion current ($\sim 731 \mu\text{A cm}^{-2}$), corresponding to a corrosion rate of $\sim 3.8 \text{ nmol s}^{-1} \text{ cm}^{-2}$. Although the tests in 1 M Na_2SO_4 are useful to compare the corrosion behaviour of the different inks, they cannot deliver quantitative information on the rate of zinc corrosion in a zinc sulfate electrolyte. *In-situ* electrochemical mass spectrometry was used to gain insight into the corrosion of printed zinc electrodes in real operating conditions. At the open circuit potential, *i.e.* no current flowing in the cell, the zinc electrode with 5% carbon black produces $\sim 0.14 \text{ nmol s}^{-1} \text{ cm}^{-2}$ of hydrogen in stationary conditions (Figure 4.12-c), which is much lower than the corrosion rate estimated from the Tafel analysis. The rate of hydrogen evolution only changes marginally during charge-discharge experiments (Figure 4.12-d). However, the amount of zinc ink that can be loaded onto the working electrode for the *in-situ* experiments is extremely low ($\sim 0.1 \text{ mg}$), because of the proximity of the working electrode to the membrane separating the electrolyte from the vacuum chamber of the mass spectrometer. This impedes an accurate measurement of the mass of zinc on the working electrode, preventing a direct comparison with the results of the Tafel analysis.

Table 4.3: Tafel fitting of the linear sweep voltammograms in 1 M Na_2SO_4 .

	CB 5%	CB 3%	CB 1%	CB 0%
β_a (mV/decade)	117	87	140	98
β_c (mV/decade)	161	165	164	53
i_{corr} (mA)	731	698	634	45
E_{corr} (V)	-1.11	-1.11	-1.06	-0.98

Additionally, it is difficult to predict how the rate of hydrogen evolution would scale when three-dimensional electrodes are considered. Despite the challenges presented by a quantitative analysis, both the Tafel method and the *in-situ* mass spectrometry indicate that the zinc electrodes are progressively corroding in aqueous environment, even if they retain a stable plating and stripping potential over more than 500 h of cycling, corresponding to a cumulative capacity of 500 mAh cm^{-2} (comparable with the typical lifespan reported for ZIB cathodes).²⁷³ The reasons for the stable charge-discharge behaviour of the printed electrodes and their corrosion mechanism was further investigated with *post-mortem* characterization, as discussed in the next section.

2.4. *Post-mortem* characterization

The retention of the three-dimensional structure of the printed electrodes at high depth of discharge was assessed with *ex-situ* SEM imaging after 5 h of continuous discharge at 5 mA cm^{-2} (Figure 4.13-a,b), corresponding to the stripping of $\sim 10\%$ ($\sim 30 \text{ mg cm}^{-2}$) of the total amount of zinc from

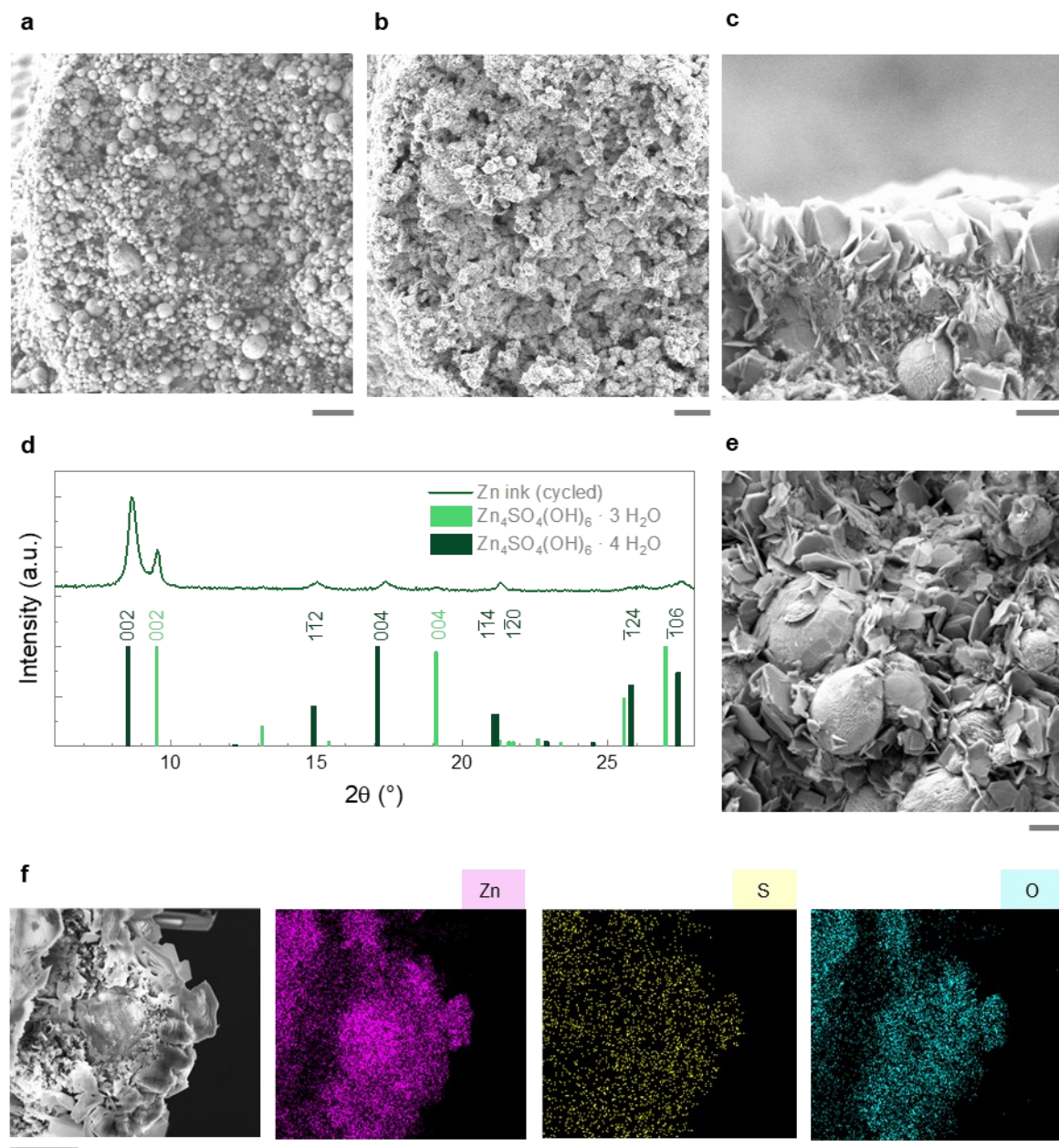


Figure 4.13: (a,b) SEM imaging of the cross section of a printed electrode (5% carbon black ink) before (a) and after (b) continuous discharge for 5 h at 5 mA cm^{-2} (scale bars are $20 \mu\text{m}$); (c) SEM imaging of the cross-section of a printed electrode after 500 h of galvanostatic cycling at 1 mA cm^{-2} , showing zinc hydroxysulfate platelets growing perpendicular to the surface (scale bar $2 \mu\text{m}$); (d) *ex-situ* XRD on the zinc anode after galvanostatic cycling; (e) SEM imaging of the cross-section of a printed electrode after 500 h of galvanostatic cycling (1 mA cm^{-2}), showing zinc hydroxysulfate platelets growing between the zinc particles (scale bar $2 \mu\text{m}$); (f) EDS analysis on the layer of zinc hydroxysulfate covering the surface of the cycled electrode (scale bar $2 \mu\text{m}$).

the electrode. The filaments remain dimensionally stable, even though the zinc network is progressively dissolved during the discharge process, as evidenced by cross-sectional SEM (Figure 4.13-b), which presents large pores resulting from the oxidation of zinc to Zn^{2+} . The pores observed after discharge in SEM might also be attributed to the evolution of gaseous species, in particular hydrogen, inside the electrode structure. The evolution of hydrogen caused by zinc corrosion in mildly acidic electrolytes determines a local increase in the pH of the electrolyte, according to the reaction:



It must be noted that the pores observed in cross-sectional SEM might also form during the destructive sample preparation process, when cutting the electrode with a doctor blade. The evolution of hydrogen around the zinc particles causes the mechanical detachment of the particles from the bulk of the filament. As a consequence, the particles can fall off from the electrode cross-section, leaving a void.

The change in pH associated with Equation 4.1 determines the precipitation of insoluble by-products, as observed on the surface of the 3D printed samples after electrochemical cycling (Figure 4.13-c,e). Thick platelets with an approximately hexagonal shape grow between the zinc particles in the inner structure of the printed electrodes (Figure 4.13-e). The platelets also grow on the surface of the electrode (Figure 4.13-c), forming a porous layer $\sim 200 \mu\text{m}$ in thickness. EDS mapping

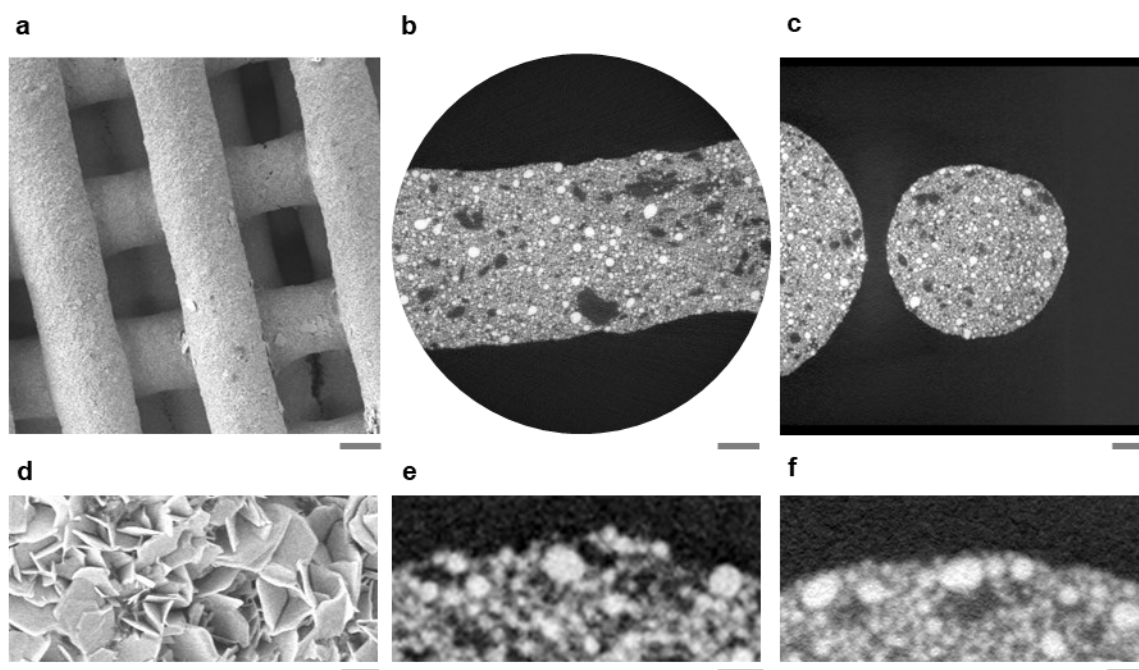
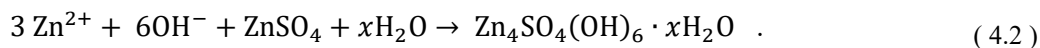


Figure 4.14: (a) SEM imaging of a 3D printed zinc electrode (5% carbon black) after charge-discharge for 250 h at 1 mA cm^{-2} (scale bar $200 \mu\text{m}$); (b,c) tomographic slices of a 3D printed zinc electrode (5% carbon black) after charge-discharge for 250 h at 1 mA cm^{-2} (scale bars are $100 \mu\text{m}$); (d) high magnification SEM image of the surface of the electrode in panel (a), scale bar is $2 \mu\text{m}$; (e,f) X-ray tomographic slices comparing the surface of an uncycled electrode (e) and a cycled electrode (f), scale bars are $20 \mu\text{m}$.

indicates that the platelets mainly consist of zinc, sulfur and oxygen (Figure 4.13-f), and their crystal structure matches well with zinc hydroxysulfates with different hydration (as shown by *ex-situ* XRD, Figure 4.13-d). The hydroxysulfate platelets likely precipitate as a consequence of the local increase in pH, according to the reaction:²⁷⁴



The dimensional stability and distribution of zinc hydroxysulfates was further characterized on a 5% carbon black electrode after 250 h of continuous charge and discharge at 1 mA cm^{-2} . The outer morphology of the electrode appears unaltered after electrochemical cycling (Figure 4.14-a), with no crumbling or cracking of the printed filaments. Although the printed electrode present stable cycling with a small overpotential of $\sim 45 \text{ mV}$, the electrode surface appears completely covered with zinc hydroxysulfates (Figure 4.14-d). X-ray tomography was performed on the electrode to further characterize the structure of the printed filaments after electrochemical cycling. The filaments do not show any inner cracks (Figure 4.14-b,c), which confirms the excellent structure retention indicated by SEM. The presence of zinc hydroxysulfates cannot be resolved from the tomographic analysis, and the tomograms appear identical to the uncycled samples. This is probably a result of the small size of the hydroxysulfate platelets and their low absorption coefficient when compared to metallic zinc. Therefore, X-ray tomography cannot be used to identify the distribution of hydroxysulfates inside the printed electrode. Even in the proximity of the surface, the continuous layer of corrosion by-products coating the electrode cannot be resolved (Figure 4.14-e,f). The contrast difference between the zinc particles and the pores and carbon black aggregates inside the filament appears lower in the cycled sample, which might be a consequence of the formation of hydroxysulfates with higher absorption coefficient than carbon. This is coherent with SEM analysis, showing the presence of hydroxysulfate platelets through the entire cross-section of the electrodes.

In order to study how the growth of zinc hydroxysulfates affects the kinetic of charge transfer in the zinc electrodes, electrochemical impedance spectroscopy tests were performed on the printed structures after galvanostatic cycling (Figure 4.15). The impedance spectra of symmetric cells are characterized by two depressed semicircles, associated with the transfer of charges through the inert layer covering the electrode (R_i and Q_i in Figure 4.15-c) and to the charge transfer resistance at the interface with zinc (R_{ct} and Q_{dl}). The interface charge transfer resistance R_{ct} is typically quite large for zinc ions, between 10 and 100Ω , because of the hindrance to desolvation and charge transfer encountered by divalent zinc ions.²⁷⁵ In symmetric zinc foil electrodes, the diameter of the second semicircle suddenly drops after $\sim 70 \text{ h}$ of continuous charge-discharge, as a result of the growth of zinc dendrites that short circuit the cell, leading to a reduction in the charge transfer resistance (as indicated by the drop in plating-stripping potential, Figure 4.15-d).²⁷⁵ Conversely, the charge transfer resistance R_{ct} of the 3D printed electrodes remains approximately stable for $\sim 200 \text{ h}$ of repeated charge-discharge, indicating that no short circuit occurs, owing to the lower surface current that

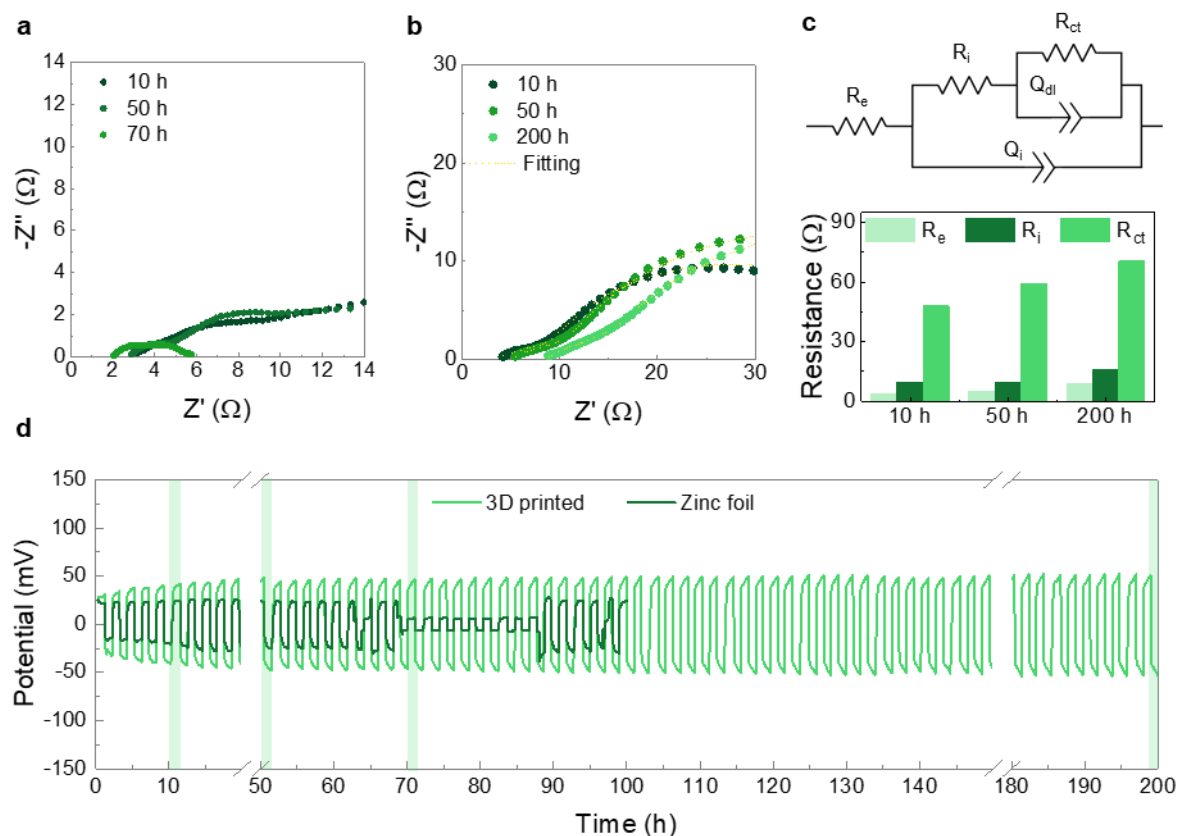


Figure 4.15: (a) EIS on the symmetric zinc foil cell at different cycling times; (b) EIS on the symmetric 3D printed cell (5% carbon black ink) at different cycling times; (c) equivalent circuit used to fit the impedance data (top) and histogram reporting the variation in the model resistances over cycling (bottom) for the symmetric 3D printed electrodes (5% carbon black ink); (d) plating-stripping potential for the symmetric zinc foil and 3D printed cell at a constant charge-discharge current of 1 mA cm^{-2} (the times at which EIS was performed are highlighted in green).

prevents the growth of dendrites. Nonetheless, R_{ct} shows a slight increase over cycling (Figure 4.15-c and Table 4.4), attributed to the growth of a film of by-products on the zinc particles. The resistance of the electrolyte R_e also increases over time, either as a consequence of the irreversible loss of zinc ions that precipitate forming insoluble zinc hydroxysulfates, or because of the formation of hydrogen bubbles that adhere to the electrode surface and reduce the active area in contact with the electrolyte. The transport resistance in the inert hydroxysulfate layer remains approximately constant in the first 50 h of cycling (Table 4.4) and only increases from $\sim 9.4 \text{ } \Omega$ to $\sim 16.2 \text{ } \Omega$ after 200 h of continuous charge-discharge. The small increase in the transport resistance can be attributed to the porous nature of the zinc hydroxysulfide layer, which can be easily infiltrated by the electrolyte. It is important to point out that the overall increase in the equivalent-circuit resistances observed during cycling is relatively small, especially if compared to the passivation of zinc electrodes in alkaline electrolyte under an anodic scan ($R_{CT} > 400 \text{ } \Omega$ and $R_i > 200 \text{ } \Omega$).²⁷⁶ For this reason, the cell plating-stripping overpotential remains stable over hundreds of hours of continuous cycling.

Table 4.4: EIS fitting parameters for the symmetric 3D printed cell (5% carbon black ink) after different cycling times.

	10 h	50 h	200 h
$R_E (\Omega)$	3.5	5.0	8.6
$R_i (\Omega)$	9.7	9.4	16.2
$Q_i (\text{mF s}^{n-1})$	19.8	16.2	21.5
n_i	0.32	0.35	0.35
$R_{CT} (\Omega)$	48.0	59.1	70.6
$Q_{DL} (\text{mF s}^{n-1})$	12.9	14.9	10.4
n_{DL}	0.75	0.74	0.77

3. Conclusions

The fabrication of aqueous ZIBs and ZHCs with 3D-structured anodes is crucial to meet the demand for energy storage devices with high energy densities and long cycling life. This chapter presented two possible approaches to formulate aqueous inks to 3D-print zinc anodes *via* DIW. In the first section, the destabilization of PEDOT:PSS dispersions to obtain an electroactive gel binder was discussed. The PEDOT:PSS ink has high storage modulus at rest and high yield stress, but undergoes irreversible microstructural transformations under shear that hinder the extrusion of stable and self-supporting ink filaments. This behaviour was attributed to the biphasic nature of the dispersing medium, consisting of a strongly bound polymeric coacervate and a polymer-depleted liquid phase. The second section of the chapter investigated polyvinyl alcohol as a highly hydrophilic polymeric binder with strong specific interactions with the surface of zinc particles. Unlike PEDOT:PSS, PVA is not electroactive nor electrically conductive, therefore a conductive additive, carbon black, was introduced into the system and its effects on the electrochemical properties of the printed electrodes were investigated. The printed structures with higher concentration of carbon black have lower plating-stripping potential and they retain their conductivity irrespective of the surface oxidation of zinc particles. Compared with zinc foil electrodes, the 3D printed anodes are not affected by the growth of dendrites, as evidenced by *ex-situ* SEM and electrochemical impedance spectroscopy, as a consequence of their lower local current density. However, the zinc particles inside the printed anodes continuously corrode in aqueous electrolytes, determining the formation of inert zinc hydroxysulfates, as demonstrated by *in-situ* mass spectrometry and *ex-situ* EDS and XRD. The hydroxysulfate layer is highly porous, thus it does not block the charge transfer processes inside the printed structures, ensuring stable electrochemical cycling for more than 500 h.

The characterization of the printed anodes presented in this section in a full cell assembly and the integration with suitable printed cathodes and electrolytes, in order to fabricate a fully printed battery, will be discussed in the next chapter.

Chapter 5

Printing of Full Batteries

The previous chapters have presented the fabrication of three-dimensional electrodes for electrochemical energy storage devices *via* DIW. In particular, the printed systems discussed so far consisted of a single electrochemically-active material, namely graphene or zinc. However, rechargeable batteries typically combine multiple functional elements, *i.e.* anodes, cathodes, electrolytes and separators, each presenting specific composition and properties, as outlined in Chapter 1. Extrusion-based printing techniques, such as DIW, allow the integration of diverse active components into a multi-material device, owing to their design and material versatility.²⁷⁷ At the same time, DIW also offers the opportunity to simplify battery assembly, reducing the number of manufacturing steps and functional components required to fabricate a full cell.^{54,57} Most of the research on 3D printed aqueous batteries has investigated the fabrication of a single battery component, primarily the anode or cathode, *e.g.* *via* the growth of electrode materials on printed conductive scaffolds.^{278,279} However, printing multiple battery components in a single manufacturing process would greatly reduce the energy cost and processing time, and enable the direct integration of multicomponent energy storage devices into portable electronic systems.

This chapter will discuss the integration of printed cathodes and electrolytes with the 3D printed zinc anodes presented in Chapter 4, demonstrating the fabrication of fully-printed aqueous batteries. In particular, the first two sections of the chapter will deal with the formulation of inks based on ZIB cathode materials, and the fabrication and electrochemical characterization of printed woodpile cathodes for ZIBs. Two different cathode materials are considered in this work: manganese oxide, a widely studied transition metal oxide initially proposed for primary zinc batteries; and vanadium disulfide, a layered transition metal dichalcogenide that has recently attracted interest as a novel cathode material for ZIBs. The synthesis, characterization and 3D printing of these materials will be presented in Section 1 and 2. Section 3 will discuss the formulation of a printable gel electrolyte, drawing inspiration from the colloidal processing of ceramic suspensions. The direct deposition of the gel electrolyte between 3D printed interdigitated electrodes eliminates the need for a glassy-fibre separator and enables the direct fabrication of a full-battery on a pre-patterned current collector, as demonstrated in Section 4. The characterization of the interdigitated battery, and its use to power a portable system, are also discussed at the end of the chapter.

1. Hydrothermal VS₂ cathodes

Zinc-ion batteries are primarily based on metallic zinc anodes, owing to the low cost, high energy density and conveniently low redox potential (-0.76 V vs SHE) of zinc.²⁸⁰ In contrast, the research on cathodes is still at an early stage, with a variety of different materials identified as promising cathodes for ZIBs. The choice of the cathode active material plays a crucial role in the performance of the full electrochemical cell, controlling the charge-storage capability, energy density and rate performance of the battery. ZIB cathode materials typically store energy through the reversible intercalation of ions into their crystal structure, which can present one-, two- or three-dimensional diffusion pathways.^{281,282} However, Zn²⁺ ions have a high charge density, almost double the charge density of Li⁺, which is detrimental for the intercalation kinetic and the structural stability of the electrodes.²⁸³ Although Zn²⁺ ions are coordinated by water molecules in aqueous electrolytes, which can partially buffer their charge density, these coordination complexes have a large radius (~ 4.30 Å), which hinders the intercalation of hydrated ions into conventional cathode materials.²⁸³

Layered transition metal dichalcogenides (TMDs) have recently attracted great interest as energy storage materials, presenting high surface area and large two-dimensional diffusion channels.²⁸⁴ The consecutive layers in the crystal structure of TMDs are held together by weak van der Waals forces, resulting in a large interlayer spacing which enables the rapid diffusion and the reversible insertion and extraction of multivalent ions.²⁸⁴ Additionally, the transition metal centres typically exhibit multiple oxidation states, allowing for multi-electron redox reactions and enhancing the capacity that can be stored in the cathode. Among TMDs, molybdenum and tungsten sulfide have been widely investigated as energy storage materials for supercapacitors and alkali-ion batteries.^{285–289} However, the thermodynamically-stable phase of these materials is semiconductive, with a bulk bandgap > 1.2 eV, which hinders the charge transfer and rate capability in three-dimensional electrodes with long transport distances.^{290,291} Vanadium disulfide VS₂, on the contrary, has a metallic character with a reported conductivity $\sim 3 \times 10^3$ S cm⁻¹, an interlayer distance ~ 5.7 Å and it is stable in air and in aqueous environment.²⁹² Similarly to other TMDs, high-purity VS₂ can be synthesized by chemical vapour deposition or solid-state reaction; nonetheless, these methods require high temperatures, they are incompatible with solution processing and they cannot be easily scaled up to formulate concentrated inks for DIW. Solvothermal and hydrothermal reactions can instead provide large amounts of active material with a controlled particle size and morphology, eliminating the need for mechanical milling to formulate DIW inks. Sun *et al.*⁴¹ demonstrated that hydrothermal VS₂ can achieve a high capacity (205.3 mAh g⁻¹) and rate capability (135.4 mAh g⁻¹) when tested as a cathode for ZIBs. They suggested that the intercalation of zinc ions in VS₂ follows a two-step mechanism, with the formation of Zn_{0.20}VS₂ at a potential ~ 0.57 - 0.75 V vs. Zn/Zn²⁺, followed by the further intercalation of Zn²⁺ to form Zn_{0.44}VS₂ at ~ 0.90 - 1.04 V vs. Zn/Zn²⁺. Other reports have suggested different stoichiometries for the intermediate discharge phases, although

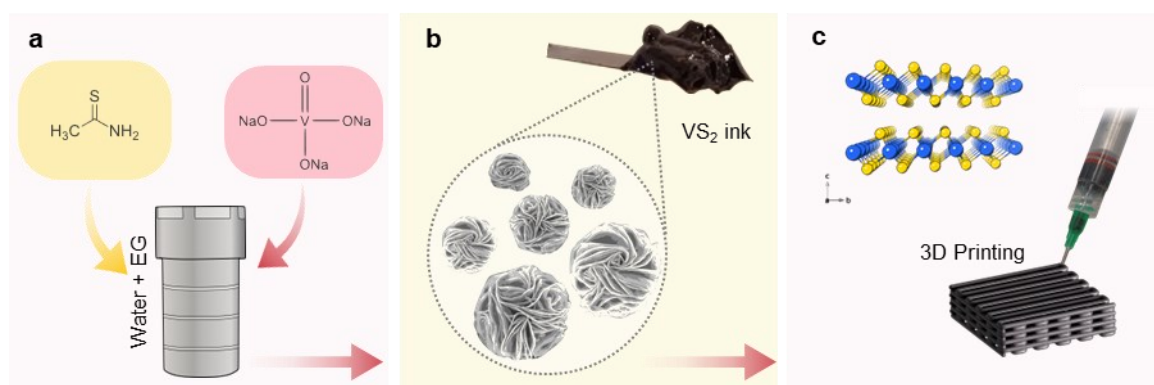


Figure 5.1: Schematic showing the hydrothermal synthesis of VS₂ (a), the formulation of a VS₂ ink (b) and the printing of woodpile VS₂ cathodes (c) (inset showing the layered crystal structure of VS₂).

they agree on the insertion charge storage mechanism.⁴⁰ Additionally, Yu *et al.*²⁹³ demonstrated that the capacity of VS₂ electrodes can be enhanced by tailoring the potential window in which the cathodes operate, in order to form a stable layer of oxide on the VS₂ particles. The resulting VS₂/VO_x electrodes achieve higher capacity (301 mAh g⁻¹) and greater stability (75% capacity retention after 3000 at 1 A g⁻¹) than bare VS₂.

Despite these promising results, the studies on VS₂ electrodes for ZIBs so far have mainly considered coin cells, which are difficult to integrate in wearable devices. On the contrary, extrusion-based printing techniques, which are able to meet the demand for shape customization, have not yet been extensively explored. This section will present the processing of hydrothermal VS₂ to formulate inks for DIW, and the characterization of the 3D printed electrodes for aqueous ZIBs.

1.1. Synthesis and physical characterization of VS₂

Vanadium disulfide was synthesized *via* a hydrothermal method, starting from Na₃VO₄ and thioacetamide as the water-soluble precursors for vanadium and sulfur, respectively (Figure 5.1-a). When the reaction mixture is heated to 160°C, thioacetamide molecules start hydrolysing, releasing HS⁻ ions which react with vanadium to form VS₂ platelets. The use of a different precursor for vanadium, namely NH₄VO₃, did not lead to the formation of vanadium disulfide, whereas partially amorphous platelets made of vanadium oxides and hydroxides were obtained instead (Figure 5.2-c,g). This is probably caused by the different reactivity of the two precursors in water and the different pH of the reaction environment (~ 12 for a 55 mM Na₃VO₄ solution *vs.* ~ 6 for NH₄VO₃), which influences the hydrolysis mechanism for thioacetamide and the stability of the vanadate species. It has been shown that, in a more alkaline environment, thioacetamide quickly hydrolyses into ammonia and thioacetate CH₃COS⁻, and subsequently the thioacetate reacts to slowly release sulfide ions.¹⁴² On the contrary, in acidic environment, thioacetamide quickly releases hydrogen sulfide and acetamide, which is then slowly hydrolysed to produce ammonia. The fast release of

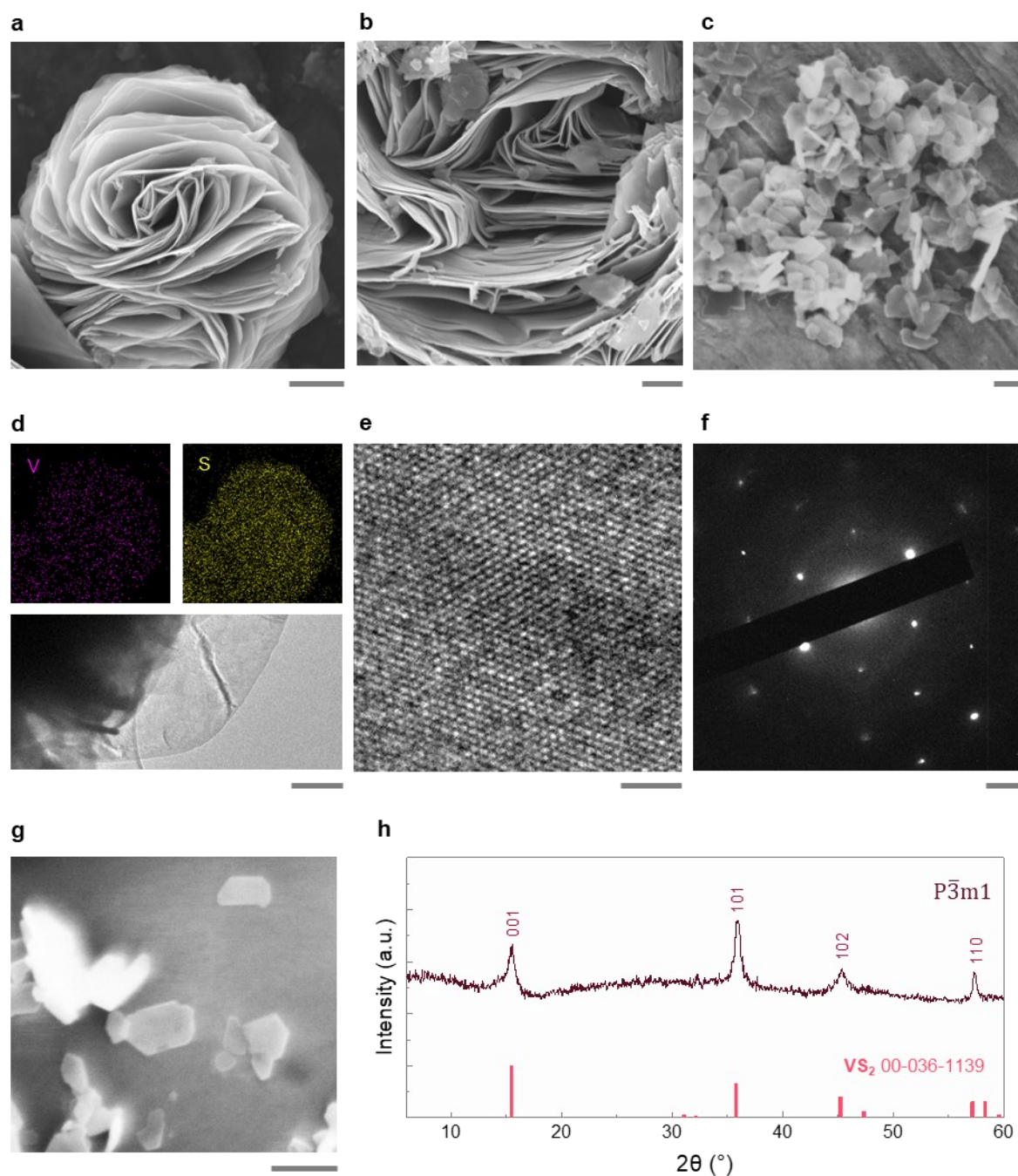


Figure 5.2: (a-c) SEM imaging of the reaction products obtained from the hydrothermal synthesis in water/EG with Na₃VO₄ precursor (a), in water with Na₃VO₄ precursor (b) and in water with NH₄VO₃ precursor (c), the scale bars are 1 μ m, 1 μ m and 100 nm respectively; (d) EDS mapping of the VS₂ microflowers in panel (a) and TEM imaging of a petal of the VS₂ microflowers (scale bar 200 nm); (e) HR-TEM of the VS₂ microflower petals (scale bar 2 nm); (f) SAED pattern of VS₂ microflowers along the (101) plane (scale bar 2 nm⁻¹); (g) high-magnification SEM imaging of the nanoplatelets obtained from the NH₄VO₃ precursor (scale bar 100 nm); (h) powder XRD pattern of the VS₂ microflowers.

hydrogen sulfide in a more acidic environment (*i.e.* in the NH₄VO₃ solution) might lead to the quick formation of small VS₂ nuclei, which then grow to form thin platelets. The thin platelets can be easily oxidised to form amorphous oxides and hydroxides, which are thermodynamically more stable in the sulfide-depleted reaction environment. This hypothesis can explain why the platelets

obtained from the NH_4VO_3 precursor have an approximately hexagonal shape (Figure 5.2-g), even though their atomic structure is predominantly amorphous. This might also be the reason why recent reports have managed to successfully synthesize VS_2 from a NH_3VO_4 precursors by buffering the solution pH at ~ 12 with the addition of ammonium hydroxide.^{40,294} Nonetheless, the formation of VS_2 might also proceed through the direct reaction of thioacetamide with the vanadium centres, with no preliminary hydrolysis step.¹⁴² In this case the rate of reaction typically increases with increasing pH,²⁹⁵ thus the acidic conditions of the NH_4VO_3 precursor might inhibit the formation of sulfides, with the preferential growth of oxides in the hydrothermal conditions. The lower solubility of the NH_4VO_3 precursor and different reactivity of the vanadium centre might also play a role in formation of different reaction products.

The hydrothermal reaction between Na_3VO_4 and thioacetamide leads to the formation of large platelets with irregular morphologies, which stack on each other to form aggregates $> 20 \mu\text{m}$ in lateral size (Figure 5.2-b). The addition of ethylene glycol (EG) to the reaction mixture promotes the growth of smaller platelets, which aggregate to form individual microflowers $\sim 5 \mu\text{m}$ in diameter (Figure 5.2-a). The different morphology obtained in the mixed water/EG solvent can be attributed to the lower dielectric constant and higher viscosity of EG compared to water, which hinders the growth of VS_2 crystals leading to the formation of spherical microflowers.²⁹⁶ Additionally, ethylene glycol can also act as a reducing agent, promoting the reduction of V^{5+} to V^{4+} during the synthesis. The microflower morphology simplifies the formulation of VS_2 inks, since they do not require additional milling processes to obtain small particles that can be ejected throughout fine nozzles ($< 500 \mu\text{m}$) without causing blockages. The elemental composition of the hydrothermal VS_2 was studied with EDS analysis, which confirmed that the individual microflowers consist of vanadium and sulfur (Figure 5.2-d). All the diffraction peaks in the powder XRD spectrum (Figure 5.2-h) match well with the 1T phase of VS_2 (space group $\text{P}\bar{3}\text{m}1$). TEM imaging indicates that the structure of the microflowers consists of thin petals, each made of highly crystalline regions (Figure 5.2-d,e). The SAED pattern in Figure 5.2-f can be assigned to the (101) plane of 1T VS_2 , in good agreement with the XRD pattern (Figure 5.2-h), which shows an unusually intense (101) reflection at 35.8° .

XPS was performed on the VS_2 samples synthesized with and without the addition of ethylene glycol, *i.e.* on the large VS_2 flakes and on the VS_2 microflowers (Figure 5.3). The high-resolution spectrum of the V $2p$ core level electrons shows three distinct doublets which indicate the coexistence of three different oxidation states for vanadium (Figure 5.3-b,d). In each doublet, the V $2p_{1/2}$ peak is broader than the corresponding $2p_{3/2}$ peak because of the Coster–Kronig effect.²⁹⁷ The doublet at higher binding energies (517.0 eV and 525.4 eV in Figure 5.3-d) agrees well with the values reported for the $2p_{3/2}$ and $2p_{1/2}$ core level electrons of V^{5+} , whereas the doublet at 516.4 eV and 523.6 eV can be associated with V^{4+} core electrons.^{298,299} The doublet at 514.0 eV and 521.4 eV corresponds to lower oxidation states, probably V^{2+} , originating from the reduction of the V^{5+} precursor during the synthesis. The V^{4+} doublet is dominant in both spectra, accounting for more than

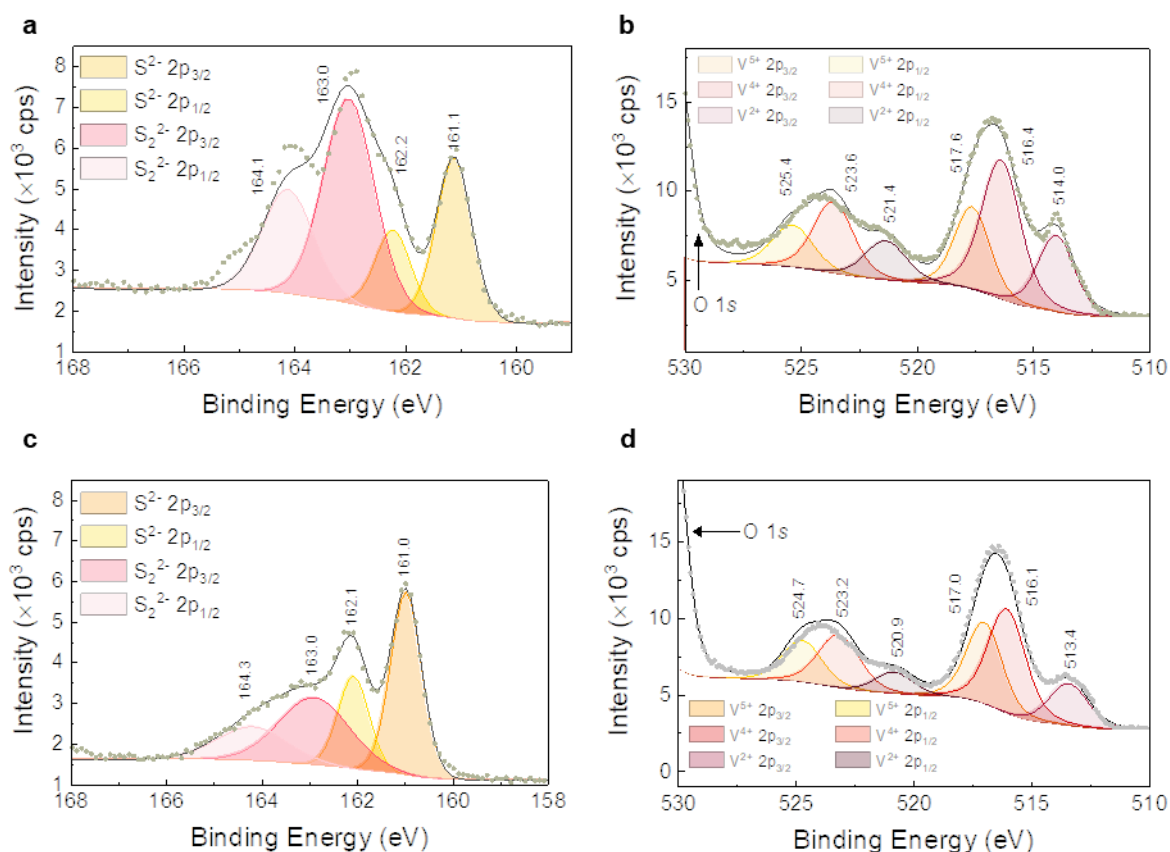


Figure 5.3: (a,b) XPS spectra for the core level electrons of S 2p (a) and V 2p (b) of VS₂ synthesized in water; (c,d) XPS spectra for the core level electrons of S 2p (c) and V 2p (d) of VS₂ synthesized in water/EG.

45 at% of the surface composition of the samples, whereas the presence of V⁵⁺ (< 25 at%) arises from the surface oxidation of the microflowers in air, with the formation of a thin and amorphous layer of oxide on the VS₂ flakes. The S 2p spectra also present two doublets, a lower energy doublet at 161.0 eV and 162.1 eV (Figure 5.3-c) arising from the core level electrons of the sulfide ions in VS₂, and a doublet at higher energies (164.3 eV and 163.0 eV), which is a typical feature of polysulfides. The presence of polysulfides on the surface of VS₂ is probably caused by the excess of free sulfides in the reaction system, as observed for the hydrothermal precipitation of heavy metals sulfides in the presence of thioacetamide.³⁰⁰ The XPS spectrum of the sample synthesized in the presence of ethylene glycol shows a weaker polysulfide doublet, probably a consequence of the reducing effect of EG, which prevents the oxidation of sulfide ions to form polysulfides.

1.2. Ink formulation and 3D printing

The VS₂ microflowers obtained from hydrothermal synthesis can be easily redispersed in water to formulate inks for DIW. However, an appropriate polymeric binder must be added to the dispersion to stabilize VS₂ against sedimentation and provide the ink with the desired rheological properties.

Aqueous binders used to process battery electrodes and to formulate inks for 3D printing, such as polyacrylic acid, polyvinyl alcohol and polysaccharides, typically contain hydrophilic and polar moieties along their carbon backbone.^{54,109} In particular, hydroxyl and carboxyl moieties promote water solubility and form specific interactions with the particles of active material. However, in the case of the VS₂ inks, vanadium cations can leach into the aqueous solution (as discussed in Section 1.3) and strongly crosslink the hydroxyl and carboxyl moieties of the binder through the formation of coordination bonds. As a result, the ink is converted into a brittle rubber during mixing, that cannot be processed *via* DIW. For this reason, poly(vinylidene fluoride) (PVDF) was selected as the binder for the VS₂ ink, owing to its chemical stability and lack of reactive groups. Although PVDF does not form specific interactions with the particles of active material (as discussed in Chapter 4), it can still effectively ensure good adhesion between the components of the ink and enhance the structural stability of the printed electrodes after solvent removal. One of the main drawbacks of PVDF is its high hydrophobicity and limited solubility in aqueous solutions. PVDF is instead highly soluble in dipolar aprotic solvents, which are often hazardous for human health and the environment. In particular, N-methyl-2-pyrrolidone (NMP), a toxic and teratogenic organic solvent, is typically employed in the processing of PVDF-based electrodes. Dimethyl sulfoxide (DMSO) is a safer and bio-based alternative to NMP, but it has only recently started to be studied for the fabrication of battery electrodes *via* conventional casting processes.¹⁰⁸ Here, the use of DMSO to formulate PVDF-based inks for VS₂ electrodes will be investigated.

The VS₂ inks were prepared starting from a dispersion of carbon black (CB) in DMSO. Carbon black acts as a conductive additive, improving the conductivity of the printed filaments, and as a rheology modifier for the printing process, endowing the ink with a yield-stress rheology. Carbon black consists of conductive particles with fractal shape, which can form loosely interacting clusters in solution.³⁰¹ The individual CB particles within each cluster are in a dynamically arrested state, but the clusters are free to diffuse in the solution. When a critical concentration of particles is reached, the density of the clusters increases, forming a percolated network that can simultaneously bear mechanical loads and conduct electrons.³⁰² The critical concentration of CB particles for the formation of a physically bonded network was investigated with oscillatory rheology (Figure 5.4). The DMSO suspensions with a CB mass fraction ~ 2.7 wt% exhibit a viscoelastic response, with the storage and loss moduli strongly dependent on the oscillation frequency in the linear viscoelastic region (Figure 5.4-a). Although the response is mainly elastic for frequencies higher than 2 Hz, the suspension has a liquid (viscous) behaviour at rest (*i.e.* $\omega \rightarrow 0$), which is unsuitable for the formation of self-supporting three-dimensional structures. When the mass fraction of particles reaches ~ 5.3 wt%, the viscoelastic moduli become independent of frequency, with a predominantly elastic response ($G' \sim 950$ Pa *vs.* $G'' \sim 55$ Pa at 1 Hz) indicating the formation of a physically-bonded gel made of carbon black clusters. The gel-like response is associated with the onset of a finite yield

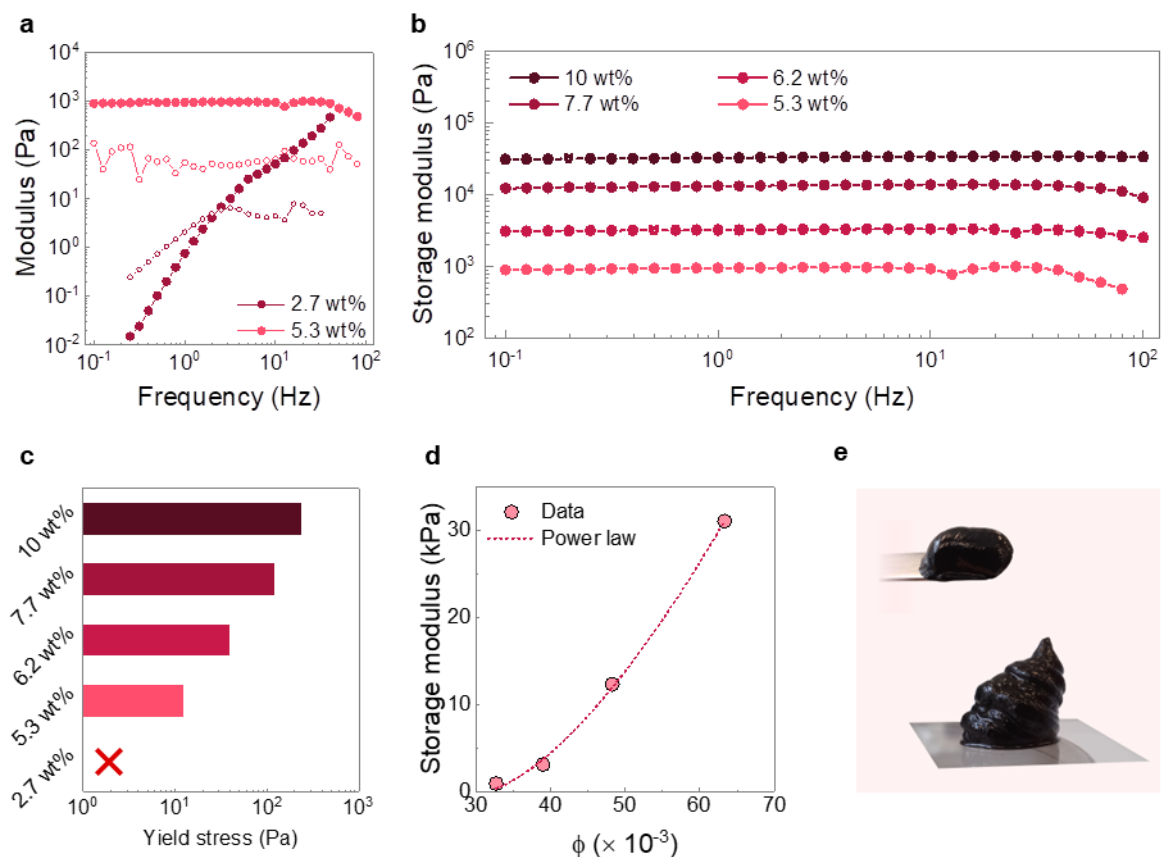


Figure 5.4: (a) Oscillatory frequency sweep of the 2.7 wt% and the 5.3 wt% carbon black dispersion in DMSO (closed circles represent G' , open circles G''); (b) oscillation frequency sweep reporting the storage modulus of different CB dispersions in DMSO as a function of the oscillation frequency; (c) yield stress for the CB dispersion in DMSO at different mass fractions, the 2.7 wt% suspension does not exhibit a yield-stress behaviour; (d) storage modulus of the CB dispersions in DMSO as a function of the CB volume fraction and power-law fitting; (e) digital photographs of the 10 wt% CB-DMSO paste,

stress ~ 12 Pa for the 5.3 wt% suspension, as determined from amplitude sweep tests (Figure 5.4-c). The yield stress and storage modulus gradually increase with the concentration of carbon black particles (Figure 5.4-b,c), reaching a value of ~ 235 Pa and $\sim 3 \times 10^4$ Pa at a mass fraction of ~ 10 wt%. Above the gelation point, the storage modulus has a power-law dependency on the volume fraction of CB, similarly to flocculated suspensions of ceramic particles.³⁰³ The critical volume fraction for gelation ϕ_c is around 3.1%, corresponding to a mass fraction of ~ 5 wt%, as determined from a power law fitting of the oscillatory data (Table 5.1 and Figure 5.4-d). At concentrations

Table 5.1: Results of the power-law fitting of the storage modulus values as a function of CB volume fraction

Power-law model	G'_0 (Pa)	ϕ_c	n
$G' = G'_0 \left(\frac{\phi}{\phi_c} - 1 \right)^n$	2.9×10^5	3.1%	1.5

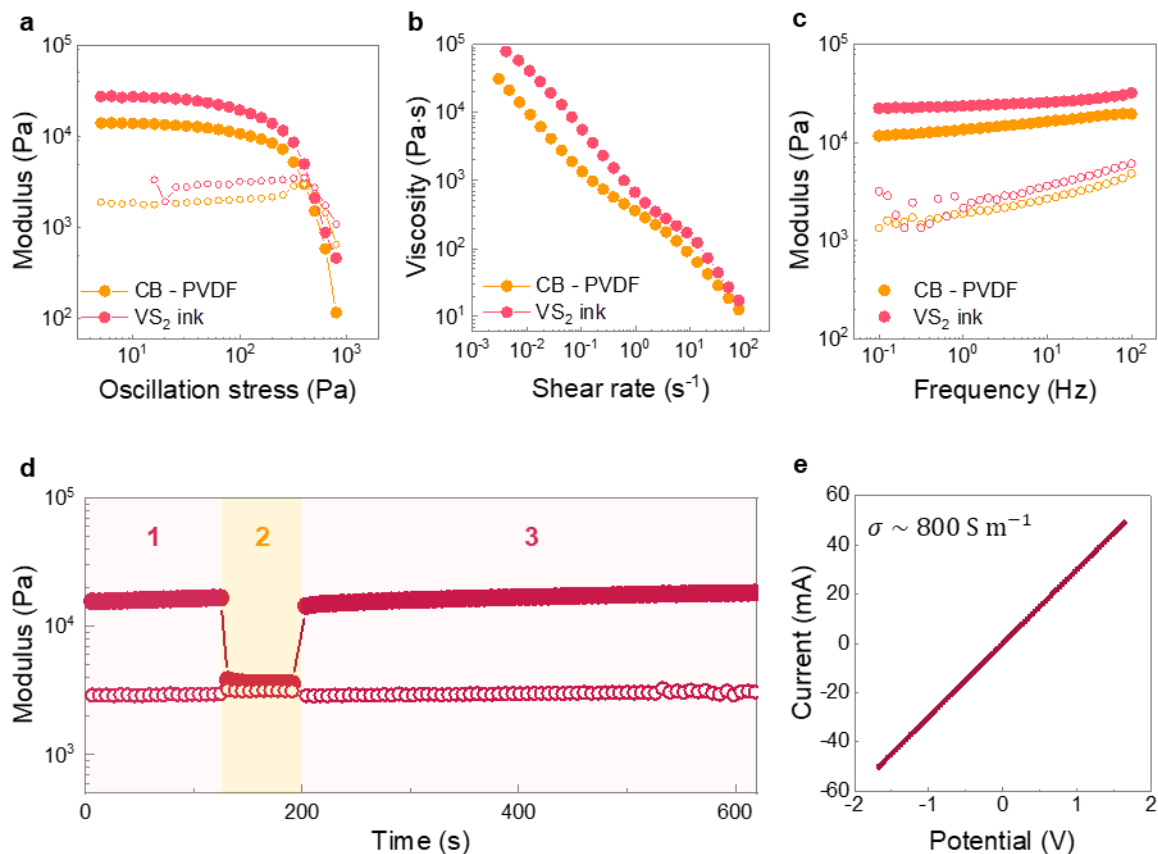


Figure 5.5: (a) Amplitude sweep tests on the CB-PVDF paste and on the VS₂ ink (closed circles represent the storage modulus, open circles the loss modulus); (b) flow curve for the CB-PVDF base paste and the VS₂ ink; (c) frequency sweep tests on the CB-PVDF paste and on the VS₂ ink (closed circles represent the storage modulus, open circles the loss modulus); (d) three interval thixotropy test on the VS₂ ink at an oscillatory stress of 10 Pa (region 1 and 3) and 450 Pa (region 2), closed circles represent the storage modulus, open circles the loss modulus; (e) I-V curve for the CB-PVDF paste.

higher than 10 wt% the carbon black dispersion becomes inhomogeneous, presenting hard particle aggregates in a stiff gel phase.

PVDF was added to the 10 wt% carbon black dispersion to bind the particles together and retain the structural integrity of the printed electrodes after drying. The addition of PVDF determines an increase in the yield stress of the carbon black dispersion to ~ 400 Pa, as a consequence of thickening action of the polymer. The PVDF-CB paste can be used on its own as an ink for the printing of conductive structures, presenting an electrical conductivity of $\sim 800 \text{ S m}^{-1}$ (Figure 5.5-e). Alternatively, electroactive materials can be added to the base PVDF-CB paste to formulate inks for battery electrodes. The inks for the VS₂ cathodes were obtained by dispersing VS₂ microflowers into the PVDF-CB paste under shear mixing. The printability of the VS₂ ink predominantly relied on the yield stress rheology of the base CB paste, hence this ink formulation could be easily adapted to print different energy storage materials. The addition of VS₂ microflowers slightly enhanced the yield stress and storage modulus of the dispersion (from ~ 400 Pa to ~ 450 Pa and from $\sim 1.3 \times 10^4$

Pa to $\sim 2.3 \times 10^4$ Pa, respectively, Figure 5.5-a,c), but the overall rheological behaviour was not significantly altered. Importantly, both the VS₂ ink and the base paste exhibited a solid-like response in the limit of small amplitudes (Figure 5.5-a,c) and a liquid-like, shear-thinning response during flow which facilitates extrusion (Figure 5.5-b). The shear thinning behaviour arises from the progressive disruption of the particle network, with the formation of particle clusters with smaller hydrodynamic volume.³⁰¹ The breakdown of the physical interactions holding the network of particles together should be highly reversible, so to quickly recover an elastic response after extrusion and prevent the collapse of the filaments. Three-interval thixotropy tests indicate that the storage modulus of the ink was quickly restored to its equilibrium value after complete fluidization, achieved by the application of an oscillatory stress equal to the yield stress (~ 450 Pa, Figure 5.5-d).

The high storage modulus and yield stress of the VS₂ inks, alongside the fast recovery of their elastic properties after shear, enabled the fabrication of woodpile electrodes made of several stacked layers (Figure 5.6-a). The printed filaments consist of a continuous network of conductive CB particles, which disperses and supports the individual VS₂ microflowers, as evidenced by SEM imaging (Figure 5.6-b,c). This enables the fast transport of electrons from the external circuit to the microflowers, which act as the functional centres for charge storage in the three-dimensional structure of the electrode.

1.3. Electrochemical characterization

The electrochemical properties of the hydrothermal VS₂ microflowers were characterized in a two-electrode setup, using zinc foil as the counter electrode. Two aqueous electrolytes were employed for the tests: a conventional 3M ZnSO₄ electrolyte and a water-in-salt electrolyte (WISE), consisting

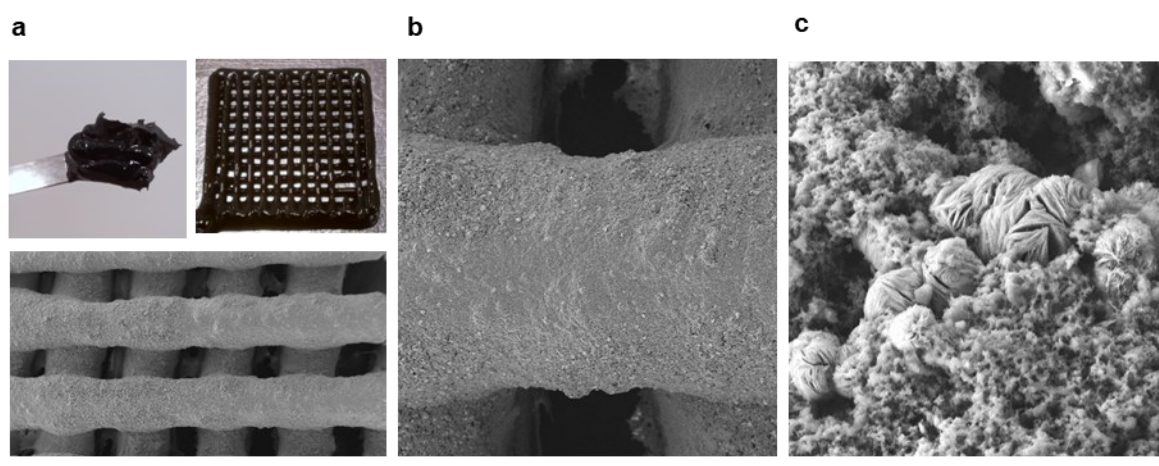


Figure 5.6: (a) VS₂ ink (top left) and 3D printed woodpile VS₂ electrode (top right), SEM imaging of the 3D printed woodpile VS₂ electrode (bottom), scale bar 500 μm; (b) SEM imaging of a printed strut making up the structure of the VS₂ electrodes (scale bar 100 μm); (c) high-magnification SEM image of the surface of the printed VS₂ electrode displaying microflowers surrounded by CB particles (scale bar 5 μm).

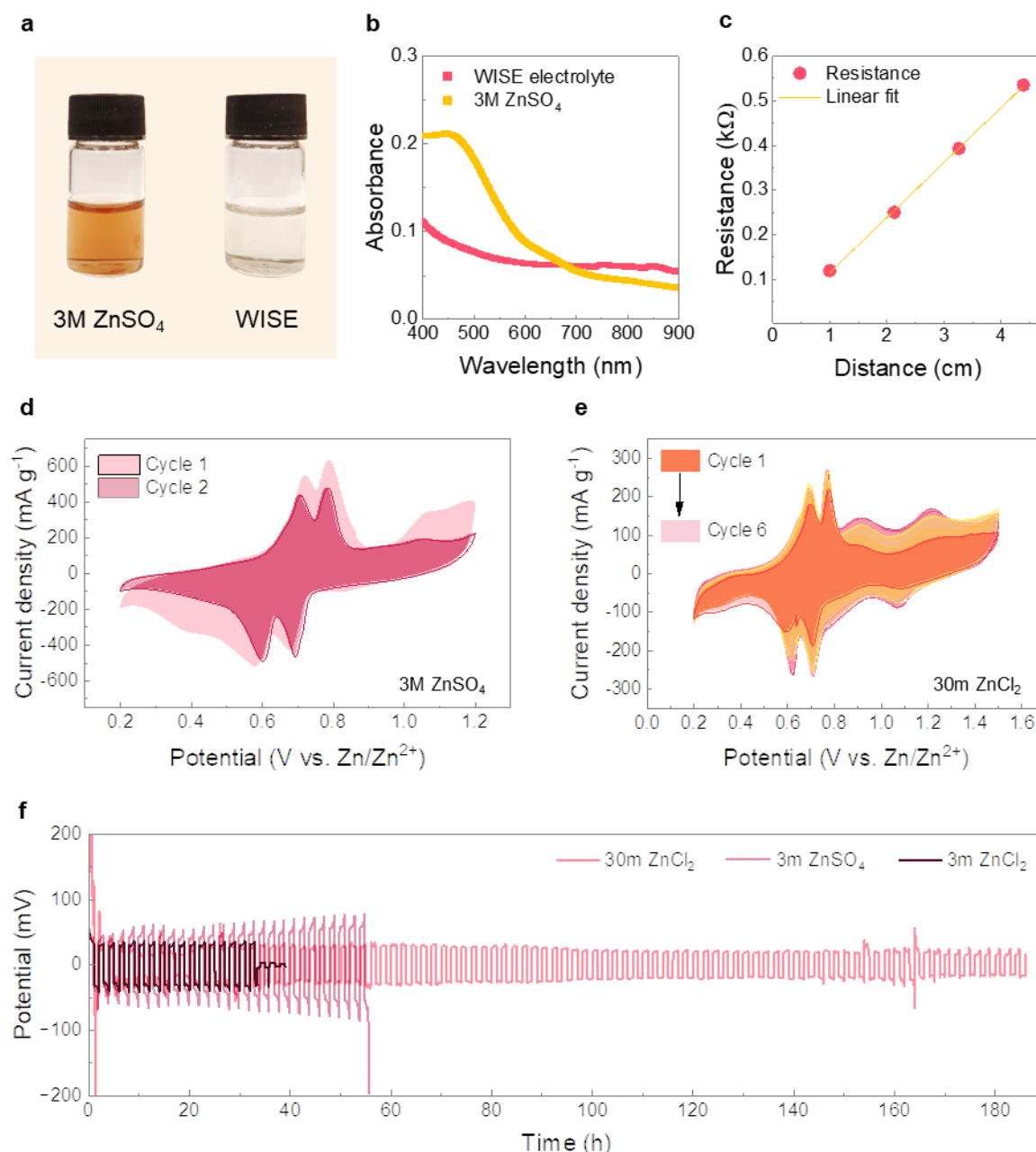


Figure 5.7: (a) Digital photograph of the ZnSO₄ and WISE electrolytes after electrochemical cycling of VS₂ electrodes; (b) UV-vis spectroscopy on the ZnSO₄ and WISE electrolytes after cycling; (c) resistance of the WISE electrolyte at increasing distance between the stainless steel electrodes, as determined from the high-frequency real intercept of impedance spectra; (d,e) cyclic voltammetry of the VS₂ electrodes vs. zinc foil in a 3M ZnSO₄ and WISE electrolyte; (f) plating-stripping tests on symmetric zinc foil cells in different electrolytes (10 mA cm⁻²).

in a highly concentrated (~ 30 m) solution of ZnCl₂. Vanadium disulfide gradually dissolves in the conventional 3M ZnSO₄ electrolyte, as evidenced by a change in the colour of the solution, which turns bright yellow during charge and discharge (Figure 5.7-a). The strong UV-vis absorption below ~ 550 nm arises from the presence of VO₂⁺ ions in the electrolyte, probably associated with the fast oxidation of vanadium disulfide in the acidic aqueous environment.³⁰⁴ On the contrary, the WISE

electrolyte does not show any notable absorption peak in the visible range, remaining clear during electrochemical cycling. The higher stability of VS_2 in the WISE electrolyte can be attributed to the low thermodynamic activity of water in the system, resulting from the absence of free (uncoordinated) water molecules.³⁰⁵ In particular, owing to the low molar ratio between H_2O and Zn^{2+} in the ZnCl_2 WISE (~ 1.8), not all zinc ions can form octahedral coordination complexes with water, resulting in a molten hydrate structure.^{45,306} The strong bonding between Zn^{2+} and H_2O prevents water molecules from reacting at the electrode interface, and hinders the formation of undesirable side products, stabilizing the active material.⁴⁵ However, WISE electrolytes typically present high viscosity, associated with the strong interaction between the charged species in the solution, which determines a lower ionic conductivity in comparison with conventional electrolytes.³⁰⁷ The conductivity of the WISE electrolyte was measured with blocking (non-faradaic) stainless steel electrodes in a symmetric cell configuration. The tests were performed at different electrode spacing to eliminate the contribution of contact resistance (Figure 5.7-c). The ionic conductivity of the WISE electrolyte ($\sim 0.37 \text{ S m}^{-1}$) is significantly lower than a conventional ZnSO_4 electrolyte ($\sim 6.3 \text{ S m}^{-1}$, Section 3) but it is in line with other water-in-salt electrolytes based on lithium and sodium ions ($\sim 0.1 - 1 \text{ S m}^{-1}$).³⁰⁷

The high concentration of ions in the WISE electrolyte can enhance the stability of both the VS_2 cathode, hindering the dissolution of vanadium, and of the metallic zinc anode, suppressing zinc corrosion and promoting a more uniform zinc plating.^{45,306} The performance of zinc anodes in the WISE electrolyte was investigated with plating-stripping tests in a symmetric cell configuration (Figure 5.7-f). Despite the lower ionic mobility and higher viscosity, the cell with the WISE electrolyte maintains a stable plating-stripping potential $\sim 30 \text{ mV}$ for more than 200 h at a high current density of 10 mA cm^{-2} . In contrast, the 3M ZnCl_2 cell experiences a short circuit after $\sim 34 \text{ h}$ of cycling, whereas the 3M ZnSO_4 cell presents a sudden overpotential increase after $\sim 56 \text{ h}$, probably caused by the formation of insulating species on the electrode surface (Figure 5.7-f). When tested in the WISE electrolyte, the VS_2 electrodes also show a more stable charge storage response, with a redox current progressively increasing during the first five activation cycles and then stabilizing (Figure 5.7-e). On the contrary, in the conventional ZnSO_4 electrolyte the current decreases during CV cycling, as a result of the dissolution of the active material from the electrode (Figure 5.7-d). The sharp redox peaks in the region $0.6 - 0.8 \text{ V vs. Zn/Zn}^{2+}$ can be attributed to the two-step intercalation of zinc ions into the layered structure of VS_2 , already observed in a conventional ZnSO_4 electrolyte⁴¹. However, the WISE electrolyte is stable in a larger electrochemical potential window than the conventional ZnSO_4 electrolyte ($1.3 \text{ V vs. } 1 \text{ V}$ for 3M ZnSO_4), providing access to additional redox peaks in the range $1 - 1.5 \text{ V vs. Zn/Zn}^{2+}$ (Figure 5.7-e). Even at slow scan rates (0.1 mV s^{-1}), these peaks appear significantly broader than the peaks associated with zinc intercalation, which indicates that they might originate from pseudocapacitive processes at the surface of the active material.³⁰⁸

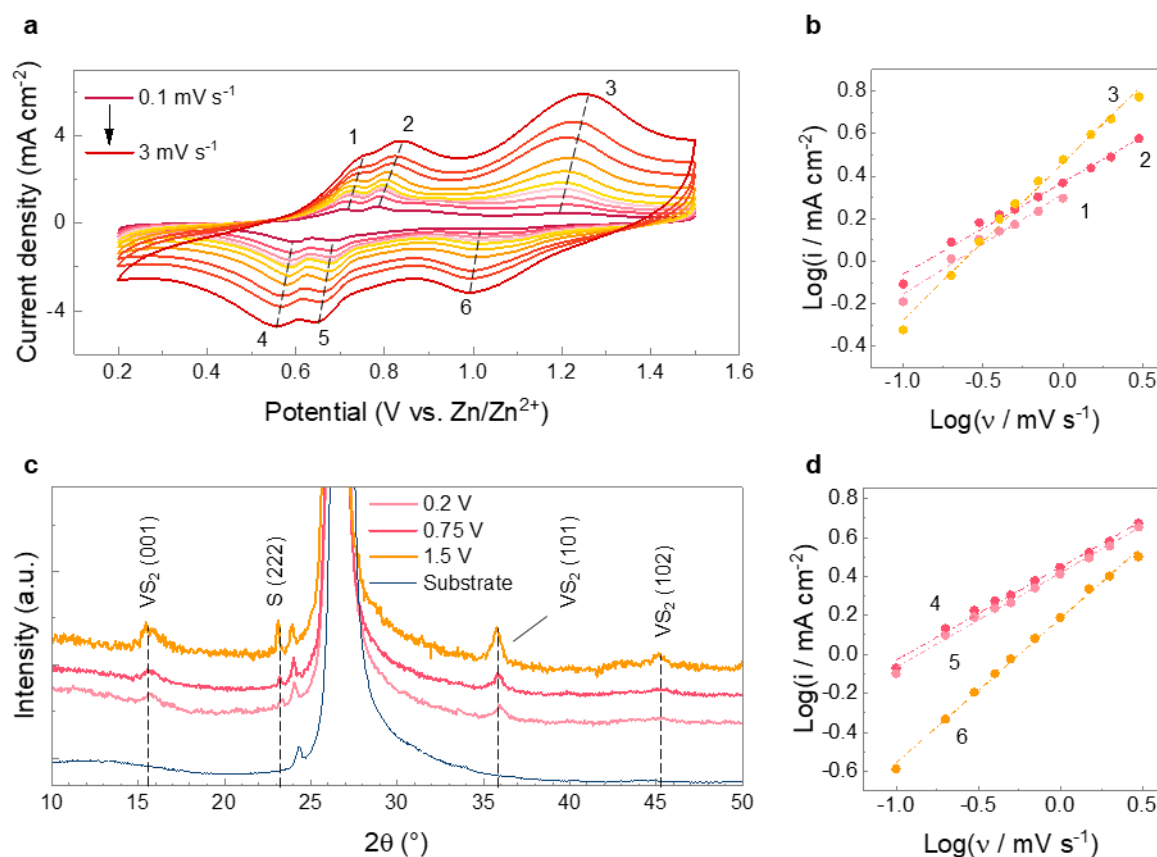


Figure 5.8: (a) Cyclic voltammetry on a VS_2 electrode in the WISE electrolyte at different scan rates; (b) power-law fitting for the oxidation peak current as a function of scan rate; (c) *ex-situ* X-ray diffraction on the VS_2 electrode charged to different potentials; (d) power law fitting for the reduction peak current as a function of scan rate.

The nature of the charge storage process for the VS_2 electrode in the WISE electrolyte was further investigated fitting the CV current response at different scan rates with a power law (Equation 2.23). While at lower scan rates the first two redox peaks (peaks 1 and 2 in Figure 5.8-a) are the most intense, at faster scan rates the redox peak in the range 1 – 1.5 V vs. Zn/Zn^{2+} (peak 3) become predominant. The peak current follows a power law dependency on the scan rate ($i = a v^b$, Figure 5.8-b,d) with a b exponent ~ 0.5 for the oxidation peaks 1 and 2 (and the corresponding reduction peaks 3 and 4) and ~ 0.75 for the oxidation peak 3 (and the corresponding reduction peak 6). This indicates that the charge storage process is diffusion-limited for the first two peaks, as expected for the intercalation of zinc ions in VS_2 , whereas it has a more capacitive nature (b closer to 1) for the high-potential peaks. The charge storage for peak 3 and 6 might be associated with the surface oxidation of VS_2 , as suggested by recent studies on VS_2/VO_x heterostructures.²⁹³ *Ex-situ* X-ray diffraction on the VS_2 electrodes at different states of charge does not show any variation in the VS_2 reflections, indicating that the bulk material is not completely converted into amorphous oxide upon charging to 1.5 V vs. Zn/Zn^{2+} . Previous *in-situ* studies have reported a shift in the (001)

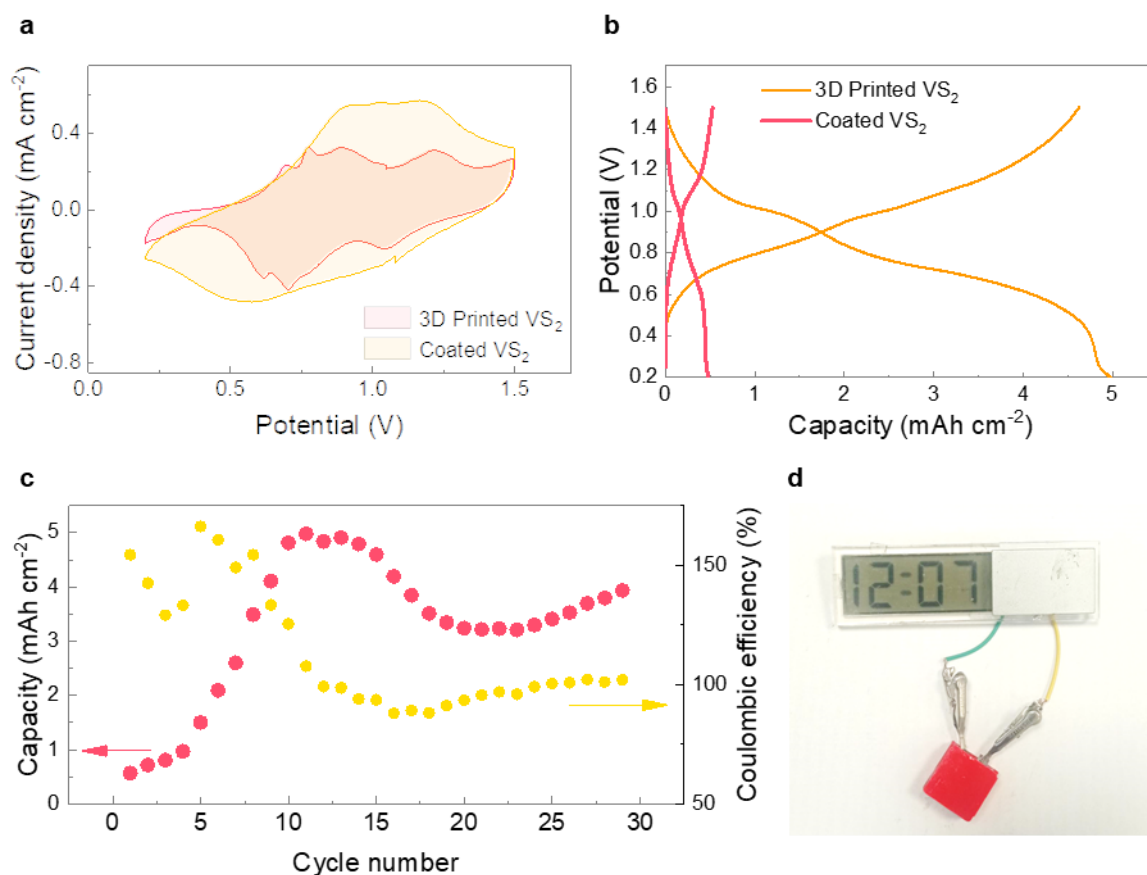


Figure 5.9: (a,b) Cyclic voltammetry (0.1 mV s^{-1}) and galvanostatic charge-discharge (0.2 mA cm^{-2}) of the 3D printed and tape-casted VS₂ electrodes in the WISE electrolyte; (c) capacity and coulombic efficiency as measured from GCD of the VS₂ cathodes in the WISE electrolyte; (d) digital photograph of the encapsulated battery powering a LCD clock.

reflection during charging, attributed to the reduction in the *c*-lattice parameter of VS₂ after zinc deintercalation.⁴⁰ However, a shift of the (001) peak cannot be resolved from *ex-situ* diffraction (Figure 5.8-c), probably owing to the relaxation of the material during sample preparation.³⁰⁹ An additional peak at $\sim 23^\circ$ appears when the material is charged to 0.2 V, and becomes significantly more intense upon charge to 1.5 V. This peak might be associated with the (222) reflection of elemental sulfur, which is formed during the surface oxidation of VS₂.

After an initial electrochemical activation, the 3D printed woodpile electrodes achieve a significantly higher areal capacity than conventional tape-casted electrodes ($\sim 4.98 \text{ mAh cm}^{-2}$ vs $\sim 0.48 \text{ mAh cm}^{-2}$, Figure 5.9-a,b). In particular, after encapsulation in a 3D printed PLA case, the VS₂ battery could power an LCD display (Figure 5.9-d). Nonetheless, the VS₂ electrodes require an initial electrochemical activation to achieve their highest capacity and they are not stable over repeated galvanostatic cycling. At a current density of 0.2 mA cm^{-2} , the cathodes keep activating for the first ~ 12 cycles, probably owing to the surface conversion of VS₂ to oxides (presenting higher charge storage capability) or to a better infiltration of the electrolyte inside the three-dimensional

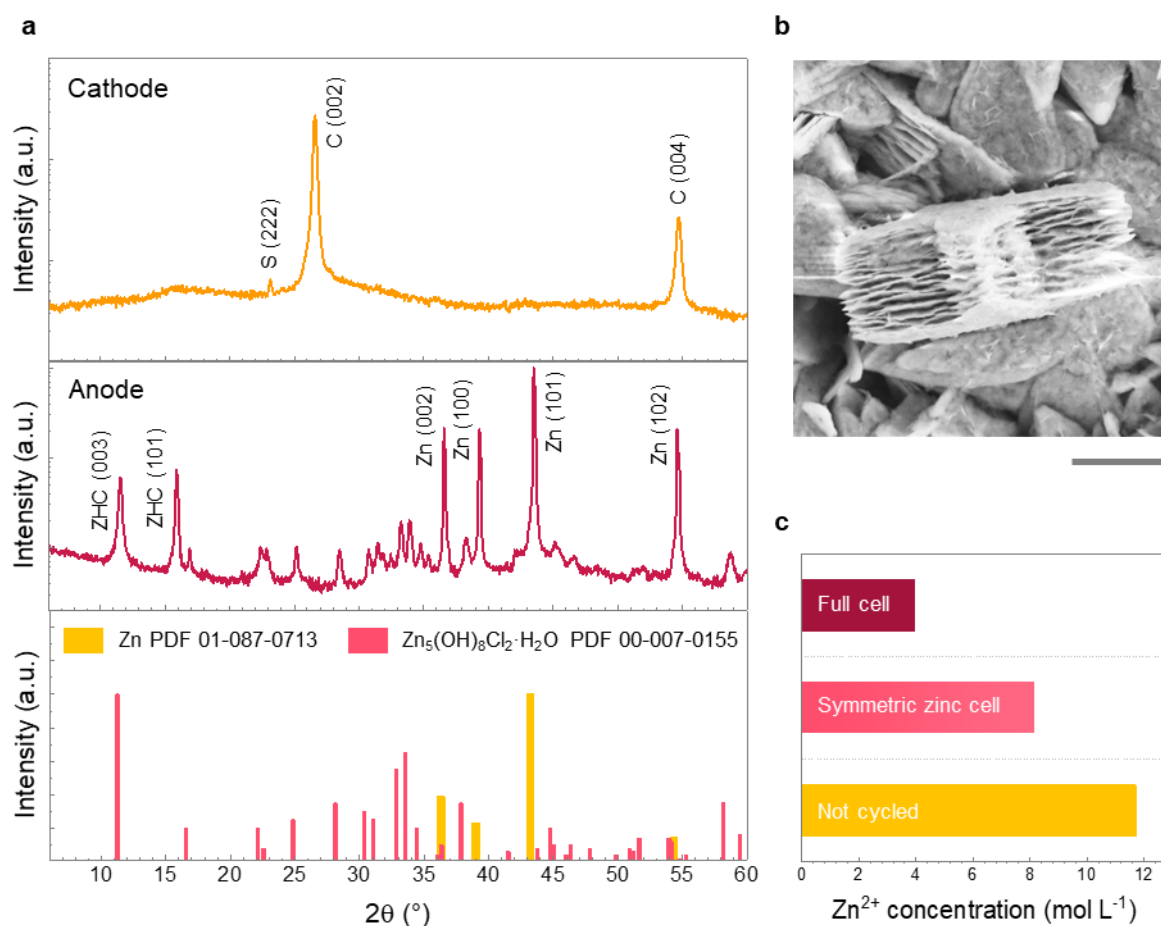


Figure 5.10: (a) XRD pattern on the cycled zinc anode (top), cycled VS₂ cathode (middle) and PDF reference patterns for Zn and Zn₅(OH)₈Cl₂·H₂O, a logarithmic scale was used to plot the experimental data to better visualize low intensity peaks; (b) SEM imaging of the Zn₅(OH)₈Cl₂·H₂O platelets growing on the surface of the anode during cycling (scale bar 5 μm); (c) concentration of zinc ions in the cycled electrolytes, determined with complexometric titration.

electrode. After a small interval in which the cathodes show a stable electrochemical response, their discharge capacity starts fading, dropping to $\sim 3.2 \text{ mAh cm}^{-2}$ after 22 cycles. Notably, during the activation process the coulombic efficiency is higher than 100%, suggesting that the increase in capacity is caused by a progressive conversion of the VS₂ microflowers, rather than an initial incomplete wetting of the electroactive material.

To better understand the causes of the capacity decrease after activation, *ex-situ* tests were performed on the cycled samples (Figure 5.10). The surface of the cycled anodes appears covered by hexagonal and star-shaped particles, made of exfoliated layers containing zinc, oxygen and chlorine (Figure 5.10-b). The peaks in the *ex-situ* XRD pattern of the anodes can be assigned to metallic zinc and to zinc hydroxychloride hydrate Zn₅(OH)₈Cl₂·H₂O (ZHC), which constitutes the hexagonal platelets on the surface of the cycled electrodes (Figure 5.10-a). The formation of ZHC platelets was unexpected, considering the ability of concentrated ZnCl₂ WISEs to prevent the growth of side products demonstrated in recent reports.⁴⁵ Notably, the formation of inert products containing dead

zinc might deplete the electrolyte of zinc ions, transforming the WISE electrolyte in a conventional ZnCl_2 electrolyte. The concentration of zinc ions in the electrolyte was measured before and after cycling with a complexometric titration technique, employing ethylenediaminetetraacetic acid (EDTA) as the ligand for Zn^{2+} . In symmetric-cell and full cell configuration, the concentration of zinc ions drops from $\sim 11.7 \text{ mol L}^{-1}$ to $\sim 8.2 \text{ mol L}^{-1}$ and $\sim 4 \text{ mol L}^{-1}$, respectively (Figure 5.10-c). The value obtained for the full cell represents an upper limit concentration for zinc ions, since vanadium ions, which can also be coordinated by EDTA, might also be present in the electrolyte. These results show that during electrochemical cycling, the concentration of the WISE electrolyte decreases, leading to conditions that are more favourable for VS_2 dissolution. Nonetheless, the concentration of zinc ions cannot only decrease as a consequence of the formation of $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$, since the formation of 1 mol of hydroxychloride requires 5 mol of zinc chloride and 8 mol of water. Other irreversible processes must happen in the system, *e.g.* the irreversible conversion of VS_2 into inert zinc-rich phases after zinc intercalation (as suggested by the discharge capacity, which is higher than the charge capacity in the first GCD cycles). *Post-mortem* XRD on the VS_2 cathodes

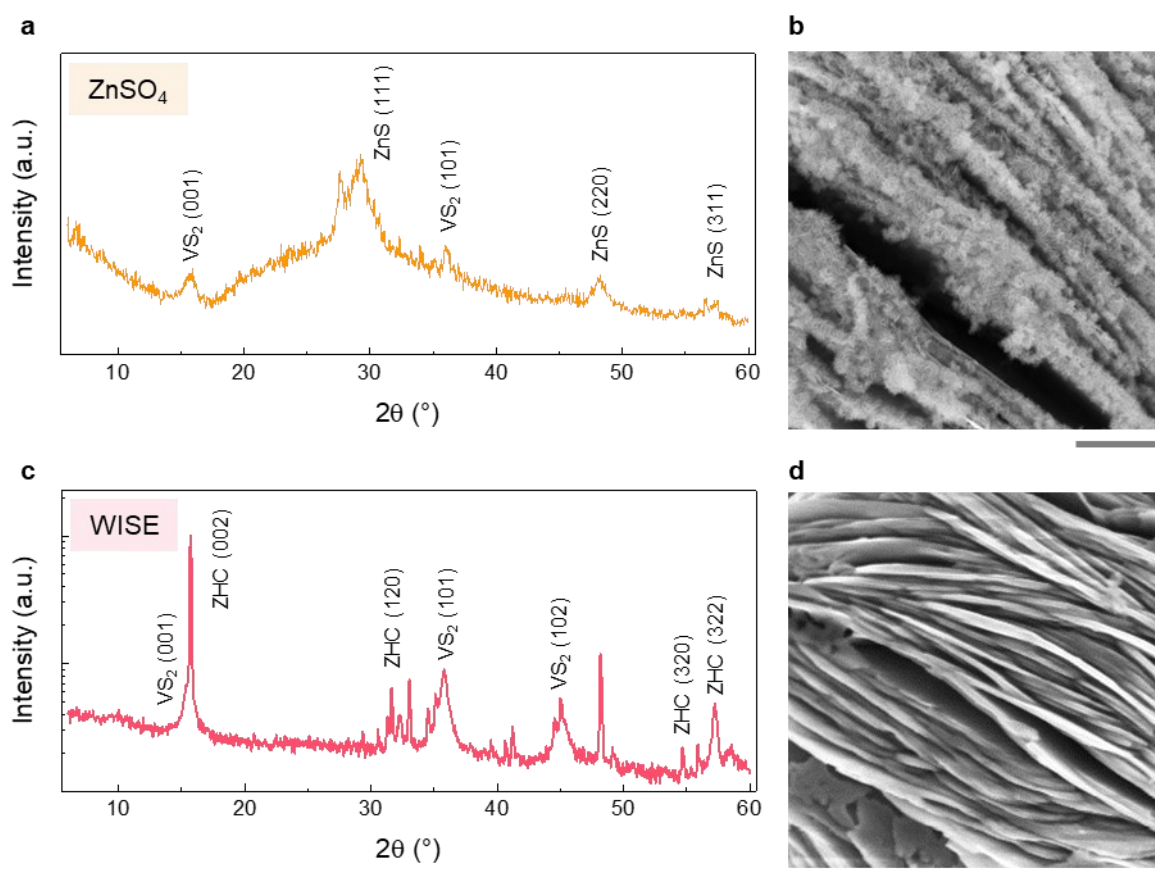


Figure 5.11: (a) XRD pattern of hydrothermal VS_2 soaked in 3M ZnSO_4 for 14 days, matching with VS_2 (PDF 00-036-1139) and ZnS (PDF 01-080-0020); (b) SEM image of the of hydrothermal VS_2 soaked in 3M ZnSO_4 for 14 days (scale bar 1 μm); (c) XRD pattern of hydrothermal VS_2 soaked in WISE for 14 days, matching with VS_2 (PDF 00-036-1139) and ZHC (PDF 00-045-0819); (d) SEM image of the of hydrothermal VS_2 soaked in WISE for 14 days (scale bar 1 μm).

shows only peaks associated with graphitic carbon (arising from carbon black and the graphite substrate), but no peaks associated with VS_2 , which suggests an amorphization of the material during cycling (Figure 5.10-a, top panel). The amorphization of VS_2 might be caused by oxidation in the acidic ZnCl_2 electrolyte, which becomes progressively less concentrated, and by the formation of amorphous phases upon zinc intercalation. The small peak at $\sim 23^\circ$ could arise from the formation of elemental sulfur during the oxidation of VS_2 , as already observed after a single charge cycle to 1.5 V.

These results indicate that VS_2 is not stable during electrochemical cycling, exhibiting irreversible phase conversions and unstable capacity. Recent studies have demonstrated that the intercalation capacity of VS_2 can be stabilized operating a controlled oxidation of the material surface, either with an electrochemical treatment or by soaking VS_2 in an aqueous solution.^{293,310} In particular, when soaked for several days in an aqueous solution, the surface of VS_2 nanosheets can be converted to oxides through a dissolution-oxidation mechanism.³¹⁰ The effect of prolonged soaking in different electrolytes was investigated for the hydrothermal VS_2 microflowers. In a conventional ZnSO_4 electrolyte, the surface of the VS_2 petals became rough and irregular after soaking, indicating the conversion of VS_2 to other phases (Figure 5.11-b). Two new broad peaks appear in the XRD

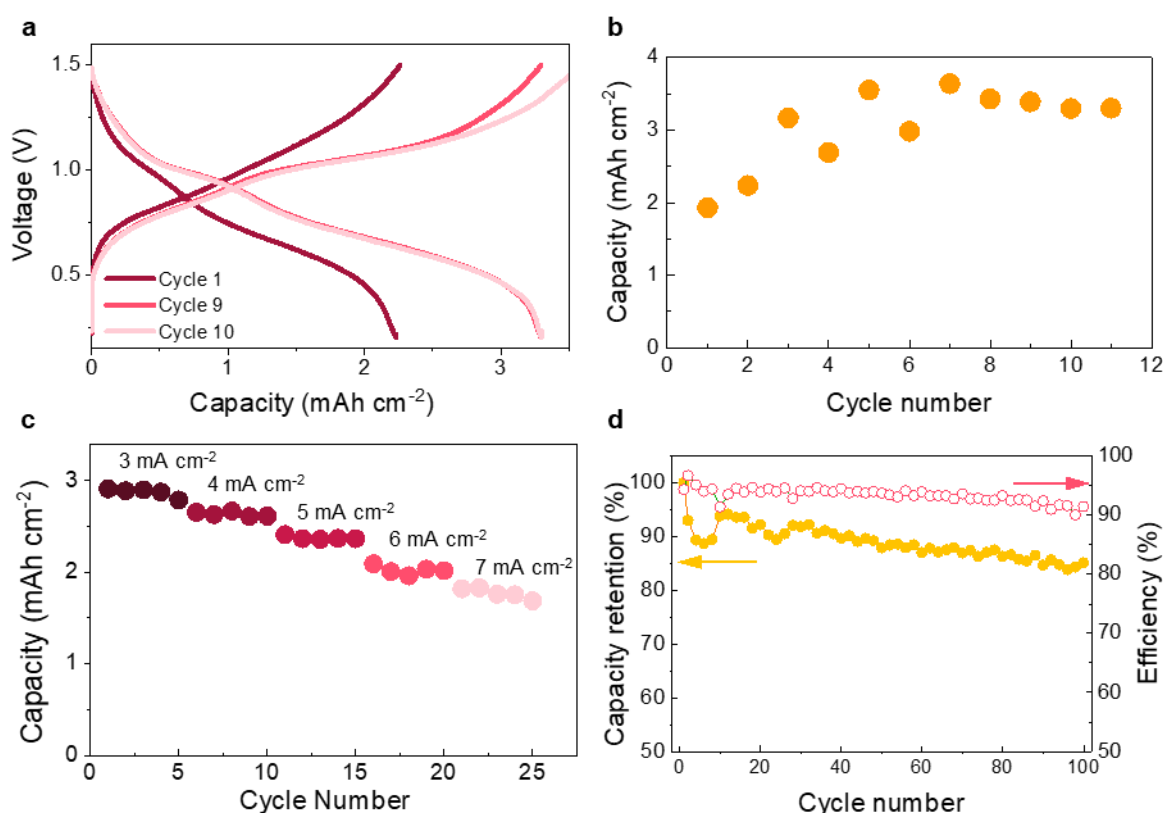


Figure 5.12: (a,b) Charge-discharge on 3D printed VS_2 cathodes after soaking in WISE for 14 days; (c) rate capability of the VS_2 cathodes after soaking in WISE for 14 days; (d) capacity retention and coulombic efficiency of the VS_2 cathodes after soaking in WISE for 14 days.

pattern of the material, at $\sim 29^\circ$ and $\sim 48^\circ$, which might be associated with the formation of micro-crystalline zinc sulfide (Figure 5.11-a). On the contrary, the petals of the VS_2 soaked in the WISE electrolyte remain smooth, and only the peaks of VS_2 and zinc hydroxychloride can be observed in XRD (Figure 5.11-c,d). The electrodes soaked in WISE for 14 days have a more stable electrochemical response (Figure 5.12). Although they still present a gradual activation during the first 8 cycles (from $\sim 1.9 \text{ mAh cm}^{-2}$ to $\sim 3.3 \text{ mAh cm}^{-2}$, Figure 5.12-a,b), the electrode capacity is then stable over repeated cycling, with a capacity retention $> 80\%$ after 100 cycles at 1 mA cm^{-2} (Figure 5.12-d). At a high current density of 7 mA cm^{-2} , the areal capacity remains higher than 1.7 mA cm^{-2} , indicating good rate capability (Figure 5.12-c).

2. Manganese oxide cathodes

Manganese oxide has been widely studied as a cathode material for rechargeable zinc ion batteries, owing to the natural abundance, low cost and safety of manganese.³¹¹ It is generally agreed that the charge storage process in manganese oxide cathodes follows an intercalation mechanism, with the co-insertion of Zn^{2+} and H^+ ions, often associated with a reversible phase conversion of the active material.^{38,311,312} Depending on the crystal phase of manganese oxide, the positive ions can be intercalated into the layered or tunnel structure of MnO_2 or react with MnO_2 to form new zinc-rich phases.^{312,313} Manganese oxide can be easily synthesized with scalable and water-based reaction methods, such as hydrothermal synthesis and electrodeposition from aqueous electrolytes.^{38,314} Here, the oxidative electrodeposition of amorphous manganese oxide to functionalize 3D printed graphene structures was investigated for ZIB cathodes.

2.1. Electrodeposition on printed scaffolds and physical characterization

The conductive scaffolds for the electrodeposition of manganese oxide were fabricated *via* DIW, using the graphene capillary ink presented in Chapter 3. This approach has the advantage to be easily adaptable to different high-performing cathode materials, e.g. V_2O_5 and several polymorphs of MnO_2 .³¹⁴⁻³¹⁷ Manganese oxide was grown on the conductive graphene scaffolds with an oxidative electrodeposition process from a solution of manganese(II) acetate. The electrodeposition of manganese oxide is a two-step process, leading to the formation of an MnOOH intermediate which is then oxidized to MnO_2 , as detailed in Chapter 2 (Equations 2.1-2.3). The potential for electrodeposition was optimized with linear sweep voltammetry (Figure 5.13-a) in a three-electrode configuration. The current response of the working electrode starts rapidly increasing ~ 0.5 V *vs.* Ag/AgCl , indicating the onset of Mn^{2+} oxidation at the printed carbon electrode. At ~ 0.8 V *vs.* Ag/AgCl the current starts decreasing as a result of the depletion of Mn^{2+} ions in the proximity of the electrode, whereas above ~ 1 V *vs.* Ag/AgCl the oxidation of water (oxygen evolution reaction, OER) becomes predominant, with a rapid increase in the anodic current. To evaluate the fraction of the anodic current which contributes to OER and to Mn^{2+} oxidation, respectively, the high-potential region of the voltammogram (> 1.5 V *vs.* Ag/AgCl) was fitted with the Butler-Volmer equation, assuming that the contribution of Mn^{2+} oxidation is negligible in this region (Figure 5.13-a). Around 0.7 V *vs.* Ag/AgCl , most of the anodic current goes into the oxidation of manganese ions (shaded areas in Figure 5.13-a), with only $\sim 5\%$ of the total current contributing to OER; thus this potential was chosen for the electrodeposition of manganese oxide.

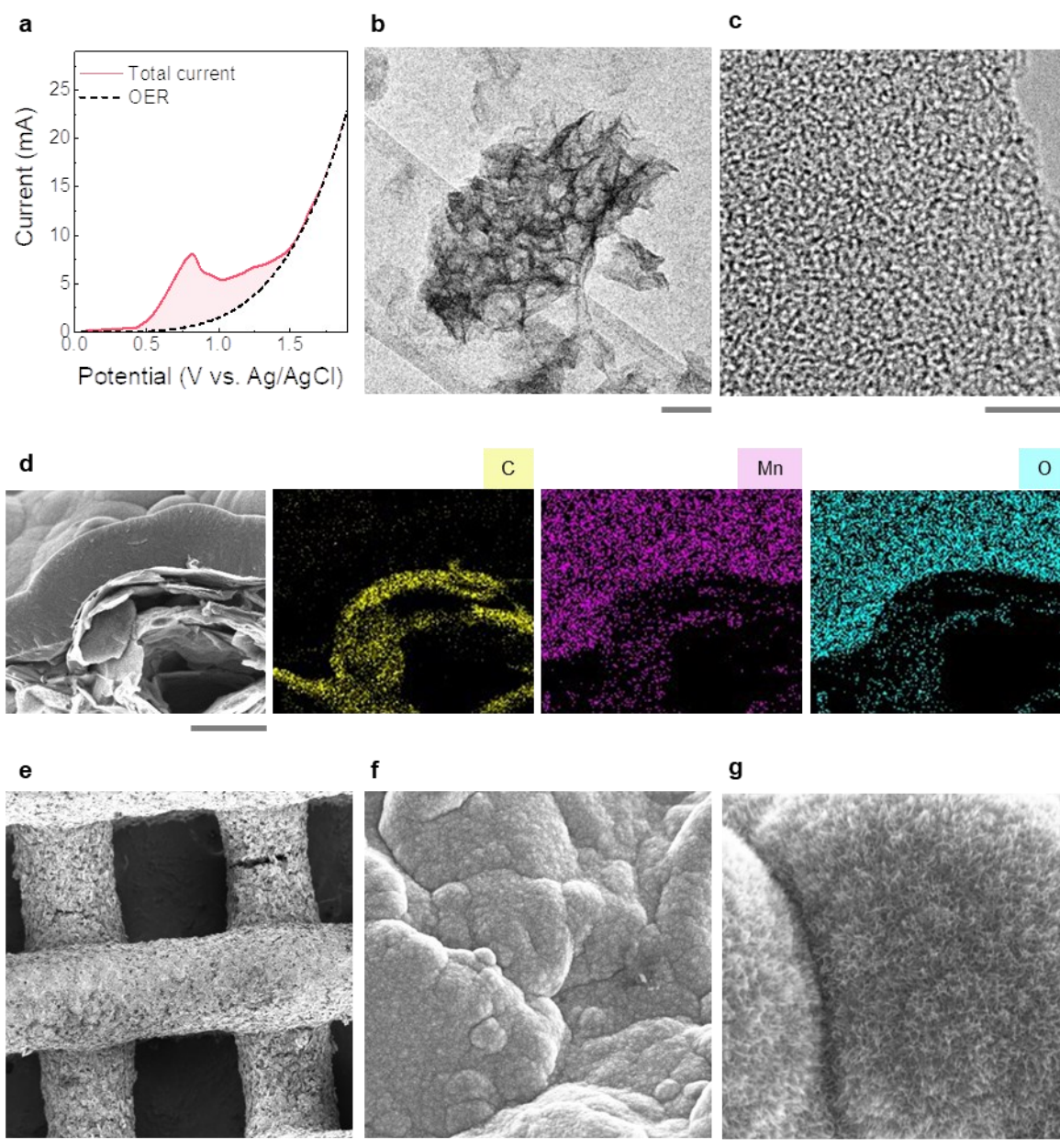


Figure 5.13: (a) Linear sweep voltammetry on a graphene electrode in 0.1 M $\text{Mn}(\text{CH}_3\text{COO})_2$ and 0.1 M Na_2SO_4 solution; (b,c) TEM and HR-TEM on the manganese oxide sheets grown on graphite nanoplatelets (scale bars 50 nm and 5 nm, respectively); (d) SEM cross-sectional image showing a thick layer of manganese oxide growing on the external surface of a graphene electrode, and corresponding EDS mapping (scale bar 5 μm); (e-g) SEM imaging on the external surface of a 3D printed graphene electrode after functionalization with manganese oxide (scale bars 500 μm, 5 μm and 1 μm, respectively).

The electrodeposited manganese oxide forms aggregated nanosheets ~ 100 nm in size on the surface of the graphene platelets, as shown by TEM imaging (Figure 5.13-b). The nanosheets are completely amorphous (Figure 5.13-c), similarly to recent reports on electrodeposited MnO_2 from manganese acetate electrolytes³¹⁴ The amorphous nanosheets form a continuous layer covering the external surface of the electrode, as evidenced by SEM imaging and EDS analysis (Figure 5.13-d,f,g). The coating follows the surface topography of the graphene nanoplatelets, presenting a

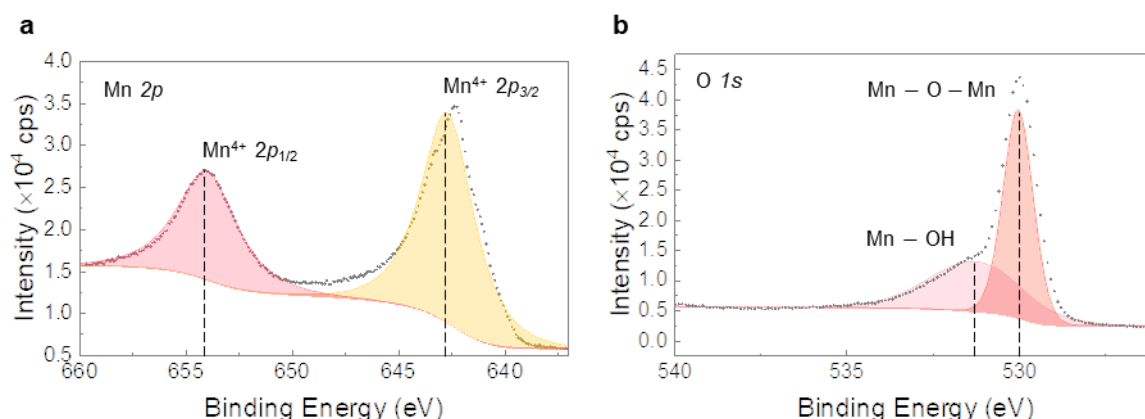


Figure 5.14: (a) High-resolution XPS spectrum of the Mn 2p core level electrons; (b) high-resolution XPS spectrum of the O 1s core level spectrum.

moosy appearance (Figure 5.13-g), which can enhance the electroactive surface area in contact with the electrolyte. The macroscopic architecture of the electrodes is not altered during the electrodeposition process (SEM image in Figure 5.13-e), owing to the mechanical stability of the graphene scaffolds.

The oxidation state of manganese in the amorphous manganese oxide was further investigated with XPS (Figure 5.14). The high resolution spectrum for Mn 2p confirms the presence of Mn^{4+} , as indicated by the binding energy of the Mn $2p_{3/2}$ peak in Figure 5.14-a (~ 642.6 eV).³¹⁸ The O 1s spectrum can be deconvoluted into two peaks, at ~ 530.0 eV and ~ 531.2 eV, which can be associated with the different chemical environment of the oxygen core level electrons in Mn-O-Mn and Mn-OH, respectively.³¹⁹ The hydroxyl functionalities are probably formed on the surface of manganese oxide in aqueous environment.

2.2. Electrochemical characterization

The electrochemical properties of the manganese oxide electrodes were tested in a 2 M ZnSO_4 electrolyte in a full cell configuration. The anodes were fabricated with DIW, using the zinc ink presented in Chapter 4, with a content of carbon black of 5%. Manganese sulfate (0.2 M) was added to the electrolyte to stabilize manganese oxide against dissolution. Recent studies have shown that, during discharge, manganese oxide is reduced to MnOOH , which disproportionates into MnO_2 and soluble Mn^{2+} ions, causing a net loss of active material.³²⁰ If additional manganese ions are present in the electrolyte, they can be oxidized on the surface of the cathode during charge, compensating for the loss of manganese oxide during the discharge process. The cyclic voltammogram of the printed ZIBs in 2 M $\text{ZnSO}_4 + 0.2$ M MnSO_4 exhibits a single oxidation peak ~ 1.58 V during the first cycle, which turns into two partially convoluted peaks at ~ 1.57 V and ~ 1.61 V in the following cycles (Figure 5.15-a). The single oxidation peak in the first cycle is probably associated with the

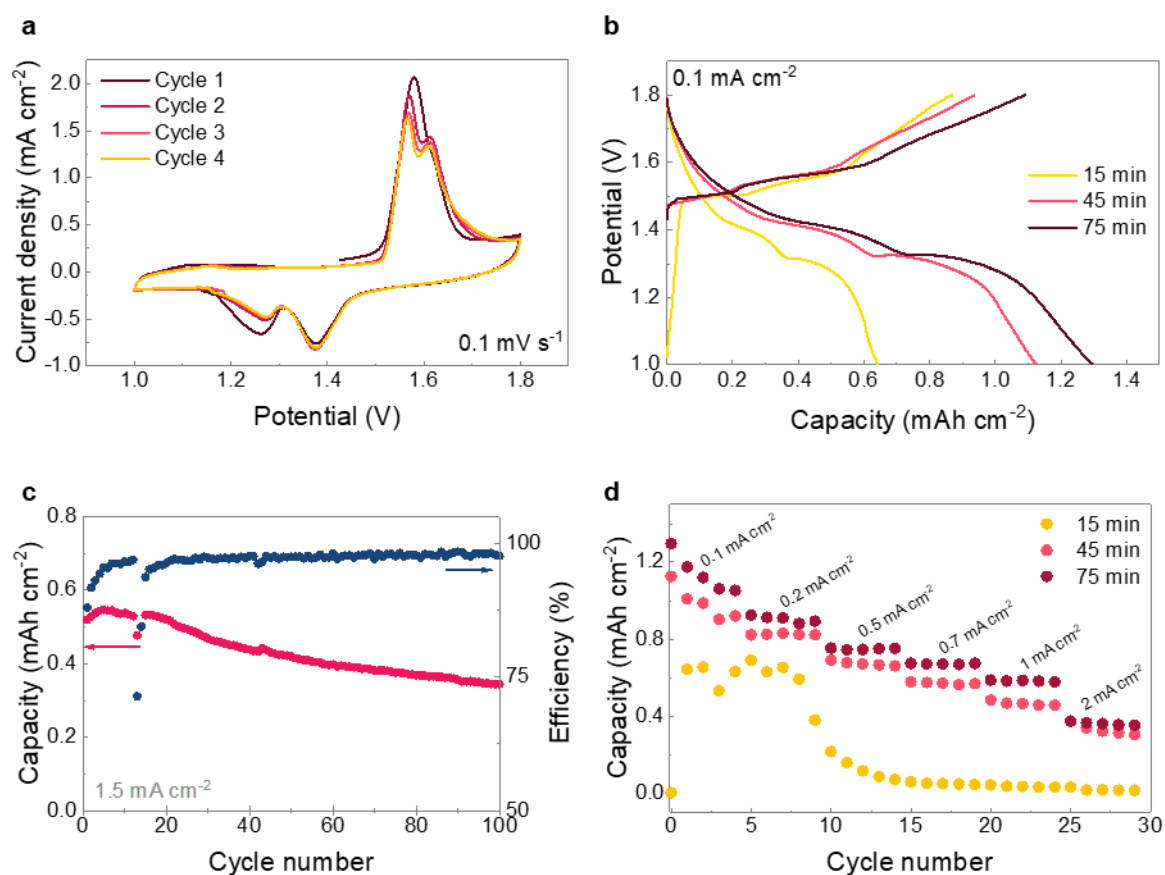


Figure 5.15: (a) Cyclic voltammogram on the electrodeposited MnO₂ cathodes in a full cell configuration vs. a 3D printed zinc anode; (b) comparison of the galvanostatic charge-discharge for electrodeposited MnO₂ cathodes at different electrodeposition times; (c) capacity retention and cycling stability of the electrodeposited MnO₂ cathode; (d) rate capability of the electrodeposited MnO₂ cathodes at different electrodeposition times.

initial oxidation of Mn²⁺ in the electrolyte, since no reduced phases are present in the positive electrode. The two stable redox peaks appearing from cycle 2 could arise from the conversion of the amorphous manganese oxide to ZnMn₂O₄, from the reaction with H⁺ to form MnOOH, or from a combined mechanism, as recently discussed in the literature.^{313,320,321} The areal capacity of the full cell increases with the electrodeposition time, as a result of the higher loading of electroactive material on the cathode scaffold. The cell with the highest mass loading of MnO_x (75 min electrodeposition at 0.7 V vs. Ag/AgCl) reaches an initial capacity of ~ 1.3 mAh cm⁻², as demonstrated by galvanostatic-charge discharge tests at 0.1 mA cm⁻² (Figure 5.15-b). The low initial coulombic efficiency in GCD tests is probably caused by the oxidation and subsequent deposition of Mn²⁺ (Figure 5.15-c); after the first cycles, the coulombic efficiency progressively increases reaching ~ 97% after 10 cycles, and remains approximately constant over ~ 100 cycles. The cell capacity remains stable during the first ~ 20 cycles, and then progressively decreases; however, it still exhibits a capacity retention ~ 66% after 100 cycles (Figure 5.15-c). The 75 min cell shows the best rate

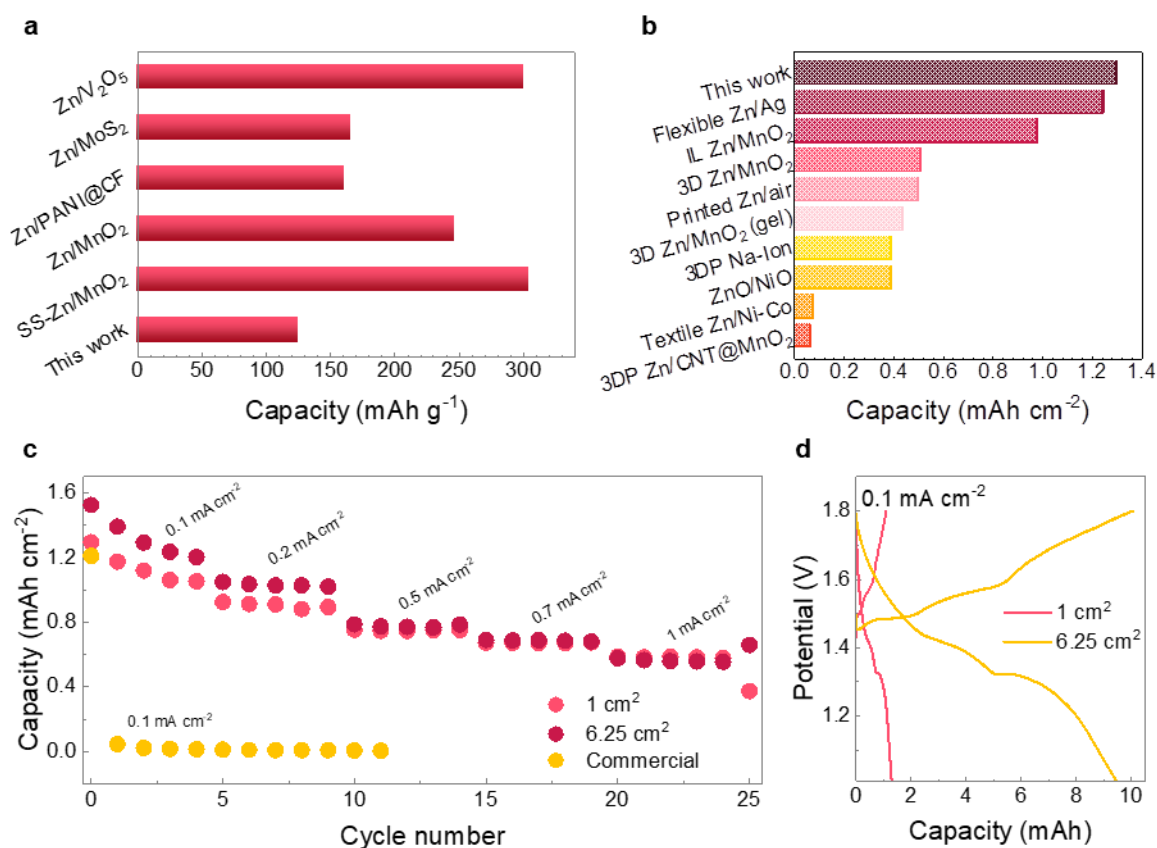


Figure 5.16: (a) Comparison of the gravimetry capacity of the printed MnO₂ cell with literature ZIBs (references in Appendix A2); (b) comparison of the areal capacity of the printed MnO₂ cell with literature ZIBs and other batteries (references in Appendix A2); (c) rate performance of the printed MnO₂ cells with different footprint areas and of a commercial ZIB; (d) galvanostatic-charge-discharge on the MnO₂ cells with different footprint areas.

performance, retaining the highest capacity when tested at increasing current densities in the range 0.1-2 mA cm⁻² (Figure 5.15-d).

The performance of the 75-min cell was compared to state-of-the-art aqueous devices, to assess the viability of employing printed electrodes to power portable electronics. The printed devices have a gravimetric capacity that is comparable with recently-reported zinc ion batteries fabricated with conventional tape-casting methods, although V₂O₅ and crystalline MnO₂ have higher gravimetry charge-storage capability (Figure 5.16-a). Nonetheless, the areal capacity of the printed cell surpasses previous reports on ZIBs, owing to the high areal mass loading of the electrodes (Figure 5.16-b). The performance of the printed battery was further compared to a commercial zinc battery, based on a MnO₂ cathode and a ZnCl₂ electrolyte, with a footprint area of 6.25 cm². The initial capacity of the commercial battery is slightly smaller than the printed ZIB (~ 1.2 mAh cm⁻² vs. ~ 1.3 mAh cm⁻²), but it drops to 0.04 mAh cm⁻² after the first discharge cycle (Figure 5.16-c). While the commercial ZIB can only be used as a primary battery, the printed ZIB retains a stable capacity over repeated discharge at increasing current density. Additionally, it was possible to further

enhance the capacity of the printed battery increasing its footprint area from 1 cm^{-2} to 6.25 cm^{-2} (*i.e.* the same footprint area as the commercial battery) and the diameter of the printed filaments from $410\text{ }\mu\text{m}$ to $800\text{ }\mu\text{m}$. The higher electrochemically active surface area for manganese electrodeposition resulted in an enhancement in the areal capacity ($\sim 1.5\text{ mAh cm}^{-2}$) and total capacity of the cell ($\sim 9.5\text{ mAh}$ *vs.* ~ 1.3 for the 1 cm^{-2} cell), Figure 5.16-d.

3. Colloidal zinc electrolyte

The vast majority of studies on DIW for energy devices has investigated the fabrication of EESD electrodes, overlooking the other cell components. In particular, printable electrolytes are needed to manufacturing full electrochemical cells *via* 3D printing, facilitating the integration into electronic systems. A notable exception is represented by the work of McOwen *et al.*,⁸⁵ who developed a printable electrolyte for lithium-ion batteries which can wet and conform to the electrode surface after deposition. The printability requirements for the electrolyte ink typically differ from the electrode inks, as anticipated in Chapter 1. In particular, while the electrode inks should form self-standing structures with no sagging and buckling, the electrolyte inks must be optimized to promote wetting and infiltration into the electrodes, in order to maximize the contact area with the electroactive material. Liquid electrolytes possess high ionic conductivities ($\sim 1\text{-}10\text{ S m}^{-1}$ for ZIB aqueous electrolytes) and ensure good wetting of the electrode surface;³²² nonetheless, they cannot be easily processed with DIW owing to their Newtonian rheology, and pose leakage risks during manufacturing and operation of the electrochemical cell. In contrast, gel electrolytes often exhibit a favourably high viscosity or yield-stress rheology and are less prone to leakage. Gel electrolytes typically rely on inert additives, *e.g.* polymers or ceramic oxides such as polyvinyl alcohol or TiO_2 , to achieve the desired rheological and mechanical properties.^{322,323} Here, the use of a colloidal suspension of fumed SiO_2 was investigated to formulate yield-stress electrolytes for printed ZIBs.

3.1. Flow behaviour and simulations

The electrolyte inks were formulated starting from a colloidal dispersion of fumed silica in water (5 wt%). The suspension is electrostatically stabilized by the negative surface charges of silica, arising from the hydrolysis of the silanol groups on the particle surface.³²⁴ Similar colloidal dispersions of alumina and titanates have been proposed as inks for the fabrication of functional ceramic components with DIW.^{118,325,326} Colloidal dispersions of charged particles can be gelated by tailoring the ionic strength or pH of the solution, in order to screen the electrostatic repulsion and promote the formation of attractive interparticle interactions. For example, in a recent study monovalent (Na^+) and divalent (Ba^{2+}) cations were used to gelate barium titanate suspensions for DIW processing.³²⁷ The divalent cations can screen the surface charge of ceramic particles much more efficiently, resulting in a gel with higher storage modulus and yield stress. Following a similar approach, zinc sulfate was used here to destabilize the colloidal suspension of silica particles, providing a functional gel that can be used as an electrolyte in ZIBs. After the addition of ZnSO_4 (2 M), the silica suspensions turns into a translucent gel, as demonstrated by vial inversion tests (Figure 5.17-a). The gel electrolyte behaves as a solid material with a predominantly elastic response at rest ($G'_{eq} \sim 5.2 \times 10^3\text{ Pa}$ vs. $G''_{eq} \sim 70\text{ Pa}$) as indicated by its oscillatory frequency response at low strain

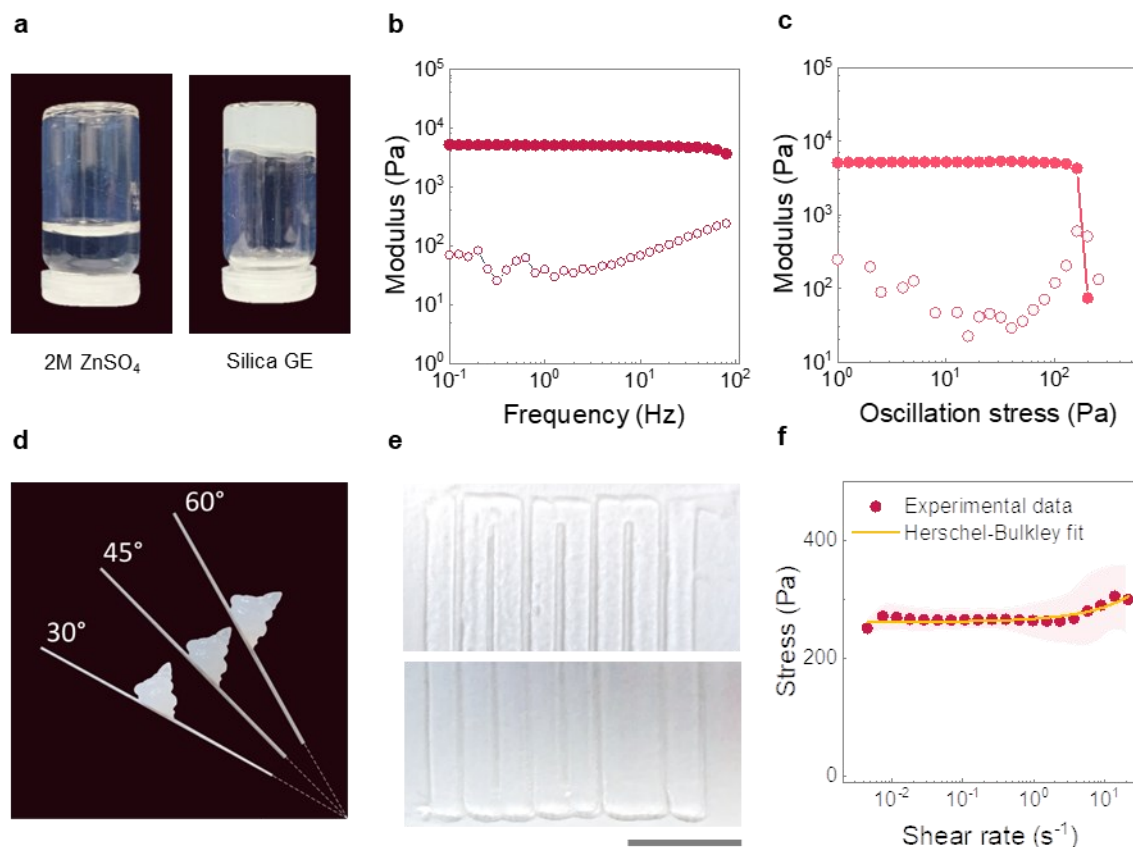


Figure 5.17: (a) Vial inversion tests on a 2 M ZnSO₄ solution before and after the addition of fumed silica (5 wt%); (b) oscillatory frequency sweep on the silica gel electrolyte within the LVE (G' close circles, G'' open circles); (c) oscillatory amplitude sweep on the silica gel electrolyte at an oscillation frequency of 1 Hz (G' close circles, G'' open circles); (d) self-standing gel electrolyte on a slate ad different angles; (e) 3D printed gel electrolyte, one printed layer (top), two printed layers (bottom), scale bar 1 cm; (f) flow ramp and Herschel-Bulkley fitting for the gel electrolyte.

amplitudes (Figure 5.17-b,d). The elastic response and the rest value of the storage modulus are preserved when a shear stress smaller than 180 Pa is applied to the ink, as shown in the amplitude sweep in Figure 5.17-c. When the shear stress reaches ~ 180 Pa, the ink suddenly transitions to a liquid state, and can thus be deposited by extrusion-based printing processes (Figure 5.17-e). The flow behaviour of the electrolyte was further investigated with rotational flow tests (Figure 5.17-f). The experimental data were fitted with a Herschel-Bulkley model, providing a flow index $n \sim 0.7$,

Table 5.2: Results of the Herschel-Bulkley fitting for the flow curve of the gel electrolyte.

Herschel-Bulkley model	τ_0 (Pa)	K (Pa s ⁿ)	n
$\tau = \tau_0 + K \dot{\gamma}^n$	262	5.4	0.7

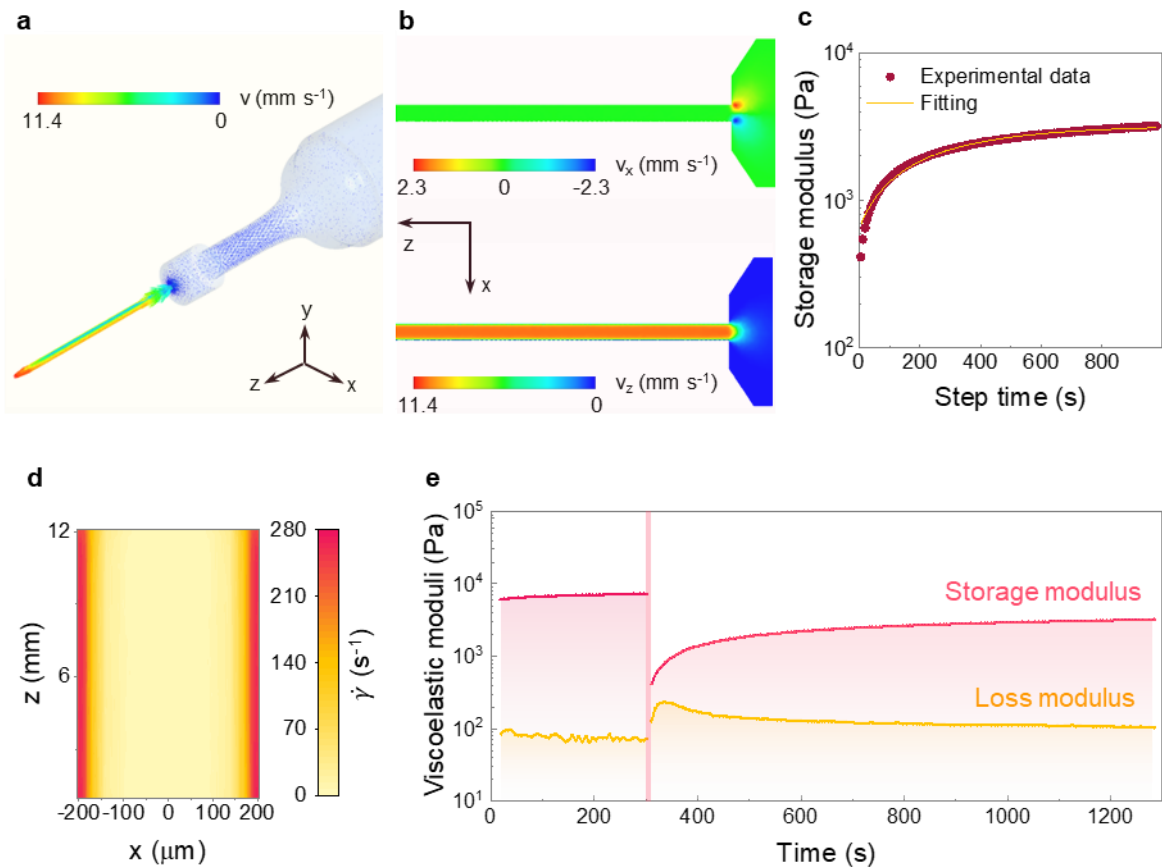


Figure 5.18: (a) Velocity profile of the gel electrolyte in the extrusion cartridge and nozzle determined with CFD simulations (extrusion speed 6 mm s^{-1}); (b) velocity profile (x - and z -component of the velocity vector) inside and in the proximity of the extrusion nozzle; (c) storage modulus recovery and exponential fitting of the 3ITTs in panel (e); (d) shear rate profile inside the printing nozzle; (e) 3ITTs on the gel electrolyte, after a continuous rotational shear at 280 s^{-1} (region highlighted in pink).

which is indicative of the shear thinning behaviour of the electrolyte (Table 5.2). In the case of attractive gels of colloidal particles, the shear thinning arises from the breakdown of particle aggregates under shear, with the formation of smaller flocs.¹⁶³

The Herschel-Bulkley parameters obtained from the fitting of the experimental flow curve were used to simulate the flow behaviour of the ink during the extrusion process. As discussed in Chapter 3, during the extrusion of a yield-stress ink only the outer region of the material is sheared, while the inner core moves forward by plug flow. Determining the relative size of the sheared region is fundamental to evaluate the viscoelastic properties of the ink after extrusion, especially for thixotropic inks with a slow recovery kinetic. As evidenced by the CFD simulation in Figure 5.18-a,b, the velocity profile of the ink inside the printing cartridge is negligible, and the ink experiences the highest shear inside the printing nozzle. The extrusion flow in the nozzle is predominantly a shear flow (*i.e.* the only non-zero component of velocity is v_z and it does not depend on z), which supports the use of shear rheometry to determine the printability of the ink. Elongational components v_x and

v_y are observed only immediately before the nozzle entrance, owing to a sudden change in the geometry of the extrusion channel at the interface between the cartridge and the nozzle (Figure 5.18-b). The shear rate $\dot{\gamma}$ was calculated from the velocity profile in the nozzle, as shown in Figure 5.18-d. The central region of the extrudate, presenting a diameter $\sim 200 \mu\text{m}$, experiences a small shear rate upon extrusion $< 10 \text{ s}^{-1}$. In contrast, $\dot{\gamma}$ reaches a maximum value of $\sim 280 \text{ s}^{-1}$ in the sheared region near the nozzle wall. The recovery of the ink viscoelastic properties after shear at 280 s^{-1} were investigated with three-interval thixotropy tests (3ITTs, Figure 5.18-e). The storage modulus does not instantly recover to the equilibrium value, presenting a value $\sim 400 \text{ Pa}$ immediately after shear. The storage modulus progressively recovers over time, following an exponential growth (Figure 5.18-c), with a time constant of $\sim 320 \text{ s}$. 3ITTs demonstrate that the outer region of the ink behaves as a mechanically-weak gel during the first minutes after extrusion. The lower storage modulus can promote the adhesion and infiltration of the ink into the printed electrodes; at the same time, the presence of an unyielded core can support the electrolyte structure preventing leakage outside of the footprint area of the device.

3.2. Electrochemical properties

The electrochemical properties of the gel electrolyte were tested in a symmetric cell, with blocking stainless steel electrodes (Figure 5.19-a). The electrochemical impedance curves progressively shift towards higher resistance when the distance between the electrodes is increased. The intercept with the real axis, representing the combined transport resistance of the electrolyte and the contact resistance at the clip interface, linearly increases with the electrode distance. The ionic conductivity of the electrolyte was calculated by a linear fitting of the resistance data (Figure 5.19-b), in order to eliminate the contribution of contact resistance. The electrolyte exhibit an ionic conductivity $\sim 6 \text{ S m}^{-1}$, significantly higher than other gel electrolytes reported for zinc ion batteries (Figure 5.19-c). Nonetheless, the low transference number of the silica gel electrolyte (~ 0.36) indicates that only a small fraction of the charge is carried by Zn^{2+} ions, since the structure of the colloidal gel is not able to immobilize the sulfate anions in the solution.³²⁸ In particular, silica particles lack positively-charged functional groups that can hinder the diffusion of anions, which are instead commonly present in zwitterionic or polysaccharide-based gel electrolytes.^{328–330} For its high conductivity and low transference number the silica gel electrolyte is more similar to conventional liquid electrolytes. However, when the gel electrolyte was tested in a symmetric cell configuration, it ensured a stable plating and stripping for more than $\sim 360 \text{ h}$, whereas the cell with a conventional 2 M zinc sulfate electrolyte died after $\sim 210 \text{ h}$ (Figure 5.19-e). This might be explained considering the lower pH of the gel electrolyte, which is unfavourable for the growth of zinc hydroxysulfates, and the mechanical hindrance offered by the gel electrolyte to the growth of dendrites between the electrodes. Additionally, the gel electrolyte exhibit a coulombic efficiency $\sim 97 \%$ at a plating-stripping current

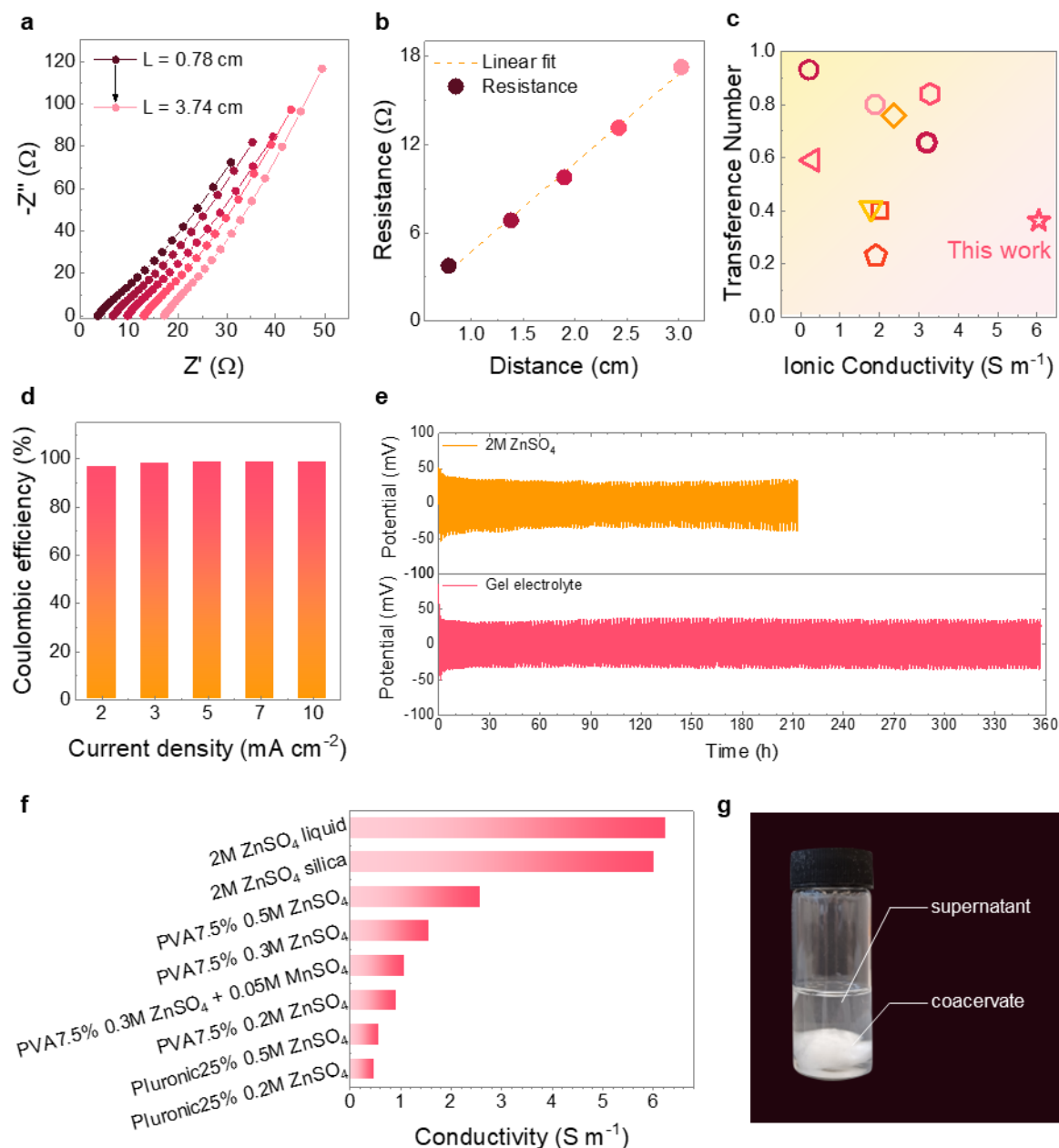


Figure 5.19: (a) Electrochemical impedance spectroscopy on the gel electrolyte at increasing distance between the stainless steel electrodes; (b) resistance of the gel electrolyte (determined from EIS) as a function of the distance between the stainless steel electrodes; (c) comparison of the transference number and ionic conductivity of the gel electrolyte with zinc-ion gel electrolytes recently reported in the literature (references in Appendix A2); (d) coulombic efficiency of the gel electrolyte at different current densities; (e) galvanostatic plating-stripping tests on a symmetric zinc foil cell in different electrolytes; (f) comparison of the ionic conductivity of the gel electrolyte with other zinc-ion gel electrolytes formulated using PVA and Pluronic F127 binders; (g) digital photograph of a PVA gel electrolyte at high concentration of zinc sulfate (2 M), showing the phase separation of the electrolyte and the formation of a coacervate.

of $2\ mA\ cm^{-2}$, which increases to $\sim 99\ %$ when a current of $10\ mA\ cm^{-2}$ is considered (Figure 5-19-d). When compared to electrolytes based on polymeric binders used for DIW, the silica electrolyte has the highest conductivity, close to the conductivity of a 2 M $ZnSO_4$ liquid electrolyte (Figure 5.19-f). Pluronic F127 and PVA cannot be used to formulate concentrated zinc electrolyte, since

the high ionic strength of Zn^{2+} in this systems hinders gelation, causing the formation of a inhomogeneous polymer coacervate (Figure 5.19-g).

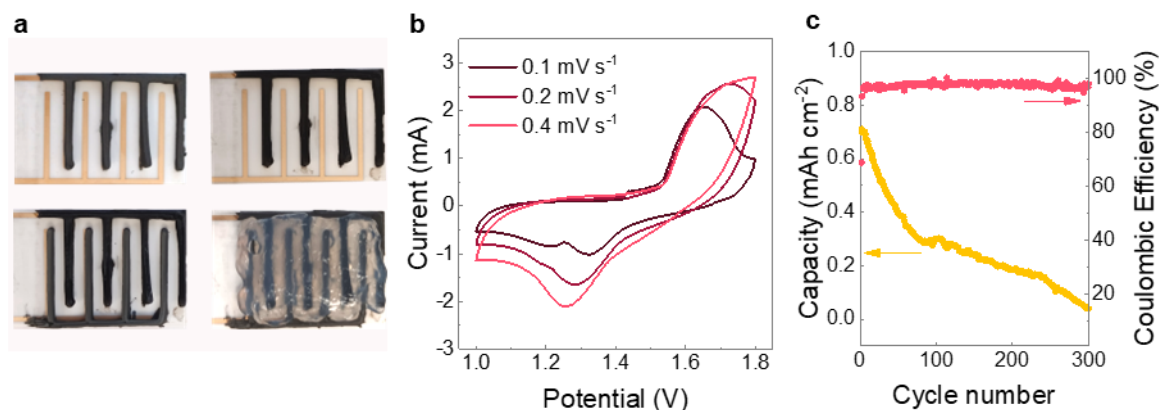


Figure 5.20: (a) Digital photographs showing the fabrication steps for the interdigitated battery: printing of the graphene electrode (top-left), electrodeposition of MnO₂ (top-right), printing of the zinc electrode (bottom-left), printing of the gel electrolyte (bottom right); (b) cyclic voltammogram on a fully-printed interdigitated battery encapsulated in epoxy resin; (c) capacity retention and coulombic efficiency of a fully printed interdigitated battery.

4. 3D printed interdigitated batteries

This section presents the integration of printed cathodes, anodes and electrolytes to demonstrate the fabrication of a fully printed battery. The cathode chosen for this purpose is based on electrodeposited manganese oxide. Although the vanadium disulfide cathodes presented in Section 1 achieved higher initial capacity, the need for organic solvents during processing makes them less appealing for aqueous devices. Additionally, vanadium has a higher specific cost and lower safety than manganese, which complicates the application of vanadium cathodes in wearable devices. The zinc anodes are printed using the zinc ink (with 5 wt% carbon black) discussed in Chapter 4. The research presented in this section is under consideration for intellectual property protection.

The fully printed batteries were fabricated printing interdigitated zinc and graphene electrodes onto a pre-patterned gold current collector (Figure 5.20-a). After electrodeposition and drying, the silica gel electrolyte was printed in the gaps between the electrodes and the cell was encapsulated in epoxy resin. The cyclic voltammogram of the printed cell exhibits similar peaks as the woodpile electrode tested in a conventional electrolyte (Section 2). However, the two oxidation peaks are completely convoluted in a broad peak ~ 1.65 V, which progressively shifts towards higher potentials when the scan rate is increased (Figure 5.20-b), owing to the high contact resistance of the system. The fully printed battery delivers a capacity of 0.7 mAh at a current density of 2.25 mA. However, the capacity rapidly fades during the first 100 cycles, despite presenting a high coulombic efficiency ($\sim 98\%$).

The possibility to connect two printed batteries in series to power a commercial Bluetooth proximity sensor was further demonstrated (Figure 5.21-a). The series of the two cells operates in a

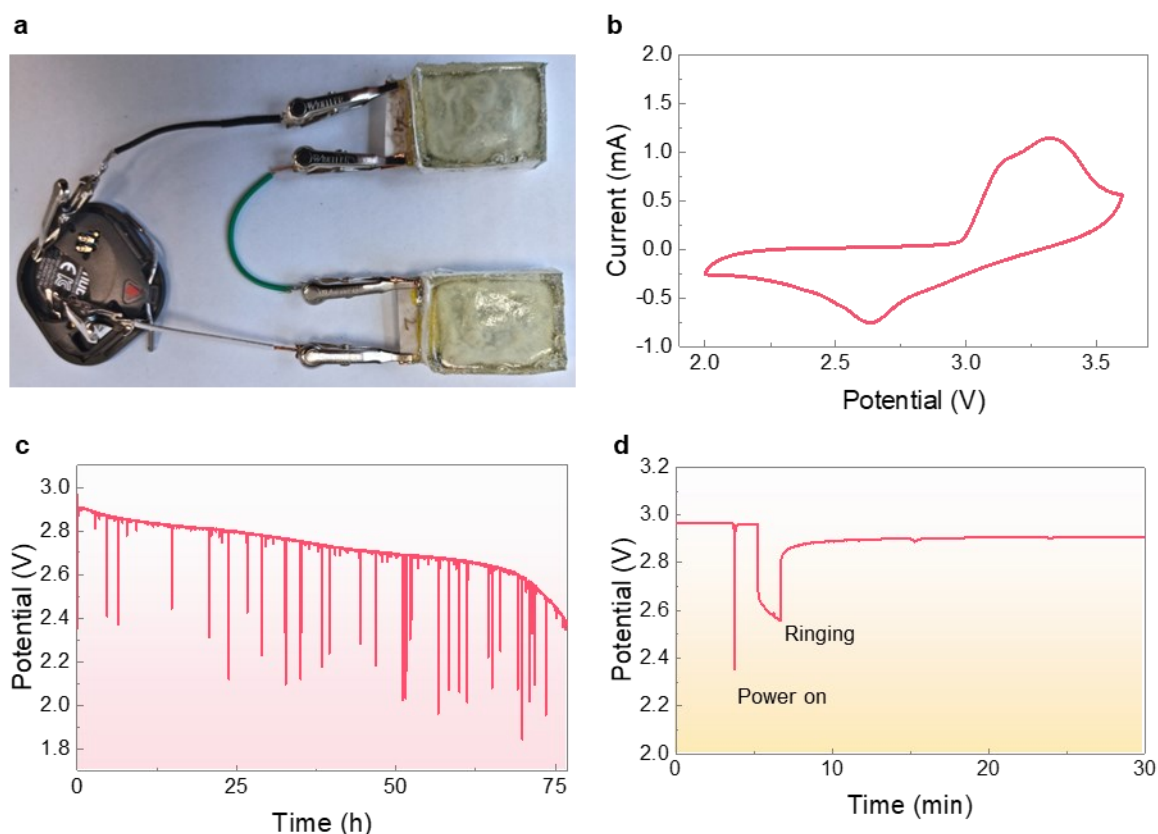


Figure 5.21: (a) Digital photograph of two encapsulated interdigitated batteries connected to a Bluetooth proximity sensor; (b) cyclic voltammogram on the series of two interdigitated batteries; (c,d) potential of the series of two interdigitated batteries connected to the Bluetooth sensor as a function of the operation time.

potential window 2-3.6 V (Figure 5.21-b), and can thus be used as a replacement for conventional lithium-ion batteries (nominal voltage ~ 3.6 V). The voltage drop of the battery was monitored during operation (Figure 5.21-c,d), demonstrating a continuous operating time of > 75 h. This life time is significantly lower than commercial lithium ion batteries, presenting a discharge time of several months. Nonetheless, compared to commercial LIBs, the fully-printed ZIB presented here has a customizable design, higher safety and easier disposal at the end of its lifecycle.

5. Conclusions

The fabrication of energy storage devices entirely through a 3D printing process would enable direct integration into portable electronic systems, reducing the manufacturing costs and processing time. This chapter presented the fabrication of fully-printed zinc-ion batteries *via* DIW and investigated their electrochemical performance. Firstly, printable cathodes based on vanadium disulfide and manganese oxide were developed. A non-aqueous ink was necessary for the processing of VS₂ electrodes, containing PVDF as the binder. The lack of specific interactions between PVDF and the active material, alongside the chemical and thermal stability of the polymer, makes this ink formulation easily adaptable to other cathode materials. Additionally, the ink formulation proposed here is safer and more sustainable than inks based on NMP, owing to the choice of DMSO as the dispersing solvent. Nonetheless, the polymeric binder is not capable of preventing the dissolution of VS₂, and the capacity retention and rate capability can only be stabilized inducing the controlled growth of an oxide layer on the surface of the active material. In contrast, the cathodes based on manganese oxide present a more stable cycling behaviour, and they can be manufacturing through a completely water-based process. In order to assemble fully-printed devices, a gel electrolyte, presenting an ionic conductivity similar to liquid electrolytes, was developed. The gel electrolyte can be process with DIW, and, owing to its thixotropic rheology, it is able to wet the electrodes after extrusion and prevent leakage during processing and operation.

The fully-printed batteries consisting of interdigitated zinc anodes, manganese oxide cathodes and a silica gel electrolyte could be used to power a Bluetooth proximity sensor for > 75 h of continuous operation. Even though this value lags behind the discharge life of commercial lithium-ion batteries, the ZIB has the advantage of safe and abundant active materials, simpler end-of-life disposal and customizable design.

Chapter 6

Conclusions

1. Concluding remarks

The fabrication of aqueous energy storage devices with innovative manufacturing methods, such as 3D printing, holds significant promise for the future development of portable and wearable electronics. Among 3D printing methods, Direct Ink Writing can address the environmental issues associated with conventional manufacturing processes, while simultaneously enhancing the design flexibility, energy density and rate performance of aqueous EESDs.

The aim of this work was to demonstrate the potential of DIW for the fabrication of aqueous supercapacitors, hybrid capacitors and batteries. In particular, we proposed new ink formulations and assessed their suitability for EESDs with customized design and satisfactory electrochemical figures of merit. We started by validating the use of highly-concentrated graphene and graphene/CNTs aqueous suspensions as inks for the fabrication of supercapacitor electrodes, which do not require post-printing reduction through chemical processes or annealing at prohibitively high temperatures. We demonstrated that the graphene electrodes are also suitable for the electrodeposition of manganese oxide, to obtain customizable cathodes for ZIBs. We then proposed novel water-based ink formulations for zinc anodes based on PVA and carbon black. The rheological characterization carried out on these inks substantiated their printability for Direct Ink Writing, enabling the manufacturing of electrodes with complex geometry and superior mechanical stability. We demonstrated that, unlike PVA, a PEDOT:PSS gel cannot serve the role of binder and rheology modifier for printable zinc inks, owing to the irreversible microstructural transformation under shear, which impedes the smooth extrusion of self-supported filaments. However, the concentration of the PEDOT:PSS binder in these inks was relatively low (~ 1.3 wt%). Recent studies suggest that higher concentration of PEDOT:PSS (> 5 wt%) can provide gels with better printability;^{135,136} therefore, the investigation of highly-concentrated PEDOT:PSS inks could be a promising route to overcome the printability issues highlighted in this work. Highly-concentrated PEDOT:PSS suspensions can improve the homogeneity of the ink, providing a more stable gel matrix for the extrusion process; however, the higher cost of the ink should also be considered, and justified in light of the electrochemical performance of the printed devices.

We also successfully developed a printable gel electrolyte for ZIBs with an ionic conductivity close to liquid electrolytes, and a favourable rheological response for electrode wetting. A key advantage of the inks demonstrated lies in the use of water as the dispersing solvent, representing a notable departure from previous reports on 3D-printed ZIB electrodes based on NMP. All the electroactive materials could be processed using aqueous binders except for VS_2 . We successfully formulated an ink containing chemically-inert PVDF in DMSO for the printing of VS_2 electrodes, highlighting the safety benefits of DMSO when compared to other polar aprotic solvents.

The presence of a conductive phase inside EESD electrodes is fundamental to achieve high active material utilization and retain good performance at high discharge currents and over repeated cycling. As a consequence, the zinc and vanadium inks developed in this work required the addition of carbon black, whereas the graphene ink and MnO_2 electrodes could rely on the superior electrical conductivity of graphene nanoplatelets. It would be important to set a conductivity target to use as a benchmark in the formulation and optimization of inks for EESD electrodes. Nonetheless, setting a specific target value of conductivity for an electrode is extremely challenging, since the optimal conductivity range depends on the maximum discharge rate required by the application and on the geometry, porosity and microstructure (size and distribution of the active material particles) of the electrode. An initial guideline for the optimization of the electrode conductivity could be provided by state-of-the-art cathodes for lithium-ion batteries (we do not consider anodes since they are usually made of highly conductive graphite, less affected by conductivity issues). Lithium nickel manganese cobalt oxide (NMC) electrodes typically present a conductivity $< 100 \text{ S m}^{-1}$,^{331,332} significantly lower than the conductivity of the electrodes presented here. Nonetheless, the thin tape-casted NMC cathodes reported in literature are very different electrochemical systems compared to the 3D electrodes discussed in this work. In particular, 3D woodpile electrodes are expected to require higher conductivities, since electrons have to travel paths longer than 1 mm (depending on the electrode thickness), compared to $\sim 100 \mu\text{m}$ in thin film electrodes. In contrast, lower values of conductivity might be satisfactory for interdigitated electrodes, since the distance between the active material and current collector can be smaller than woodpile devices. Only rate capability testing and impedance spectroscopy can confirm whether the electrode conductivity is sufficient for the application chosen, highlighting charge transfer limitations associated with electronic transport.

In this work, the rate capability, charge transfer kinetic and superior energy and power density of the 3D printed devices, alongside the degradation and ageing mechanisms occurring inside the electrodes and electrolyte, was unveiled with a combination of physical and electrochemical characterization tools. We demonstrated that compact electrodes made of graphene exhibit significant irreversible ohmic loss in comparison to 3D printed woodpile structures with similar aspect ratio. Our experiments also confirmed that the vertical thickness of graphene woodpile electrodes can be increased up to 6 layers without manifesting any notable hindrance to charge transport, allowing for printed supercapacitors with competitive areal energy and power densities. The addition of

carbon nanotubes to the graphene electrodes made it possible to increase the electrode thickness to 12 layers, delaying the decline in the gravimetric capacity and coulombic efficiency. The excellent areal and energy density exhibited by the graphene and graphene/CNTs electrodes are mainly a consequence of the use of graphene rather than reduced graphene oxide, providing high electron conductivity, and of the high mass loading and 3D architecture of the electrodes. In this work, we mainly focussed on the optimization of the electrode thickness to achieve the highest areal energy density, power density and rate capability, but we did not perform a systematic study on the optimization of the overall design of the electrodes, which could further enhance the areal electrochemical performance. In particular, the capacitance of the symmetric devices could be further enhanced by optimizing the mass and design of the positive and negative electrode independently, to account for the different surface area accessible to the electrolyte anions and cations. When gravimetric properties are considered, the GNP electrodes are outperformed by carbonaceous materials with higher specific surface area, such as carbon aerogels and activated carbon, presenting higher gravimetric capacitance and specific energy. This is a crucial point to consider when assessing the use of GNP electrodes for real applications, since low specific weight could be a more appealing figure of merit than high areal energy for certain markets.

Through microstructural characterization and CFD simulations on the graphene electrodes, we also established a correlation between the flow history experienced by the ink during the manufacturing process and the inner microstructure of the electrodes, providing evidence that shear forces can align the graphene platelets in the extruded filaments. Additionally, our results indicate that the three-dimensional structuring of zinc anodes enhances their cycle life. In particular, the 3D-printed zinc electrodes proposed here exhibit lower plating-stripping overpotential and higher coulombic efficiency than conventional zinc foil electrodes, as a result of the lower local current density on the surface of the electrodes. Even though *post-mortem* characterization shows the formation of zinc hydroxysulfates during operation, we argued that the porous hydroxysulfate layer does not block the charge transfer processes inside the printed structures, resulting in long cycling stability. For VS_2 electrodes, we showed that a water-in-salt electrolyte can enhance the cycling life and stability above conventional ZnSO_4 electrolytes, hindering the dissolution of vanadium. Nonetheless, we demonstrated that even in a water-in-salt electrolyte, the stability of 3D printed VS_2 electrode is insufficient for application in aqueous batteries, in the absence of a preliminary stabilization involving a partial conversion of the active material.

I believe that, among the chemistries developed in this work, the printed zinc hybrid capacitors and zinc-manganese oxide batteries hold great promise, considering the low cost and safety of the raw materials, the simplicity of the ink formulation and printing process and the good electrochemical performance achieved. On the other hand, vanadium disulfide is significantly more toxic and expensive compared to the other active materials presented in this work, and it is highly unstable in aqueous environment. The high conductivity and large inter-layer spacing of VS_2 can probably be

better exploited in non-aqueous systems, while vanadium oxides (primarily V_2O_5) would be more suitable for high-performance aqueous ZIBs. Printed electrodes based on graphene and graphene/CNTs achieved excellent areal properties in a symmetric supercapacitor setup. However, considering the predominance of activated carbon in the supercapacitor market, and the high conductivity and relatively low gravimetric performance of thick graphene nanoplatelets, we believe these electrodes can be better employed for hybrid aqueous devices or functionalized for battery applications. The use of functionalized conductive scaffolds with tailored geometry is an excellent method to achieve high-rate electrodes from high-energy density active materials limited by a low electrical conductivity.

Throughout this work, we also provided insight into the limitations of conventional testing methods and validated the use of alternative characterization tools for the assessment of the electrochemical performance and degradation of 3D printed EESDs. In particular, we evaluated the use of a chronoamperometric method, previously proposed for supercapacitors, for the rapid characterization of the rate capability of 3D-printed electrodes with long discharge times, providing a dense array of data points in a short time and in a wide rate window. Our research suggests that the chronoamperometric method provides the same results as galvanostatic charge-discharge tests, provided that the electrode and electrolyte degradation is negligible during testing. We also argued that Tafel tests do not provide a reliable measurement for the corrosion rate of zinc anodes, demonstrating how electrochemical mass spectroscopy is instead able to deliver quantitative information on the corrosion of zinc in real battery electrolytes.

Finally, we demonstrated the fabrication of interdigitated graphene devices and proposed the integration of different ink formulations to manufacture fully-printed aqueous ZIBs, characterizing their performance for the practical integration into portable electronic systems. We demonstrated a fully-printed ZIB able to power a Bluetooth sensor for over 75 h, based on safe and abundant active materials, which is expected to be significantly more environmentally sustainable than conventional lithium-ion batteries. It must be noted that, although the chemistries explored in this work are based on relatively abundant active materials and aqueous electrolytes, the sustainability of the devices need to be studied with a more holistic and quantitative approach, starting from the extraction and processing of the raw materials to the end-of-life and disposal of the cells. Life-cycle assessment (LCA) is a common method to examine the environmental impact of EESDs,³³³ and it can provide a better understanding of the sustainability of the devices developed in this work. Comparative cradle-to-gate LCA studies on different battery chemistries have already been presented, suggesting that zinc-ion batteries can be significantly more sustainable than lithium-ion batteries.⁴ Nonetheless, these studies only considered conventional manufacturing methods at the lab scale, *e.g.* tape casting; further studies, accounting for new manufacturing processes (such as 3D printing) on a commercial scale, are required to shed light on the environmental impact of the aqueous devices presented in this work.

2. Technological relevance of this work

The 3D printed EESDs developed throughout this work present appealing features for the market of portable and wearable electronics. We demonstrated the fabrication of electrodes and devices with tuneable geometry, which can be further optimized and miniaturized for integration into electronic systems with unconventional size and shape constraints. Additionally, the geometric versatility of the printed devices allows complete design freedom for the development of new wearable systems, in contrast to the currently available technologies. The EESDs here developed are safe, based on non-flammable aqueous electrolytes and non-toxic materials, and can thus better tolerate mishandling and overcharging. The absence of safety systems, and the resulting simplification of the battery management electronics in aqueous EESDs, can reduce the production costs. However, the slow production speed of 3D printing processes and low consistency in the performance of the printed devices would undoubtedly result in higher per-unit costs compared to mass production methods. Therefore, we expect our devices to be particularly suited for a market requiring small production runs, where complex geometries and customization are crucial requirements, and which can better tolerate higher per-unit costs compared to mass-produced electronics. We believe a possible market presenting these features is represented by customized biomedical devices, such as robotic prosthetics.

Robotic prostheses consist of mechatronic components, including motors, sensors and micro-controllers, which emulate the functions of human neuromuscular system. EESDs are typically used as power supplies for the components of robotic prostheses.³³⁴ However, the small size of prostheses typically limits the space available for batteries, constraining the size and processing capability of the electronic components.³³⁴ The 3D printed EESDs proposed in this work can fit in the complex structures of highly customized prostheses, and their design can be easily tailored to accommodate the size and shape of different devices. Further development is nonetheless needed in terms of capacity and cyclability, to ensure battery operation at a battery discharge power > 10 W for several hours of continuous use (capacity ~ 4000 mAh) and over hundreds of charge-discharge cycles.³³⁵ This enhancement are expected to come primarily from the optimization of the cell chemistry, *e.g.* the use of additives that prevent electrode degradation and corrosion. A rational optimization of the electrode geometry, having in mind the geometric constraint of commercial prosthetic devices (*e.g.* a robotic hand), would also narrow the gap between the performance of the devices developed in this work and the requirements of commercial prostheses. Should these enhancements prove insufficient to meet the performance target, the ink formulation principles developed in this work could still be adapted to non-aqueous chemistries, in particular high-energy lithium-polymer batteries.

3. Future works

3.1. Graphene and graphene-CNT electrodes

- The microstructural investigation of the graphene electrodes demonstrated that the extrusion process can influence the alignment of platelets inside the extruded filaments. The identification of a quantitative relationship between the degree of platelet alignment and the extrusion parameters, *e.g.*, printing speed and residence time inside the nozzle, was hindered by the possible presence of wall slip during extrusion. Further experiments, systematically measuring the degree of platelet alignment at different residence times, together with rheological models taking into account the ink microstructure in the proximity of the nozzle wall, can shed light into the extent of wall slip. The identification of a relationship between the microstructure of the electrodes and the controllable parameters of the DIW process would be of great interest to optimize charge transport and mechanical properties.
- The electrochemical characterization of interdigitated graphene supercapacitors indicates high interface resistance, owing to the absence of a current collector and to the long ionic and electronic transport paths. The design of the interdigitated electrodes (length of the fingers, distance between the fingers and thickness of the electrodes) provides control over the length of the charge transport paths. A systematic study on the optimal design parameters would lead to a critical improvement in the electrochemical performance of the graphene devices.
- Interdigitated graphene devices also show limited cycling stability, with fast ageing processes that we attributed to the degradation of the polymeric gel electrolyte. An investigation of alternative aqueous electrolytes with higher stability, such as water-in-salt electrolytes, is necessary to achieve the cycle life required by commercial applications.
- We demonstrated that a CO₂ laser treatment can enhance the conductivity of 6-layer graphene electrodes for supercapacitors. However, it is necessary to further investigate the penetration depth and temperature profile inside the electrodes to evaluate the possibility to apply the treatment to thicker structures.
- Our investigation shows that the areal capacity of graphene/CNTs electrodes does not significantly increase above 12 layers. We attributed this to the incomplete wetting of the electrodes in the viscous zinc sulfate electrolyte, as supported by the lower coulombic efficiency of thicker electrodes. The fabrication and testing of electrodes with optimized design to promote the electrolyte diffusion would confirm this hypothesis and identify a route to overcome the thickness limitations discussed in this work.

3.2. Zinc electrodes

- The zinc-PVA inks proposed in this work can be used to print electrodes with complex geometry and excellent shape fidelity to the original digital model. Nonetheless, the rheological tests performed on these inks indicate a certain degree of thixotropy, which is usually detrimental to achieve self-standing filaments. We attributed the good printability of the zinc inks to the large unsheared core in the extrudate (high yield stress) and to the rapid drying of the filaments during deposition. Further research should elucidate the microstructural origin of the thixotropic behaviour, and the role played by thixotropy and water evaporation during the extrusion process for the shape retention of the filaments.
- We demonstrated that the formation of a porous layer of zinc hydroxysulfates during cycling does not cause any major hindrance to charge transfer. However, the formation of dead zinc is known to rapidly reduce the coulombic efficiency in real devices, characterized by electrolyte-starved conditions and low areal loading of zinc in the anode. Testing in these conditions would provide insight into the commercial viability of the printed electrodes for different cell configurations than the one used in this work, *i.e.*, flooded pouch cells.

3.3. 3D printed cathodes and full battery

- We showed how the hydrothermal synthesis of VS_2 leads to the formation of spherical microflowers that can be directly used to formulate inks. However, the mechanism underlying the formation of VS_2 microflowers is unclear. The synthesis of VS_2 could proceed through the initial decomposition of the precursors and subsequent reaction of the products or by the direct reaction of the precursors. A better understanding of the reaction mechanism is fundamental to control the shape and size of VS_2 towards smaller and monodisperse particles. This would pave the way to the fabrication of miniaturized EESDs using micro-nozzles.
- We argued that the electrochemical processes occurring in hydrothermal VS_2 might be a combination of intercalation and surface oxidation reactions. *Ex-situ* XRD could not provide evidence of the intercalation processes, probably owing to the relaxation of the material during sample preparation. Additionally, our experimental results suggest that the active material becomes amorphous after cycling. *In-situ* XRD is necessary to establish the exact nature of the electrochemical processes occurring in the electrodes, and identify the cycling stability before amorphization.
- Our experimental results suggest that the areal capacity of woodpile manganese oxide electrodes can be enhanced by altering the electrode design (*i.e.*, footprint area, filament spacing and diameter). A systematic investigation of the optimal geometry to maximize the

energy and power density under the constraint of a fixed available volume and shape would be necessary for the integration of printed electrodes into wearable systems.

- The fully-printed battery we proposed shows higher transport resistance than woodpile electrodes in a sandwich configuration. The design of the interdigitated structure must be further optimized to promote charge transport and reduce the length of the ionic and electronic diffusion paths.
- The practical application of fully-printed batteries was demonstrated powering a Bluetooth proximity sensor. Nonetheless, the commercial viability of the fully-printed batteries must be further validated selecting target wearable systems and identifying the main figures of merit which lag behind in comparison with the available commercial alternatives. We envision that all-printed batteries present appealing features for the market of wearable biomedical sensors, such as skin temperature sensors, heart rate monitors and movements sensors. The main challenges that must be addressed for integration into these devices are: (1) need for a smaller design (miniaturization); (2) development of a printed case for ease of integration with the sensor electronics; (3) long lifespan for continuous and reliable operation; (4) low self-discharge rate. The first two requirements can be easily addressed with the 3D printing process, whereas the battery life and self-discharge rate must be enhanced incorporating additives in the active elements of the cell, *e.g.* in the electrolyte ink.

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Appendix

A1. Reactive NVP inks

This appendix will describe the formulation of a reactive ink to fabricate $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ (NVP) electrodes for sodium ion battery cathodes. The NVP ink was obtained adding a sol-gel precursor to the graphene capillary dispersion presented in Chapter 3. After printing, the electrodes are thermally annealed in inert atmosphere to decompose the precursor and form NVP.

A1.1 Ink formulation

The sol-gel precursor was formulated mixing NaOH, NH_4VO_3 and $\text{NH}_4\text{H}_2\text{PO}_4$ in a molar ratio 3:2:3. The mixture was dissolved in water with citric acid and the solution was stirred for 8 h at 80°C until a dark blue gel was obtained (**Figure A1.1-a**). The gel was dried at 80°C for 12 h in air and then ground with a ceramic mortar to obtain the sol-gel precursor. NVP for XRD measurements was synthesized by annealing the sol-gel precursor in argon for 3 h at 350°C and then for 16 h at 800°C. The NVP ink was obtained adding the sol-gel precursor to the graphene ink (Chapter 3) in a 2:5 mass ratio (NVP precursor:graphene nanoplatelets). After printing, the electrodes were dried in air overnight and then annealed in argon for 3 h at 350°C and then for 16 h at 800°C.

A1.2 Physical characterization and rheology

The formation of $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ after thermal annealing of the sol-gel precursor was confirmed by X-ray diffraction (**Figure A1.1-b**). The addition of the sol-gel precursor to the graphene ink resulted in a notable reduction in viscosity, storage modulus ($\sim 10^4$ Pa vs. $\sim 10^5$ Pa), and yield stress (~ 4 Pa vs. ~ 60 Pa) probably a consequence of the different surface tension of the primary liquid phase (**Figure A1.1-c,d**). A change in the surface tension of the dispersing medium can hinder the formation of the octanol capillary bridges between the graphene nanoplatelets, resulting in a mechanically weaker ink at rest. Nonetheless, the ink still presented a storage modulus of $\sim 9.5 \times 10^3$ Pa and a yield stress of ~ 4 Pa, sufficiently high to print woodpile electrodes made of several (2 to 6) stacked layers (**Figure A1.1-e**). As evidenced by SEM imaging, the final electrode is made of graphene nanoplatelets decorated with NVP particles (**Figure A1.1-f**).

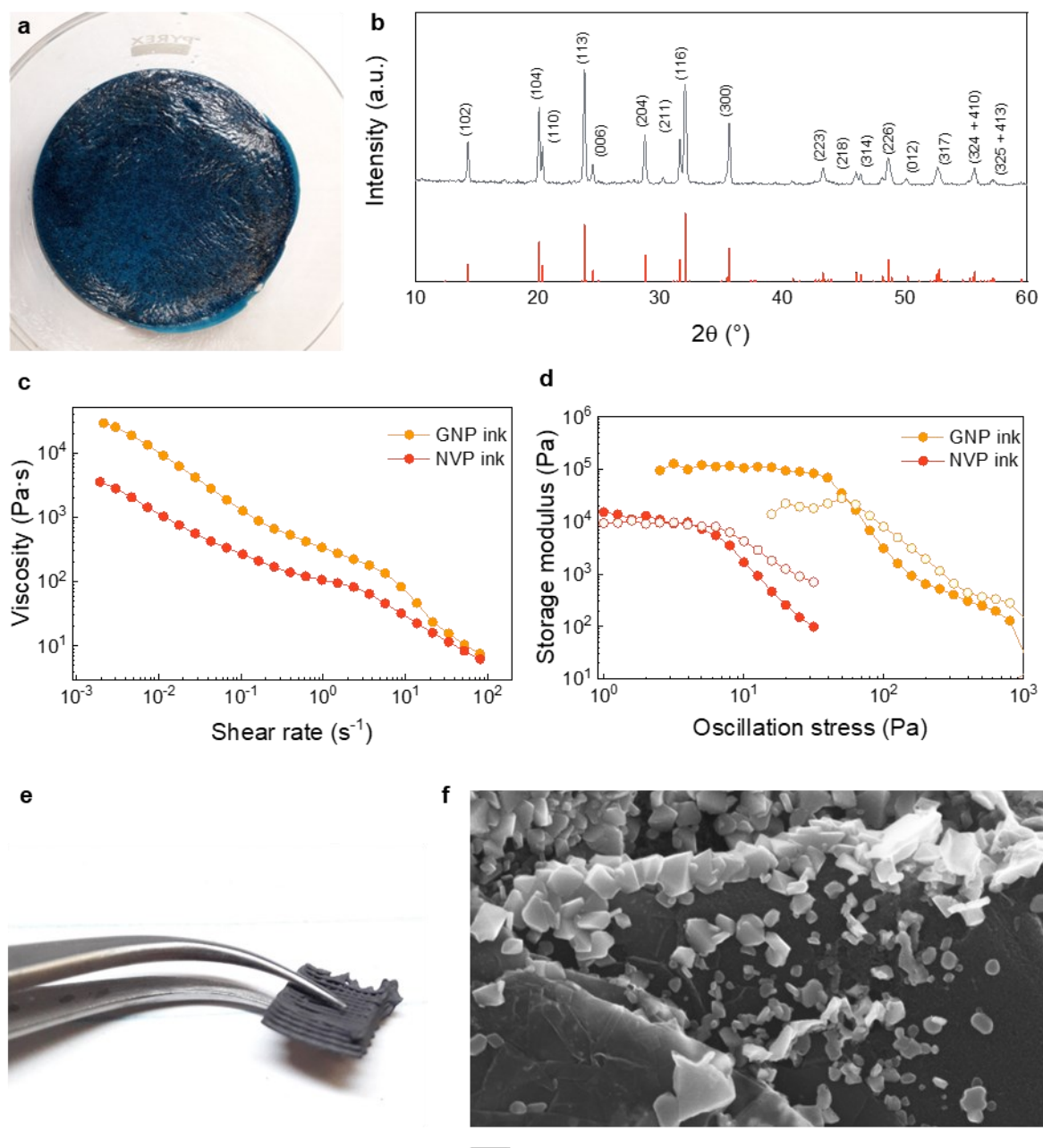


Figure A1.1: (a) Digital photograph of the sol-gel precursor employed for the formulation of the NVP inks; (b) XRD on the sol-gel precursor after annealing in argon (reference pattern PDF 96-222-5133) ; (c) flow ramp on the NVP ink and graphene nanoplatelet ink; (d) oscillatory amplitude sweep on the graphene nanoplatelet ink and NVP ink; (e) digital photograph of a 3D printed woodpile electrode; (f) SEM image of a 3D printed woodpile electrode after thermal annealing, showing NVP particles growing on the graphene nanoplatelets (scale bar 200 nm)

A2. References for the comparison plots

References for **Figure 3.4-d**: yield stress and storage modulus comparison for the graphene ink.

MXenes (1)	ref. ³³⁶
GO + Ca ²⁺	ref. ¹²⁷
MXenes (2)	ref. ⁹⁹
GO	ref. ¹²¹
Gallium alloy	ref. ³³⁷
PEDOT:PSS	ref. ¹³⁵
CNF	ref. ¹¹⁴
Holey GO	ref. ¹²⁰
GO + urea + GδL	ref. ²⁰³

References for **Figure 3.12-b**: comparison of the electrical conductivity of the graphene ink with literature values for reduced graphene oxide inks.

rGO (1)	ref. ¹²⁷
rGO (2)	ref. ¹²¹
rGO (3)	ref. ²⁰³

References for **Figure 3.17-a**: Ragone plot comparing the gravimetric power and energy density of the 3D printed graphene supercapacitors with recent carbon-based devices.

Graphene aerogel	ref. ³³⁸
Graphene xerogel	ref. ³³⁸
3D printed GAM	ref. ¹²⁷
Graphene	ref. ³³⁹
rGO/MWCNT	ref. ²⁰³
3D printed GCA	ref. ²⁰⁴
Carbon cloth	ref. ³⁴⁰

References for **Figure 3.17-b**: Ragone plot comparing the areal energy and power density of the 3D printed graphene supercapacitors with state-of-the-art carbon-based devices.

3D printed GA	ref. ²⁰⁴
rGO hydrogel	ref. ³³⁹
3D GA	ref. ²⁰³
Coaxial carbon fiber	ref. ³⁴¹
rGO film	ref. ⁵²
CDC	ref. ³⁴²
rGO + CNTs	ref. ³⁴³
Cellular rGO films	ref. ³⁴⁴
G/CNTs	ref. ³⁴⁵
S-graphene	ref. ³⁴⁶
Photoreduced graphene	ref. ³⁴⁷
Laser-reduced GO	ref. ³⁴⁸
rGO	ref. ³⁴⁹
S-doped graphene	ref. ³⁵⁰
IJP graphene	ref. ³⁵¹

References for **Figure 3.17-c**: comparison of the areal capacitance of the 3D printed graphene supercapacitors with recently reported carbon devices

(1)	ref. ³⁴⁸
(2)	ref. ³⁵²
(3)	ref. ³⁴²
(4)	ref. ⁵²
(5)	ref. ³³⁹
(6)	ref. ³⁵⁰
(7)	ref. ²⁰³
(8)	ref. ³⁴⁶

References for **Figure 3.30-b**: Ragone plot comparing the performance of the ZHCs with state-of-the-art devices.

Ti ₃ C ₂ T _x	ref. ³⁵³
rGO	ref. ³⁵⁴
MXenes	ref. ³⁵⁵
AC	ref. ³⁵⁶
3D MXenes	ref. ⁹⁹
PG	ref. ¹²⁵
GPA	ref. ²⁰³
Carbon	ref. ³⁵⁷
GO-GNP	ref. ¹⁰¹
rGO-VNQD	ref. ³⁵⁸

References for **Figure 4.11-a**: comparison of the voltage hysteresis for the plating and stripping on zinc-CB 5% structures with other zinc anodes recently reported in the literature.

MXenes@Zn (1)	ref. ³⁵⁹
MXenes@Zn (2)	ref. ³⁵⁹
TiO ₂ @Zn	ref. ³⁶⁰
CNTs@Zn	ref. ³⁶¹
Kaolin@Zn	ref. ³⁶²
MoS ₂ @Zn	ref. ³⁶³
ZrO ₂ @Zn	ref. ³⁶⁴
rGO@Zn	ref. ³⁶⁵

References for **Figure 5.16-a**: comparison of the gravimetry capacity of the printed MnO₂ cell with literature ZIBs.

Zn/V ₂ O ₅	ref. ³⁶⁶
Zn/MoS ₂	ref. ³⁶⁷

Zn/PANI@CF	ref. ³⁶⁸
Zn/MnO ₂	ref. ³⁶⁹
SS-Zn/MnO ₂	ref. ²³³

References for **Figure 5.16-b**: comparison of the areal capacity of the printed MnO₂ cell with literature ZIBs.

Flexible Zn/Ag	ref. ³⁷⁰
IL Zn/MnO ₂	ref. ²³⁴
3D Zn/MnO ₂	ref. ³⁶⁹
Printed Zn/air	ref. ³⁷¹
3D Zn/MnO ₂ (gel)	ref. ³⁶⁹
3DP Na-Ion	ref. ³⁷²
ZnO/NiO	ref. ³⁷³
Textile Zn/Ni-Co	ref. ³⁷⁴
3DP Zn/CNT@MnO ₂	ref. ²⁴⁶

References for **Figure 5.19-c**: comparison of the transference number and ionic conductivity of the gel electrolyte with zinc-ion gel electrolytes recently reported in the literature.

(1)	ref. ³⁷⁵
(2)	ref. ³³⁰
(3)	ref. ³⁷⁶
(4)	ref. ³²⁹
(5)	ref. ³²⁸
(6)	ref. ³⁷⁷
(7)	ref. ³⁷⁸
(8)	ref. ³³⁰
(9)	ref. ³²⁹

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Author/Editor	Royal Society of Chemistry (Great Britain)	End Page	2821
Date	01/01/2008	Issue	9
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Publication: Applied Materials

Publisher: American Chemical Society

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Date	01/01/2013	Issue	18
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All-Printed In-Plane Supercapacitors by Sequential Additive Manufacturing Process



Author: Myeong-Lok Seol, Inho Nam, Erick L. Ribeiro, et al

Publication: ACS Applied Energy Materials

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Author/Editor	Royal Society of Chemistry (Great Britain)	End Page	540
Date	06/01/2005	Issue	5
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