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Los Angeles

Relating Charge Transport and Exchange Behaviors by Ligand Chemistry of Carbon Dots

A dissertation submitted in partial satisfaction of the
requirements for the degree Doctor of Philosophy
in Chemistry

by

Chenxiang Wang

2023

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ABSTRACT OF THE DISSERTATION

Relating Charge Transport and Exchange Behaviors by Ligand Chemistry of Carbon Dots

by

Chenxiang Wang

Doctor of Philosophy in Chemistry

University of California, Los Angeles, 2023

Professor Richard B. Kaner, Chair

The emergence of electrochemical energy storage technologies represents a significant milestone in the pursuit of sustainable energy solutions, offering a viable alternative to fossil fuels. This shift is driven by the urgent need to mitigate environmental impacts and maximize the efficiency of renewable energy systems. Central to this advancement is the development of storage systems with improved energy density (energy stored per unit volume or mass) and power density (rate of energy delivery), crucial for high-capacity applications. Notably, the transition from traditional lithium-ion batteries with organic electrolytes to aqueous battery systems, using water-based electrolytes, brings several advantages. Aqueous batteries are inherently safer, reducing the risk of thermal runaway, vital for large-scale applications like grid storage. They also have a reduced environmental footprint, aligning with sustainability goals, and offer cost-effectiveness due to the use of water-based electrolytes and potential for cheaper materials. Furthermore, aqueous batteries often exhibit superior electrochemical stability and faster ion transport, enhancing cycle life and

rapid charging capabilities. Nonetheless, challenges persist, such as the narrow electrochemical stability window of water, which can limit operating voltage and energy density, necessitating innovative electrode and electrolyte design for performance enhancement.

The goals of this dissertation have been to investigate some fundamental properties of carbon-based electrodes, specifically carbon nanodots in their chelating chemistry, to tune the electrochemical performance in aqueous energy storage systems.

Chapter 2 discusses the role of graphene in enhancing supercapacitors, emphasizing its electrochemical and electrical attributes. Graphene's two-dimensional hexagonal lattice of sp^2 -hybridized carbon atoms, with exceptional thermal and electrical conductivity, enhances energy storage efficiency. Synthesis methods, including top-down and bottom-up approaches, are reviewed, along with the scalability of graphene production through Graphene Oxide (GO) and reduced Graphene Oxide (rGO). The chapter also explores Carbon Nanodots (CNDs) and Graphene Quantum Dots (GQDs) in energy storage. Chapter 3 focuses on using Carbon Nanodots (CNDs) and derivatives in capacitive energy storage. Strategies to increase their specific surface area and rate capability for high-performance conductive electrodes are discussed, including integrating conductive compounds and polymers. Synthesis methods of CNDs are evaluated, positioning them as components in advanced energy storage systems. Chapter 4 introduces a laser process to enhance sulfonyl compounds' performance in pseudocapacitive charge storage materials. Laser-converted carbon nanodots (CNDs) form conductive scaffolds with high surface areas, enabling efficient Faradaic processes. The resulting electrode exhibits remarkable capacitance and cycling stability, promising for advanced capacitive storage materials. Chapter 5 emphasizes electrode matching for filter electrochemical capacitors (FECs) in green electricity conversion. Effective matching improves capacitance, frequency response, voltage range, and longevity.

Analytical methodologies are employed to design a durable filter electrochemical capacitors with exceptional performance metrics. Chapter 6 explores zinc-based batteries for grid-level energy storage. A novel functionalization process using ZnCND and H-ZnCND improves zinc anodes' stability, offering a safer and efficient energy storage solution. Chapter 7 addresses the rechargeability and cycling efficiency of zinc batteries by reengineering the solid-electrolyte interface (SEI) with ZF-rich fluorinated zinc-based SEI, enhancing its mechanical properties and ionic conductivity. This approach leads to dendrite-free zinc metal anodes and promising energy density.

The dissertation of Chenxiang Wang is approved.

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2023

*Dedicated in loving memory of
my late grandmother, Yufang Luo*

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LIST OF PUBLICATIONS AND PRESENTATIONS

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3. **C. Wang**, S. Vi-Tang, X. Chang, M. Anderson, A. Huang, Z. Yang, M. El-Kady, R. Kaner “A Simple Route to Sulfonyl Porous Graphene from Carbon Nanodots for Metal-free Pseudocapacitor” *Materials Horizons*(Invited Paper), Accepted (2023).
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CHAPTER 1. INTRODUCTION

The advent of electrochemical energy storage technologies marks a significant milestone in the quest for sustainable energy solutions, offering a viable alternative to the conventional reliance on fossil fuels.^[1] This paradigm shift is driven by the urgent need to mitigate the environmental impacts of traditional energy sources and to harness the potential of renewable energy systems more effectively.^[2,3] The cornerstone of this technological advancement lies in the development of storage systems with enhanced energy density and power density.^[4] Energy density, defined as the amount of energy stored per unit volume or mass, is critical in determining the feasibility of a storage device for high-capacity applications. Power density, on the other hand, reflects the rate at which energy can be delivered, indicating the capability of the system to meet rapid power demands.^[5] In the realm of electrochemical storage, there has been a significant emphasis on improving these parameters to cater to the increasing demands of various applications, ranging from portable electronics to electric vehicles and grid storage.^[6] The development of materials and systems that can store more energy in a compact and lightweight form while delivering it at a higher rate is essential in ensuring the efficiency and effectiveness of these applications.^[7]

A key development in this field has been the transition from traditional lithium-ion batteries, which predominantly utilize organic electrolytes, to aqueous battery systems. Aqueous batteries, employing water-based electrolytes, present several advantages over their lithium-ion counterparts.^[8] Firstly, they are inherently safer due to the non-flammable nature of the aqueous electrolytes, significantly reducing the risk of thermal runaway and associated safety hazards.^[9] This safety aspect is particularly crucial in large-scale applications, such as grid storage, where the

consequences of battery failures can be catastrophic. Moreover, aqueous systems offer a reduced environmental footprint.^[10] The use of water as a solvent, as opposed to organic solvents, minimizes the ecological impact, particularly in terms of toxicity and disposal.^[11] This aspect aligns with the broader objectives of sustainability and environmental stewardship, which are integral to the development of renewable energy technologies. ^[12]The cost-effectiveness of aqueous battery systems is another significant advantage.^[13] The reliance on water-based electrolytes and the potential for utilizing more abundant and less expensive active materials can lead to a reduction in overall battery costs.^[14] This cost advantage is essential for the widespread adoption and scalability of energy storage solutions, especially in developing regions where cost constraints are a primary concern. From an electrochemical perspective, aqueous batteries often exhibit superior electrochemical stability and faster ion transport compared to lithium-ion systems.^[15] These characteristics translate into improved cycle life and faster charging capabilities, which are critical for applications where frequent cycling and rapid energy delivery are required. However, the transition to aqueous systems also presents several challenges. The narrow electrochemical stability window of water imposes limitations on the operating voltage of aqueous batteries, potentially impacting the energy density.^[16–18] Addressing this issue requires innovative approaches in electrode and electrolyte design to extend the stability window and enhance the overall performance of the system.^[15,19]

In Chapter 2, a comprehensive review of the pivotal role of graphene in enhancing the functionality of next-generation supercapacitors, which are integral to a broad spectrum of applications, from electric vehicles to grid storage.^[20] The chapter elucidates that these supercapacitors, distinguished by their high power density and cycling stability, benefit significantly from the incorporation of

graphene, given its superior electrochemical and electrical attributes. Central to this discourse is the capacitive energy storage mechanism based on the electrical double-layer capacitance (EDLC) model, which is fundamentally governed by electrostatic charge accumulation at the electrode/electrolyte interface. Graphene, characterized by its two-dimensional hexagonal honeycomb lattice of sp^2 -hybridized carbon atoms, exhibits exceptional thermal and electrical conductivity, attributed to efficient lattice vibrations and minimal phonon leakage, which are crucial for energy storage efficiency. The synthesis methodologies of graphene, encompassing both top-down and bottom-up approaches, are extensively reviewed, highlighting their respective advantages in optimizing graphene quality for energy storage purposes. Chapter 2 also delves into the scalability of graphene production, particularly through Graphene Oxide (GO) and reduced Graphene Oxide (rGO) pathways, and discusses the potential of Carbon Nanodots (CNDs) and Graphene Quantum Dots (GQDs) in energy storage, emphasizing their tunability and biocompatibility. Conclusively, the study asserts that graphene-based materials, owing to their high specific surface area and intrinsic capacitance, are poised to revolutionize supercapacitor technology, although challenges persist in exploiting these properties to their fullest potential for commercial applications. This research thus underscores graphene's transformative impact in capacitive energy storage, paving the way for more efficient and powerful supercapacitor technologies.

In Chapter 3, the focus is on the innovative utilization of Carbon Nanodots (CNDs) and their derivatives, Graphene/Carbon Quantum Dots (GQDs/CQDs), in advancing electrode materials for capacitive energy storage systems.^[21] Central to this exploration is the transformation of CNDs from inherently low-conductive entities to high-performance conductive electrodes. This

metamorphosis hinges on enhancing their specific surface area and rate capability, employing a myriad of active sites on CNDs to elevate the electrode-specific capacitance. This is effectively achieved through the integration of conductive carbon-metal compounds and conductive polymers. CNDs, characterized by a p-conjugated carbonaceous core, typically encompass a size range of 1-10 nm and are synthesized either by oxidative segmentation of larger graphitic structures or via bottom-up carbonization of molecular precursors. Their distinct attributes—high water solubility, tunable redox activity, and rich edge functionalities—render them as prime candidates for active components in electronic devices. Recent strategies to harness the potential of CNDs in supercapacitors have included converting them into high-surface-area carbon electrodes and enhancing capacitance and electrical conductivity. CNDs have been instrumental in preventing the restacking of other components, improving porosity and ion diffusion, and boosting electron transport within electrode materials. Their small size endows them with intrinsically high surface areas, facilitating interactions with a variety of electrode materials and thus augmenting the surface area and providing pseudocapacitive sites. The synthesis and preparation methods of CNDs are critically evaluated in Chapter 3, adopting the terminologies of the original studies. This comprehensive examination of CNDs positions them as formidable components in next-generation energy storage systems, particularly in EDLC electrodes, paving the way for their application in commercially viable, advanced capacitive energy storage technologies.

Chapter 4 explores an innovative approach to enhance pseudocapacitive charge storage materials, crucial for bridging the performance gap between high-energy batteries and durable, high-power capacitors.^[22] The study addresses the inherent drawbacks of sulfonyl compounds, namely structural instability and low electrical conductivity, which have historically limited their

application as electrode materials. Here we introduce a rapid, environmentally benign laser process to interconnect sulfonated carbon nanodots (CNDs), creating functionalized porous carbon foams. These laser-converted three-dimensional (3D) turbostratic carbon structures serve as conductive scaffolds with high surface areas, embedding redox-active sulfonyl groups. This unique arrangement facilitates efficient Faradaic processes, leading to a remarkable specific capacitance of 157.6 F g^{-1} . The design ensures that even at high current densities (20 A g^{-1}), the capacitance retains 78.4% of its value, attributable to the uniform distribution of redox-active sites across the graphene domains. The 3D-tsSC300 electrode variant demonstrates extraordinary cycling stability, maintaining performance over 15,000 cycles. Furthermore, when employed in flexible solid-state supercapacitors, 3D-tsSC300 achieves a high specific capacitance of up to 17.4 mF cm^{-2} , with over 91.6% capacitance retention after 20,000 charge-discharge cycles, inclusive of stress tests under 90° bending. An assembled flexible all-solid-state symmetric supercapacitor exhibits a high energy density of 12.6 mWh cm^{-3} and a power density of 766.2 W cm^{-3} , metrics normalized by the full device volumes. These figures are competitive with, or surpass, those of state-of-the-art commercial pseudocapacitors and hybrid capacitors. The supercapacitor, offering a 2 V potential window in a serial circuit, showcases the potential of this technology in metal-free energy storage devices, marking a significant stride in the field of advanced capacitive storage materials.

The focus of Chapter 5 is on enhancing electrochemical filter capacitors' (ECs) efficiency for use in green electricity conversion and integrated circuit frequency regulation. The study identifies that the optimal functionality of these ECs, surpassing traditional electrolytic capacitors in miniaturization and portability, depends critically on the harmonization of fast ion-exchange kinetics and high reversibility between the positive and negative electrodes. Discrepancies in the

charge-exchange kinetics and structural behaviors of electrode pairs are highlighted as principal constraints affecting both the instantaneous response and long-term cycling stability. The research emphasizes that effective electrode matching not only ensures high capacitance and rapid frequency response, thereby broadening the functional frequency band, but also facilitates expanded voltage range and longevity, crucial for reliable grid integration. The chapter delves into the electrochemical compatibility and degradation dynamics to unravel the coupled effects of electrode interactions on the overall capacitor performance. Analytical methodologies, including Coulombic efficiency at ultra-slow scans and resistor-capacitor capacitances at 120-Hz perturbations, are employed to quantify stable electrode potentials and frequency-response times. This approach leads to the development of a 1.8 V durable EC-based filter capacitor, characterized by exceptional performance metrics such as capacitance retention and phase angle stability over extensive cycling periods. The findings of this study offer a comprehensive blueprint for designing ECs tailored for high-voltage line filtering applications, with a particular emphasis on achieving matched charge-exchange kinetics between electrodes. This not only mitigates phase divergence-induced irreversibility but also aligns with the requirements of modern energy storage and digital communication technologies, thereby marking a significant advancement in the field of energy storage materials science.

Chapter 6 explores zinc-based batteries as a viable alternative to lithium-based systems for large-scale grid-level energy storage.^[23] This shift is driven by the ample global reserves of zinc, its inert nature, and the employment of safer, water-based electrolytes. However, Zn metal anodes in these batteries face challenges such as poor cycling stability, primarily due to irreversible dendrite formation and hydrolytic processes during charging. The study identifies the unique coordination

geometry of Zn^{2+} ions, complexed by multi-layer water ligands, which creates a significant ion diffusion barrier at the zinc anode. This results in dendritic electrodepositions and substantial hydrogen evolution, leading to corrosion and the formation of electrochemically inert compounds, thus degrading Coulombic efficiency and battery lifespan. To address these issues, the research introduces a novel functionalization process for Zn anodes using ZnCND and H-ZnCND, achieved through a solution-phase reaction with tannic acid as a crosslinker. This process results in a homogeneous coating on Zn foils, enhancing surface morphology and ensuring a stable coating during electrochemical processes. The study further explores the composition and distribution of bonding configurations within the H-ZnCND layers, revealing a gradient distribution that inhibits the formation of a distinct interphase between Zn and the surface passivation layer. This configuration ensures good wettability near the electrolyte and facilitates a homogeneous electrical field distribution around the Zn metal. By varying degrees of histidine functionalization, the research effectively modulates the coating layers' histidine and carboxylate motifs. The nitrogen-to-oxygen ratios in the coatings indicate an increasing amount of histidine, crucial for enhancing the battery's performance. This work represents a significant advancement in the field of zinc-based battery technology, offering a promising direction for developing safer, more efficient, and cost-effective energy storage solutions.

Chapter 7 investigates addressing the fundamental limitations of non-rechargeable zinc batteries, particularly in enhancing their rechargeability and cycling efficiency. The study zeroes in on the critical challenge posed by the solid-electrolyte interface (SEI) on zinc anodes, which is typically unstable and inhomogeneous, leading to low cycle efficiency and severe dendrite formation. To tackle this, the research introduces a groundbreaking ZnF_2 -rich fluorinated zinc-based SEI (ZF),

characterized by its low solubility in electrolytes, wide bandgap preventing electron tunneling, and an elevated voltage window against Zn/Zn^{2+} to avert dendritic formation. However, at higher capacities, ZF-based SEIs exhibit compromised stability due to their inelastic mechanical properties and inadequate ionic conductivity, which fail to accommodate the escalated volume changes and ion flux. To counter these shortcomings, the study proposes a novel approach of mechanical reengineering of ZF, achieved by integrating carbonyl ligands into the SEI structure, thereby enhancing its elasticity and zinc ion affinity. This strategic modification creates a gradient in the SEI's elasticity at various depths, resulting in a highly reversible, dendrite-free zinc metal anode capable of sustaining high capacities. The efficacy of this reengineered SEI is rigorously validated through a combination of nanomechanical investigations and density functional theory analyses. These assessments elucidate the correlation between the mechanical elasticity, ionic conductivity of the SEI, and the improved cycling dynamics of zinc anodes. Employing this advanced SEI, a full cell with a low negative-to-positive electrode capacity ratio of 2.01 was developed, demonstrating a $\text{Zn}||\text{LiMn}_2\text{O}_4$ cell with a substantial reversible capacity of 94 mAh g^{-1} after 120 hours, and an impressive energy density of 16.7 Wh kg^{-1} . This research not only sheds light on the mechanism linking the electrochemical behavior of zinc anodes with the SEI's mechanical properties, but also lays out a systematic methodology for designing superior SEIs, potentially applicable across various zinc battery systems like Zn-air, Zn- Br_2 , and Zn-S batteries. This study represents a significant leap in zinc battery technology, paving the way for more efficient, reliable, and scalable energy storage solutions.

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CHAPTER 2. GRAPHENE'S ROLE IN EMERGING TRENDS OF CAPACITIVE ENERGY STORAGE

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2.1 CAPACITIVE ENERGY STORAGE

Supercapacitors are among the key emerging technologies in the field of energy storage. Due to the nature of their charge storage mechanism, supercapacitors feature electrochemical characteristics complementary to those of secondary batteries, including unparalleled power density ($500 - 30,000 \text{ W kg}^{-1}$)^[1] and extended cycling life ($>100,000$ cycles)^[2]. These properties make them attractive in applications that require fast charging/discharging and long-term reliability. For example, when elevators and cranes release cargo, supercapacitors store the partial kinetic energy to be used when new cargo is lifted. In wind turbine blades, supercapacitors are broadly used in pitch control to ensure safe and steady energy conversion. In grid storage, supercapacitors regulate peak power quality by shaving pulses ranging from 0.1 to 30 s.^[3] As progress is made in increasing the energy density, power density, and cycle life, supercapacitors are promising energy storage devices to be used in various industries ranging from electric vehicles

to consumer electronics. The market of supercapacitors is forecasted to expand from \$1.4 billion in 2019 to \$3.5 billion in 2025.^[4]

Conventional capacitive energy storage is achieved through electrostatic charge deposition at the electrode/electrolyte interface. The accumulated charge concentration with respect to the bulk electrolyte is commonly described by the electrical double layer model developed by Hermann von Helmholtz.^[5] The charge stored at the biased electrode surface and the proximate layer with an equivalent counter ion population continuously increases with the potential difference between the two, limited only by the standard electrochemical potentials of the electrolyte ions and/or the stable voltage range of the electrolyte solvent, for example, in an aqueous electrolyte at 298 K, the stable voltage upper boundary is 1.23 V.^[6] The capacitance realized in this system is commonly referred to as the electrical double-layer capacitance (EDLC). The energy stored by EDLC, E , at a potential difference of ΔV between the plates is $E = \frac{1}{2} C (\Delta V)^2 = \frac{1}{2} Q \Delta V$, where C is the capacitance and Q is the charge. Thus, a pure EDLC at an ideal continuous electrode surface shows a rectangular current changes vs. potential over time, where $dV/dt = v = \text{scan rate}$, as shown in

Figure 2.1a.^[7] The capacitive charging/discharging current density is $i = C_{dl} \cdot \frac{dV}{dt} [A \cdot cm^{-2}]$ where C_{dl} is the areal specific capacitance. C_{dl} is usually constant except for instances when high scan rates are used or when the C_{dl} is measured from a porous material having significant ohmic resistance. The equivalent series resistance (ESR) in a supercapacitor can cause a non-90° phase-angle. This deviation is dependent on the frequency or scan rate. For example, in highly porous carbon EDLCs, the impedance can be characterized as a transmission line due to large ESR arising from the resistance: (1) between carbon particles and the electrolyte; and (2) between carbon

particles. This situation can be described in an equivalent circuit of the form involving a distributed capacitance and resistance (**Figure 1d**).

Additionally, pseudocapacitance can arise from electrochemical changes in the electrode materials such as Faradaic charge transfer. Even though the Faradaic processes are similar to those in batteries, the charge/discharge kinetics behave more closely to that of a capacitor. The pseudocapacitive behavior can be summarized in three aspects: (1) the input/output charge is approximately linear with respect to applied voltage; (2) at a certain scan rate, the charging/discharging current is close to a constant value (**Figure 2.1b, c**); and (3) the charging/discharging cycles show high reversibility kinetically, i.e. a nearly 100% coulombic efficiency. This was first studied in underpotential deposition on Pb and Au electrodes.^[8] In more recent studies, intrinsic pseudocapacitance was indicated in certain transition metal oxides, including RuO₂,^[9] IrO₂^[10] and MnO₂,^[11] while extrinsic pseudocapacitance in solid-state compounds and conductive polymers was achieved by size tuning, chemical doping, or crystal structure design.^[2] Redox pseudocapacitance is characterized by a series of redox reactions with continuous or overlapping potential ranges; the potential can be defined in a Nernst equation $E = E^\circ + 2.3 \frac{RT}{zF} \log \left(\frac{[\text{ox}]}{[\text{red}]} \right)$, where $\frac{[\text{ox}]}{[\text{red}]}$ is the oxidation extent in a redox pair. For example, in the RuO₂ pseudocapacitive system, electrons are transferred in a consecutive manner from one redox state to another, i.e. Ru²⁺, Ru³⁺ and Ru⁴⁺. Meanwhile a proton transfer from OH⁻ to O²⁻ at the hydration layer takes place to balance the charges. It should be noted that pseudocapacitance is often connected in parallel with the EDLC and a charge transfer resistance (R_F). R_F represents the reciprocal rate constant of the Faradaic reaction, which is usually coupled to a solution resistance,

R_s . Furthermore, a series connection of R_s and C_{dl} corresponds to the high-frequency admittance of a supercapacitor. A pseudocapacitance-dominated supercapacitor can be described in an equivalent circuit diagram (**Figure 2.1e**). A comparison of electrochemical attributes in EDLCs with pseudocapacitance was originally provided by Brian Conway and reprinted in **Table 2.1**.^[8]

2.2 GRAPHENE, A MOST VALUABLE PLAYER

Among crystalline carbon materials, graphene, the two-dimensional (2D) allotrope, offers great potential in many perspectives. In perfect graphene, carbon atoms form a two-dimensional hexagonal honeycomb lattice. It consists of an entirely sp^2 -hybridized carbon network with a carbon-carbon bond distance of 1.42 Å. The strong covalent sp^2 bonding results in efficient lattice vibrations. The absence of dangling bonds in the 2D plane minimizes phonon leakage. As a consequence, the thermal conductivity near room temperature in an isolated graphene sheet exceeds $\sim 3,000 \text{ W mK}^{-1}$,^[12] which is almost ten times that of copper. The p_z orbital, which is perpendicular to the sp^2 -hybridized 2D plane, binds with proximate carbon and forms a π band. As Linus Pauling proposed in the 1950s, the π band collectively forms a resonant valence band with high electron mobility.^[13] This is what causes an almost ballistic electrical conductivity.

2.2.1 GRAPHENE PROCESSING AND PRODUCTION

Multiple methods of making graphene or their functional derivatives have been reported, which can be categorized as either top-down or bottom-up approaches.^[14] Bottom-up graphene is, for example, achieved by molecular self-assembly of aromatic molecules in the solvent.^[15] In the first

approach, a metal substrate functionalized by thiols is employed to covalently bind to deposited aromatic molecules or by vapor phase deposition^[16]. However, with vapor deposition, monolayer graphene is obtained in a much shorter processing time (about 1 hour^[17]) Chemical conversion of aromatic self-assembled monolayer into carbon under electron irradiation and pyrolysis also effectively leads to graphene formation. Electron illumination of aromatic domains give rise to lateral crosslinking at low acceleration voltage (50–100 eV), which approximately equals to doses of ~750 electrons per molecule. By C–H cleavage and crosslinking between aromatic rings the graphene is formed.^[18] Meanwhile, the elevation of temperature to around 800 K in vacuum or inert gas enables conversion from carbonaceous molecules to a graphene lattice. The crystallographic and macroscopic properties of the resulting graphene are dependent on the annealing conditions, for example, heating temperature and substrate. Recently, a flash Joule heating method applied on cheap carbon sources, i.e. biochar, coal and coal derived products, discarded tires, and plastic waste was reported to rapidly generate graphene at gram-scale.^[19] The synthesis is solvent- and reactant-free and the obtained graphene shows a turbostratic arrangement between the stacked graphene layers. A gram of produced graphene only requires about 7.2 kJ, which could allow large scale production of graphene for industrial applications.

Due to promising scalability, top-down approaches starting from graphite as the source material are widely used. In graphite, the graphene sheets are stacked in two allotropic forms, hexagonal and rhombohedral, bonded by van der Waals forces.^[20] Graphite itself is obtained either naturally as a mineral or synthesized by subjecting non-graphitic carbons to temperatures as high as 1700 °C – 2700 °C in vacuum or inert gas.^[21] In order to obtain graphene, exfoliation is accomplished in different ways.^[22] In liquid phase, sonication can be used to generate a shock (pressure) wave upon

the collapse of cavitation bubbles. The energy produced from the shockwaves is sufficient to separate or exfoliate the individual graphite layers. Stabilizers and surfactants are often added to the liquid medium to help stabilize the resulting colloidal suspension.^[23] In contrast, shear-based exfoliation in liquid is caused by creating large viscosity gradients. This has been demonstrated using a centrifugal mixing method.^[24] However, the liquid-phase exfoliation often requires extensive use of solvent and size selection processing, which leads to difficulties in scalability.^[25] Graphite is exfoliated with high yields using this method, however, it contains high concentrations of impurities and surface-property modifying surfactants. Due to the large amounts of liquids used and generated waste in liquid exfoliation, more environmentally friendly processes such as ball-milling have been studied.^[26] In this process, the resulting shear forces of ball-milled graphite as well as the harsh impact from the balls leads to graphene platelets with a smaller particle sizes and larger surface areas. It has been previously reported that graphite passes through a nanocrystalline phase prior to amorphization during the milling process. One drawback of this process is the non-homogeneity of the resulting product. Raman spectroscopy has shown, with increasing milling time, a decrease in the crystallinity of the graphite, and an increase in the diamond-like sp^3 and fullerene-like bonding. Additionally, reduced milling times have shown the presence of graphitic ribbons as well as particles with defects, delamination, and warping.^[27]

Gas-phase exfoliation is performed in a supercritical fluid gaseous medium. A supercritical fluid is a high-density fluid with a low-surface-tension.^[28] Our group has reported a compressible gas flow exfoliation method by utilizing a series of narrow converging-diverging channels.^[29] In this process, 2D layered materials are suspended and carried through these narrow orifices using a high-pressure gas undergoing rapid expansion. The resulting 2D layered materials are exfoliated

due to the high shear rates generated by supersonic flow. This fast gas exfoliation, requiring a certain amount of solvent, has many advantages over liquid phase shear exfoliation and chemical intercalation exfoliation such as being a continuous rather than a batch-based process. Moreover, it is more environmentally friendly, versatile for multiple 2D materials, and shows reduced occurrence of defects in the exfoliated materials.

Electrochemical exfoliation uses an electrical bias in ionic aqueous or organic electrolytes.^[30] Traditionally, this has been done in aqueous media using sulfuric acid. In this process, sulfate ions are co-intercalated with water causing a stable exfoliation of the graphite sheets. Because the sulfate anion is close in size to the graphitic interlayer spacing, when sulfuric acid is used as the medium for electrochemical exfoliation, the co-intercalation of sulfate anions and water molecules generates gaseous products such as SO_2 , O_2 and H_2 .^[31] Dilute sulfuric acid becomes a widely-used medium.^[32,33] Due to the strong oxidizing nature of sulfuric acid, neutral, alkaline, or inorganic sulfate salts have been studied to produce exfoliated graphene.^[34,35] Non-organic electrolytes have also caused intense interest due to the possibility of avoiding the strong oxidative species from the electrolysis of water.^[36,37]

2.2.2 GRAPHENE-BASED MATERIALS

2.2.2.1 Graphene oxide (GO) and reduced graphene oxide (rGO)

The most scalable method to produce and process graphene is the route *via* GO.^[38] GO is obtained by graphite oxidation using strong oxidants such as H_2SO_4 , H_2O_2 and KMnO_4 .^[33,34] The oxidation process affects the surface chemistry and chemo-physical properties, and functionalities of final products. Then, reduced graphene oxide (rGO) is obtained by thermal or chemical reduction of

GO. The manufacturing of graphene-based materials from GO are on the industrial scale at a relatively low cost. However, the reduction products end up with remaining functional groups and morphological defects. As a consequence, the thermal and electrical transport is compromised in rGO. This, for example, affects the specific capacitance of rGO-based capacitors, which falls far below the theoretical capacitance of isolated graphene (550 F/g). Notably, several facile and scalable thermal reduction methods were reported including photothermal exposure, laser treatment, or microwave-induced pyrolysis. For example, free-standing rGO films was prepared by exposing GO to a xenon lamp flash.^[41] The photo-energy generated applied is about at an intensity of 1 J cm^{-2} . It induces an exothermic decomposition reaction. The input photo-energy is approximately 9 times the thermal energy to pyrolyze a $1 \text{ }\mu\text{m}$ -thick GO platelet to around $100 \text{ }^{\circ}\text{C}$, which is sufficient to induce deoxygenating reactions. The flash reduction results in gaseous products that cause rGO films expand by ten times. The electrical conductivity of the flash-reduced rGO film reaches around 10 S cm^{-1} . Another technique features rapid, clean photo-reduction and accurate fabrication of patterned film is femtosecond laser irradiation.^[42] The coherent laser beam generates highly localized heated areas with a line width ranging 0.1 from $10 \text{ }\mu\text{m}$. The rGO films formed by laser reduction have a conductivity as high as 256 S/cm . A pre-programmed laser is used to draw the patterns to form complex and delicate circuits. These processes enable the industrialization of rGO in a bulk-scale production.

2.2.2.2 Carbon nanodots (CNDs) and graphene quantum dots (GQDs)

CNDs and GQDs are considered zero-dimensional carbon materials that describe a family of organic nanoparticles with sizes below 10 nm . The structures of CNDs vary from amorphous to a

combination of sp^2 and sp^3 carbon, while GQDs strictly consists of sp^2 carbon lattice in a few layers.^[43,44] Nowadays, their potential in energy storage and conversion applications is recognized, particularly for their tunability in particle size, their low cost, and high biocompatibility.^[45] Compared with other carbon nano-allotropes, CNDs may contain multiple functional groups. The rich functionalities impart them with outstanding hydrophilicity and reactivity towards various inorganic, polymeric species.^[46] They often serve as technological platform from battery electrodes to optoelectronic devices due to their low cost and fast synthesis, nanometer dimensions and tunable surface functionalities.^[47] Typically CNDs/GQDs are nanosized graphitic domain cleaved or cut down from different types of carbon materials such as carbon fiber, CNTs, graphite powder, etc. *via* various physical or chemical techniques. Among them, hydrothermal, electrochemical exfoliation, chemical oxidation, ultrasonication are the predominant top-down methods.^[48] The bottom-up approach based on fusion and carbonization usually features higher production yield and mono-dispersity of CNDs/GQDs. Moreover, the rational design of bottom-up methods gives unique crystallite shapes, well-defined structures, and specialized functional group. The carbon sources of CNDs/GQDs synthesis are mostly small biomonomers or aromatic molecules. Bottom-up techniques include hydrothermal carbonization, pyrolysis and microwave-assisted synthesis.^[49]

CNDs/GQDs play active roles in different parts of EDLCs, such as electrodes, solid-state electrolytes and conductive additives.^[6] To incorporate CNDs/GQDs in an EDLC electrode, connecting discrete and confined carbon domains to create a spanned electron transportation channel is the top priority. Common strategies include compositing CNDs/GQDs with other carbon materials to building 3D architectures based on CNDs/GQDs. In a composite carbon

electrode, due to their nanoparticulate structures, CNDs/GQDs can be embedded and create extra pore volume with well-defined pore sizes. For example, CNDs were derived from waste zucchini biomass using a low-cost and environmental synthetic route.^[50] In a hydrothermal process the as-prepared CNDs were assembled with GO followed by reduction of HI vapor. The specific capacitance of the composite CND/rGO electrode is 374 F g^{-1} at 2 mV s^{-1} . When the scan rate was increased from 2 to 1000 mV s^{-1} , the CND/rGO electrode showed 71.7% capacitance retention. The excellent performance is due to less restacking of rGO sheets and heteroatoms introduced by HI reduction. The composite electrode is also electrochemically stable, cycling over 10,000 times at 10 A g^{-1} with a capacitance retention of 93.8%. By applying CNDs with abundant functional groups as building blocks, porous and high surface-area carbon materials are obtained. Our group has recently reported the fabrication of 3D-carbon electrodes for fast-frequency response applications of EDLCs, (e.g. AC-line filtering) derived from CNDs. Annealed CNDs based on citric acid and urea were used as precursors in a CO_2 laser carbonization process, resulting in a carbon network with an open pore structure. It was found that the reduction of the CNDs in an oxygen-free environment resulted in higher structural integrity of the 3D carbon and led to a better frequency response compared to electrodes reduced in an oxygen-containing atmosphere.^[51] Utilizing a simple and inexpensive method, high-frequency CND-carbon EDLCs were reported to have an RC time constant of 0.29 ms, a phase angle of -78° and a capacitance of 0.259 mF cm^{-2} at 120 Hz. Building on this, we have shown that CNDs also serve to patch defects in laser-reduced GO resulting in higher surface areas and conductivities.^[52,53] The addition of CNDs leads to a 130% increase of the active surface area. Compared to a laser-reduced GO, the electrical conductivity grows by about ten times. The CNDs also decrease the relaxation time from 128 ms to 7.6 ms and the minimum phase angle from -82.2° to -84.3° .

To enhance the energy density of CNDs/GQDs based devices, their other functional nanoparticles are incorporated. For example, finely and homogeneous dispersed Fe_2O_3 are nucleated on a CND platform. Within one conversion a composite aerogel is formed.^[54] The laser-assisted method generate an array of uniform Fe_2O_3 nanoparticles with diameters around 6.5 nm and forms a highly conductive carbon foam simultaneously. The Fe_2O_3 nanoparticles not only enlarge the specific surface area of the aerogel materials but also introduce pseudocapacitance. Arisen from the unique physicochemical characteristics of CNDs/GQDs, they are playing important roles also in the synthesis of active materials. CNDs/GQDs with multiple surface functional groups are scaffolds for heterogeneous nucleation, growth, or assembly of capacitive species, such as transitional metal compounds and conductive polymers. They facilitate the dispersion in solutions while preventing the agglomeration of active materials and enlarge the surface area. Meanwhile, CNDs/GQDs are advantageous conductive agents leading to a high electrical conductivity and fast charge transport and accommodate the electrode expansion/compression over the charge/discharge cycles. In addition, rich functional groups on CNDs/GQDs ensure strong electrical contact and interfacial bonding between carbon and additional components. Therefore, integration of CNDs/GQDs as a multifunctional material significantly justify and improve the electrochemical performance of electrode materials in various energy storage devices through the rational structural design and chemical modification.

2.2.3. GRAPHENE-BASED ENERGY STORAGE SYSTEMS

With enhancing mass production capability, graphene becomes a prominent material with promising applications in electronics and integrated circuits.^[55] Due to its excellent electrical and thermal properties, graphene-based devices combine highly tunable electrical and thermal conductivity to offset intense power loss and heat dissipation, which are currently the major obstacles of high-frequency electronics with compact layout.^[56] Graphene and its derivatives, e.g. rGO, carbon nanotubes(CNTs), CNDs/GQDs, etc. have an even more significant impact as supercapacitor materials.^[6,57] The 2D nature of graphene contributes to its high specific surface area ($2,630 \text{ m}^2 \text{ g}^{-1}$), leading to a high intrinsic capacitance of monolayer graphene to be $\sim 21 \text{ } \mu\text{F cm}^{-2}$.^[58] The value is highest reported value so far for a graphene-based EDLC materials. Besides, graphene-based EDLC is characterized by a low RC time constant of less than 200 microseconds, compared with ~ 1 second for typical EDLCs; as well as a phase angle of -82° at 120 Hz, approaching 90° in an ideal capacitor.^[59] The near-complete kinetic reversibility and polarization-free behavior are ascribed to high mobility and long mean free path of intrinsic charge carriers in graphene. At the same time, with respect to its intrinsic physical and chemical properties, there still remain challenges to the application of graphene in commercially available supercapacitors.^[60]

2.3 NEXT-GENERATION SUPERCAPACITORS ENABLED BY GRAPHENE AND ITS DERIVATIVES

2.3.1 SUPERCAPACITOR TRENDS & CHALLENGES

Since supercapacitors were introduced as energy storage devices, their limited energy density stemming from the surface-dependent charge storage mechanism has been their greatest weakness. In applications with high energy input/output required, such as in transportation and energy sectors, high-energy-density supercapacitors are expected to experience the highest growth.^[61] Electronic hardware built upon novel conducting/semiconducting materials is highly expected to enable next-level digital-based services and networking. Upcoming platforms such as the fifth generation technology (5G), the Internet of Things (IoT), vehicle-to-everything communication (V2X), etc. are calling for an momentous upgrade of global data traffic and mobile data that is compatible with the hardware and infrastructure.^[62] supercapacitors will play a pivotal part in these coming trends and, therefore, should be subject to revolutions in terms of their key electrochemical and electrical parameters. In the following sections, we discuss the most noteworthy parameters and analyze their impact on their performance. We will provide recent solutions to overcome the upcoming challenges of supercapacitors. These solutions specifically target the engineering challenges of graphene and its derivatives to meet the technical demands in capacitive energy storage (**Scheme 1**).

2.3.2 THERMAL STABILITY IN A WIDE TEMPERATURE WINDOW

In practical applications, most energy storage devices are subjected to a wide range of working temperatures. Supercapacitors placed in transportation equipment, such as vehicles, busses, or trains, and placed in industrial infrastructure, are often subject to change in climate. Additionally, energy storage components in consumer electronics often experience fluctuations in temperature due to the heat generated from silicon chip processors and other active components.^[42,43] Therefore, it is crucial to develop energy storage devices that are robust in large temperature

windows and even functional at extreme temperatures for use in military, mining, aerospace, and oil drilling applications.^[65] Technology has advanced to install thermal management and cooling systems, which can add weight and volume, as well as increase the energy consumption of the device.^[66] A better solution is to develop thermally stable energy storage devices. That is to study and improve the thermal stability of all the components of energy devices, such as cathodes, anodes, separators, and electrolytes.^[46,47] Additionally, temperature dependence, kinetic and thermodynamic aspects of the charge storage process must also be taken into consideration.^[69] Other issues that must be taken into account at elevated/depressed temperatures are side reactions between the electrode and electrolyte, electrolyte evaporation/freezing and chronic thermal localized stress.^[70]

Besides exceptional thermal conductivity, graphene is thermally stable up until 1000 °C where lattice fringes start to straighten up and single-loops appear.^[71] In the range of 200 – 400 K, monolayer graphene shows a negative thermal expansion coefficient, $(-8.0 \pm 0.7) \times 10^6 \text{ K}^{-1}$, which is fairly insignificant, meanwhile chemical stability is maintained.^[72] Given that graphene in EDLCs is solely dependent on the interface, not so much on thermal conditions, graphene serves as a reliable supercapacitor electrode at both elevated and depressed temperatures. A more challenging issue lies in the thermal behaviors of other components and their compatibility with the electrodes. One solution is to incorporate a thermally stable polymer matrix into liquid electrolyte systems. A flexible supercapacitor was fabricated based on a solid-state high-temperature electrolyte phosphoric acid (H_3PO_4)-doped poly-[2,20-m-phenylene-5,50-bibenzimidazole] (PBI) electrolyte, coupled with two freestanding rGO electrodes.^[73] The rGO shows stable and high thermal resistance, electrical conductivity, and mechanical strength. The

accelerated ion diffusion at an elevated temperature results in a high-rate capability and capacitance. At 160 °C, the device enhance the rate capability by ~40% and exhibit a capacitance of 170 Fg⁻¹ and 18.7 mFcm⁻². The high-thermal-tolerance of PBI renders the supercapacitor with strong cycling stability and flexibility retention at temperatures as high as 100 °C and above. The supercapacitor shows a capacitance retention of ~93% after 100,000 cycles. The all-solid-state configuration is able to withstand hundreds of bending cycles at angles ranging from 60 to 180°. Fe-doped MnO₂ nanofilm covered graphene composite and MoS₂ nanofilm covered graphene composites were developed.^[74] The graphene-based composite structures not only enable large interfacial contact between the active materials, but also build a strong adaptability over a wide temperature range. The supercapacitor shows that in the -20 °C to 80 °C temperature range, the capacitance increases from 21 to 119 F g⁻¹ at a current density of 2 A g⁻¹. The electrolyte of asymmetric supercapacitors is a heat-resistive non-aqueous copolymer gel. The copolymer was mixed with LiClO₄. Another work studied a free-standing electrode based on mesoporous rGO and single-walled CNTs. The work used a [1-ethyl-3-methylimidazolium (EMIM)][bistriflimide (TFSI)]-containing gel electrolyte.^[75] The rGO to CNT ratio plays an important role in the electrical and thermal conductivity and active surface of the electrode. The combination of rGO and CNT accommodate the voids caused by the thermal expansion of the electrodes which applies stress at the electrode/electrolyte interface. This stress, if untreated, increases with an increase in temperature. The flexible supercapacitor shows an areal specific capacitance of 330 mF cm⁻², and a volumetric capacitance of 2 F cm⁻³. At a wide temperature range from -40 to 200 °C, the device is able to store charge and remain flexible. Another high-temperature supercapacitor was built based on graphene aerogel electrodes and copolymer gel electrolyte containing ionic liquid-fumed silica nanoparticles (IL-FSN) with a controlled hybrid porous structure.^[76] As explained in **Figure**

2.2, as the temperature rises, the developed 3D graphene aerogel maintains its porous structure and high flexibility. The chemical stability of graphene at high temperatures also mitigates the side reactions that are likely to arise due to the intense thermal runaway resulted from thermochemical heating. Furthermore, the hydrogen bonds between the IL and FSN are diminished, lowering the electrolyte viscosity, which enhances ion diffusion rate and ionic conductivity. The capacitance is $1,007 \text{ F g}^{-1}$ at a temperature of 200°C .

In the low-temperature range, high capacitance is even harder to achieve due to depressed ion diffusion. A high specific surface area ($2,000 \text{ m}^2 \text{ g}^{-1}$) porous KOH-activated microwave exfoliated GO electrodes was assembled with a eutectic ionic liquid electrolyte.^[77] The interlayer mesoporous structure of the GO provides open channels for electrolyte ions. The ions freely diffuse into pores that have a diameter of less than 1 nm even at low temperatures. The final device shows a capacitance of 180 F g^{-1} and a wide electrochemical window (3.5 V). The supercapacitor was tested over a wide temperature range between -50°C and 80°C . It is the first study showing that a carbon–ionic liquid system exhibits over 100 F g^{-1} below room temperature. A supercapacitor is reported consisting of aligned nanoporous graphene and an eutectic ionic liquids electrolyte^[78]. The supercapacitor show high capacitance with temperature increases from -50 to 80°C . The monodispersed pore structure and well-defined ion channels between the electrode and electrolyte results in the high volumetric capacitance and ionic conductivity in the eutectic electrolyte at -50°C . The capacitance of supercapacitor shows a is 125 F cm^{-3} at 25°C and 106 F cm^{-3} at -50°C . The application of aqueous electrolytes is impeded at temperatures lower than 0°C . A polymer-based hydrogel is proved to be an effective solution due to non-freezable water around the hydrophilic polymer chains. The aqueous electrolyte is capable of maintaining its high ionic

conductivity which is the major strength of aqueous electrolytes in supercapacitors. A supercapacitor was studied based on biochar-reduced-graphene-oxide electrodes and polyampholyte hydrogel supported 3M KOH electrolyte.^[79] The rGO electrode is not only mechanically stable at low temperature but also provides superior compatibility with the hydrogel electrolyte. The fabricated supercapacitor shows a capacitance of 100 F g⁻¹ at a scan rate of 1 mV s⁻¹, a specific capacitance of 68 and 34 F g⁻¹ operating at -20 and -40 °C respectively. Another low-temperature supercapacitor was enabled by a nitrogen-doped mesopore-dominated hierarchical carbon (NMHC) electrodes and g-butyrolactone (GBL)/EMIMBF₄ binary electrolyte.^[80] The NMHC shows a sandwich configuration with mesoporous structure on two sides and microporous structure in the middle. The sandwich configuration facilitates ion transport at as low as -70 °C. The NMHC electrode exhibits a capacitance of 131 F g⁻¹ at -70 °C and 3.7 V.

2.3.3 EXTENDED FREQUENCY RANGE

Compared with electrolytic capacitors, sluggish ion diffusion and accumulation in supercapacitors are the main causes of capacitance loss at high AC frequencies. Given that the charge and discharge processes in supercapacitors involve the movement of ions through an electrolyte, they are not able to reach frequencies as high as conventional capacitors. One prevalent use of conventional capacitors is to smooth the left-over AC ripple on DC voltage busses that are found in most line-powered electronics. However, their relatively large size is a major drawback as they are often the largest components found in any electronic circuit, hindering the miniaturization and flexibility of many devices. In this regard, a supercapacitors' ability to store more than a magnitude of energy

per volume than conventional capacitors offers great advantages.^[81] When evaluating the capability of capacitors for AC line filtering, two figures of merit must be considered. One is the RC time constant at 120 Hz, which is because 60 Hz AC is full wave rectified to create a pure DC voltage. Another important parameter is the phase angle, which indicates how close to an ideal capacitive behavior a device is at 120 Hz. To design supercapacitors capable of this application, the electrode material must be highly conductive and interconnected to eliminate internal resistance. Additionally, the contact resistance between the electrode material and the current collector must be minimized. Finally, the electrodes must have an open structure consisting of large pores to avoid tortuous geometry for ions.^[82–84] In addition, the electrode must be thin ($\sim 10\ \mu\text{m}$) or ultrathin ($\sim 1\ \mu\text{m}$) to reduce charge transfer within the material. Since the main advantage of using supercapacitors as line frequency devices is their compact size, both areal and volumetric capacitance at 120 Hz are critical parameters.

Since the pioneering work of Miller *et al.*, there has been a large interest in utilizing graphene and other carbon materials as high-frequency devices. Miller reported that, almost entirely due to porosity differences, the transition between inductive and capacitive behavior happens over a decade in graphene versus seven decades in activated carbon.^[59] This indicates that tailoring the porous structure is key to achieving a high frequency response. The vertically aligned graphene sheets used in this study were grown on Ni substrates. These electrodes had high surface areas of $\sim 1100\ \text{m}^2\ \text{g}^{-1}$. The produced supercapacitors were then tested in KOH electrolyte, demonstrating a capacitance of $175\ \mu\text{F}$ and a phase angle of -82° at 120 Hz. They measured a RC time constant of less than $200\ \mu\text{s}$. This was achieved due to the high conductivity of graphene and its direct growth on a conductive Ni current collector. Moreover, electrodes comprising of vertically aligned

graphene show much higher capacitance ($50 - 70 \mu\text{F cm}^{-2}$) compared to electrodes with basal plane-oriented graphene ($3 \mu\text{F cm}^{-2}$). This was explained by the direct accessibility of edge places, which reduces ionic resistances.^[85] Unfortunately, the fabrication of these devices is costly and complicated. Recently, a more scalable method, namely an ultrathin printable graphene supercapacitor (UPSC) utilized poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) and electrochemically exfoliated graphene to demonstrate an AC-line filtering supercapacitor.^[86] These devices were fabricated by spray coating a gold coated sheet of PET and utilizing a poly(vinyl alcohol) (PVA)/H₂SO₄ polymer-gel electrolyte. These UPSCs achieved excellent cycling ability of 50,000 cycles without any capacitance loss as well as a large volumetric capacitance of 348 F cm^{-3} . Importantly, these devices were able to achieve a less than 1 ms RC time constant, exhibiting excellent flexibility and high rate capability at scan rate as high as 2000 V s^{-1} . Nitrogen-doped holey graphene can also be used in AC-line filtering applications.^[87] Zhou et al. reported a synthesis of the holey graphene by thermal annealing of polyvinylpyrrolidone (PVP), Fe₂O₃ nanorods and GO, followed by a chemical etching process. Holey graphene-based supercapacitors have improved rate performance and higher volumetric capacitance compared to pristine graphene materials.^[88–94] These devices were reported to have a fast frequency response and high capacitance of $203 \mu\text{s}$, 1.2 F cm^{-3} and $478 \mu\text{F cm}^{-2}$. The phase angle at 120 Hz was reported to be as low as -81.2° , similar to commercial electrolytic capacitors. This excellent performance is due to the synergy between the structural porosity of graphene and the N doping atoms. The electrode film consists of a more open microstructure and exhibits in-plane pores that provide open access to the electrolyte ions. The nitrogen atoms provide pseudocapacitance and enhance the electrical conductivity and create a hydrophilic surface on the electrodes. Recently, a supercapacitor using a ordered porous graphene film was fabricated.^[95] In this study, a 3D

graphene is fabricated by freeze-drying a GO suspension, followed by thermal annealing and subsequently vacuum filtering. The areal capacitance of resulting supercapacitors is $755 \mu\text{F cm}^{-2}$ at a frequency of 120 Hz, much higher than printed graphene ($179 \mu\text{F cm}^{-2}$) and electrochemically reduced GO ($283 \mu\text{F cm}^{-2}$).^[67,77] The compact and controlled pore structure not only provides more active sites but is also beneficial for ion diffusion. It can shorten the ion transmission pathway while maintaining high electrical conductivity.^[97,98] As a result, these supercapacitors can achieve ultra-high scan rates of $2,000 \text{ V s}^{-1}$ as well and exhibit an RC time constant of $< 1 \text{ ms}$. The resulting phase angle of -53° at 120 Hz is smaller than commercial capacitors (-85.5°), but exceed this of ultrathin printed graphene ($-55^\circ - 70^\circ$). Aside from the electrode design, the electrolyte solutions used in supercapacitors also play a crucial role. Many of the electrochemical capacitors used for AC-line filtering that have recently been reported are used in aqueous electrolytes due to their high ionic conductivity as compared to organic electrolytes. A major drawback to using aqueous electrolytes is that the voltage window is narrow ($< 1 \text{ V}$). Aluminum electrolytic capacitors used for filtering are often rated to 2V or higher. Utilizing these aqueous supercapacitors would require connecting multiple devices together to reach a suitable voltage, the pack of supercapacitor is bulkier and heavier. Therefore, it is more advantageous to design a high frequency devices at an extended voltage window. Chi et al, have reported a graphene-based organic electrochemical capacitor using electrochemically synthesized rGO with less defects and interconnected pores that is aligned in orientation.^[99] Small ($< 0.7 \mu\text{m}$) sheets of LGO were electrochemically reduced at -1.1V, followed by a reduction in an organic electrolyte. These devices had a phase angle of -80.5° at 120 Hz and an areal capacitance of $151 \mu\text{F cm}^{-2}$ with a voltage window of 2.5 V. Additionally, the devices had a fast response time of 0.219 ms and a high areal energy density of $472 \mu\text{F V}^2 \text{ cm}^{-2}$ at 120 Hz,.

2.3.4 SOLID-STATE ELECTROLYTE

Liquid electrolyte systems seem to set the ceiling for the safety, lifetime and energy density of supercapacitors. All-solid-state devices show many advantages compared to their liquid-electrolyte counterparts. They are inherently safer and easier to process, owing to the lack of flammable, toxic and volatile liquid components.^[100] Second, they exhibit great potential for a dramatic improvement in energy density which arises from the extension of the voltage window. Technologies based on solid polymer electrolytes offer a great opportunity to meet the flexible, shape-effective, and thermal management requirements dictated by today's electronic miniaturization while providing larger energy autonomy.^[101] Challenges in solid-state electrolyte supercapacitors lie in their limited ionic conductivity and electrode-electrolyte interface. In addition, the volumetric change that occurs during cycling is difficult to accommodate compared to liquid electrolytes.^[102] Recently, a particular interest arises in combining the advantages of both liquid and solid polymer electrolytes by the addition of liquid electrolytes to a polymer matrix to form gel polymer electrolytes.^[103]

GO has been recently demonstrated as a functional additive to solid-state electrolytes with high ionic conductivity. The abundant oxygen-containing groups in GO make it electrically insulating but allows it to have high proton conductivity. Another ideal feature is the high hydrophilicity, which allows for higher permeability to water molecules. Moreover, the functionalization of GO promises a room temperature GO based electrolyte which has highly tunable proton conductivity. For example, a poly(ethylene oxide) (PEO) polymer electrolyte studied with various amounts of GO added.^[104] A certain orientation of PEO crystal gives rise to isotropic ionic conductivity. The

addition of GO nanosheets impedes PEO crystallization, opens up ion transport channels. The ionic conductivity is increased and more anisotropic in a GO-added PEO electrolytes. Graphene was grown on a Na^+ superionic conductor (NASICON) to study the Na^+ conductivity, which causes interfacial resistance decreased by 10 times.^[105] The surface of the Na electrode after 1,000 hours of charge/discharge cycles remained smooth due to a fast Na^+ diffusion across the interface of the graphene coated NASICON and the Na electrode. The Na^+ diffusion was facilitated by a increased number of graphene defects. Another study focused on a laminated membrane realized by GO and functionalized nanocellulose composite. The hydroxide-conducting membrane serve as a electrolyte for flexible and all-solid-state zinc-air batteries .^[106] GO was decorated in a cellulose fibers network. Cross-linking reaction stabilizes the composite structure and leads to a minimum anisotropic swelling. In addition, the membrane shows high water retention after bending and closely attaches to the electrodes. At 70 °C, the membrane shows hydroxide conductivity of 58.8 mS cm⁻¹. Likewise, a recent study proposed graphene GQDs as solution-and solid-type supercapacitor electrolytes.^[107] After reacting with KOH, neutralized GQDs shows a high ionic conductivity and improved ion-donating capabilities. The resultant GQDs, used as the electrolytes, improved the capacitance and cyclic performance of the supercapacitors due to an enhanced ionization degree of the weak acidic oxygen-containing functional groups. Supercapacitors using GQD-KOH as the electrolyte shows a capacitance of 110 F g⁻¹ at the current density of 100 mA g⁻¹, which is double that of a supercapacitor using the same concentration of aqueous electrolyte. Another study reported a electrolyte with an ionic conductivity as high as 7.16 S m⁻¹. The electrolyte is prepared by cross-linking polyacrylic acid with methacrylated GO. It is able to withstands 950% strain and shows self-healing property.^[108] This novel electrolyte is fabricated into a self-healing and stretchable supercapacitors. These devices can withstand 300%

stretch. The effects of GO on widely used PVA gel electrolytes were investigated.^[109] An GO/PVA electrospun mat offers higher ionic conductivity retention after drying. The ionic conductivity only decrease by 38.4% when treated with $45 \pm 5\%$ relative humidity for a month at room temperature, compared to PVA electrolyte which decreases by 84.0%. The conductivity retention is attributed to the hygroscopicity of GO as well as the fibric mat substrate. A supercapacitor was laser scribed on the PVA/GO mat. The capacitance of laser-scribed supercapacitor is 9.9 mF cm^{-2} at 40 mV s^{-1} as shown in **Figure 2.3**.

2.3.5 MINIATURIZATION AND ON-CHIP ARCHITECTURE

With a growing demand for wireless sensor networks in applications such as household automation, transportation surveillance, health monitoring and environmental monitoring, the next-generation of electronics calls for material designs that promote size reduction, improve reliability and energy autonomy.^[110] High energy storage and conversion components are required to compensate for sufficient energy over prolonged periods of time for compact integrated circuits (IC).^[111] Thus, an increasing interest has arisen over the past decade in Microsupercapacitors (MSCs) and their integration on chips and flexible substrates.

MSCs are developed in a planar fashion in order to be integrated onto silicon wafers. The configuration designs are mainly classified into fiber/wire devices and in-plane interdigitated devices (shown in **Figure 2.4**).^[112] In fiber type devices, each of the two electrodes is coated on conductive fibers/wires which serve as current collectors. They are arranged in a parallel or intertwined configuration, followed by an electrolyte layer, separating the two electrodes. Some supercapacitors in coaxial-fiber configurations have also been introduced.^[113] The long ion

diffusion distance in fiber/cable devices can be an obstacle for fast ion transportation which is a requirement of MSCs. Yet this issue is well addressed in in-plane interdigitated electrodes, where both the electrodes are patterned on a single substrate. This interdigitated architecture is electrochemically favorable because: (i) of fast ion diffusion of electrolyte ions with reduced diffusion pathways in an in-plane ion channel (ii) the lack of a separator leads to simplified processing and (iii) the electrode/electrolyte interfacial area are maximized.

Methods including lithography and in-situ GO reduction have been investigated on the subject to pattern MSCs that are potentially compatible with IC devices. Our group, in 2012, introduced compact interdigitated rGO supercapacitors made by laser scribing.^[114] Utilizing a light-scribe DVD burner, we were able to reduce GO and produce mechanically robust rGO films with high electrical conductivity (1738 S m^{-1}) and specific surface area ($1520 \text{ m}^2 \text{ g}^{-1}$). The fabricated supercapacitor using the ionic liquid EMIMBF₄ exhibited a specific capacitance as high as 5.02 mF cm^{-2} (276 F g^{-1}) at 250 A g^{-1} and a wide potential window of 4 V. Template/mask assisted depositing/etching patterning was also studied. A MSC was fabricated by applying an interdigitated finger mask on a hybrid film of polypyrrole (Ppy) functionalized graphene and exfoliated graphene.^[115] Gold was then thermally evaporated on the surface to form a gold interdigitated pattern (widths of $210 \text{ }\mu\text{m}$, interspaces of $70 \text{ }\mu\text{m}$). After oxidative etching using a O₂-plasma cleaner, an interdigital MSC was obtained with a gold current collector and graphene composite electrodes. Due to a stacking between multiple layers of graphene and PPy-graphene, an optimal combination of pseudocapacitance and conductivity was achieved. The $5 \text{ }\mu\text{m}$ -thick solid state MSCs shows an areal capacitance of 196 mF cm^{-2} , and a volumetric capacitance of 377 F cm^{-3} at 10 mV s^{-1} using a $1.0 \text{ M H}_2\text{SO}_4$ aqueous electrolyte-immersed glass fiber separator.

Another mask-assisted assembly of interdigitated MSC used rGO and titanium carbide MXene ($\text{Ti}_3\text{C}_2\text{T}_x$) as electrodes.^[116] The 2D materials were deposited on the electrodes horizontally. When ions are transported in the electrolyte between the two electrodes, they can easily access the interlayer spaces. The minimization of ion diffusion distance and the increase of available surface area contribute to the areal capacitance of 2.4 mF cm^{-2} and volumetric capacitance of 80 F cm^{-3} with a PVA/ H_2SO_4 gel electrolyte at 2 mV s^{-1} . Printing techniques including inkjet and digital printing, have been widely exploited in fabricating flat electronics, such as MSCs. In spite of enormous progress in the printing technology, high-resolution MSCs realized by printing and a roll-to-roll production of MSCs are still very much challenging. An inkjet printed graphene MSC on silicon wafer was studied using polymer electrolytes (polyvinyl alcohol/ H_3PO_4).^[117] The fingers were $600 \text{ }\mu\text{m}$ wide, 4.5 mm long, with an interspacing distance of $300 \text{ }\mu\text{m}$. The printing technique is simple and efficient. The final devices exhibited an areal capacitance of about 0.1 mF cm^{-2} at $2 \text{ }\mu\text{A cm}^{-2}$ and stable cycling capability of over 1,000 cycles. In a similar project, a microfluidic channels based printing technique using capillary absorption of liquid inks is used to produce scalable graphene MSCs with high-fidelity.^[118] As shown in **Figure 2.5**, An imprint was first made on plastic substrates to create ink receivers and capillary channels, followed by a inkjet printing of functional materials. Applied by the capillary force, the inks flow into the neighboring channels, which generates complex patterns with high reliability. Using graphene and ion gel inks the inkjet technique gave rise to MSCs with minimum features as short as $20 \text{ }\mu\text{m}$. The MSC also show high capacitance retention over long cycling and bending cycles. An interesting method to fabricate graphene is by photochemical reduction. A photochemically reduced GO/ TiO_2 nanoparticle hybrid films results in an interdigitated MSC.^[119] The pattern was achieved using a 500 W high-pressure Hg lamp shedding UV irradiation on a customized photomask covered GO/ TiO_2 films for 4 hours

at ambient conditions. TiO_2 nanoparticles serve as a photocatalyst for GO reduction, as well as nano-spacers to mitigate graphene restacking and introduce more surface availability. The capacitance was measured with PVA/ H_2SO_4 gel electrolyte as 1.5 mF cm^{-2} and 233.0 F cm^{-3} at 2 mV s^{-1} . A 3D printed rGO MSC was explored.^[120] A rheological study revealed reversible jamming and break down of the GO ink when the shear rate is changed. Under the shear force created by extrusion the suspensions is printed as a viscous liquid. By adjusting nozzle size and suspension concentration, the resolution pattern is well controlled with the width of microfilament ranging from 250 μm to 1200 μm . The areal specific capacitance of the 3D printed MSC is 101 mF cm^{-2} at a current density of 0.5 mA cm^{-2} and 111 mF cm^{-2} at a scan rate of 10 mV s^{-1} using a PVA/ H_3PO_4 gel electrolyte.

2.3.6 OPTICAL TRANSPARENCY AND ELECTROCHROMISM

Transparent electronics have emerged as a significant category in the near future. Recent advances have revealed the use of wide-bandgap semiconductors for the realization of transparent electronic circuits. As optical transparent transistors, sensors, organic light-emitting diodes and a large group of electronic components become commercially available, transparent power sources and energy storage devices are the next milestones.^[121–124] Optical transparent supercapacitors require both optical transparency to visible light and high conductivity even often at a severe strain. These devices are designed to power optoelectronic devices such as liquid crystal displays, touch screens, and store energy from photovoltaics.^[125] In a typical supercapacitor, most components are opaque except for the electrolytes.^[126] Optical transparency is especially difficult for current collectors and electrode materials since they are intrinsic electrically conductive which usually involves a small bandgap. Thus, realizing high transparency and electrical conductivity in one material is

challenging. Approaches addressing the visibility of objects instead of intrinsic transparency are widely explored. Under normal lighting conditions, at viewing distances of 200-250 mm, the smallest object size that is recognizable to the naked eye is $\sim 0.058 - 0.072$ mm.^[127] Transparent supercapacitors can be fabricated if conductive current collectors or electrodes are downsized below this threshold.^[128] An alternative is to pattern electrodes with small features less than detection limit of the naked eye.^[129] Graphene and GO can potentially participate in both approaches.

Graphene is well known to retain a large specific area at reduced dimensions resulting from its 2D structure. In terms of optical performance, a monolayer graphene shows an optical absorption of 2.3%. In few-layered graphene, the transmittance follows $T = (100 - 2.3N) \%$, where N stands for the number of layers.^[130] Moreover, ultrafast optoelectronic response ($R_s \sim 60 \Omega \text{ sq}^{-1}$ at 97.7% transmittance for single-layer graphene) enables graphene as a strong candidate for integrated devices.^[131] Chemical vapor deposition (CVD) is widely used for the assembly of single-layer graphene, which has the highest light transmittance at any wavelength, however, pure graphene is flawed due to limited EDLC contribution. To increase the specific capacitance, transparent redox-active molecules can be added. For example, p-aminophenol (p-AP) was introduced in bilayer graphene, increasing the capacitance by almost 20 fold without adding any opaqueness.^[132] The thickness of the inserted redox materials is less than 2 nm with a transmittance of 75% at a 550 nm wavelength. The optical transmission is retained after bended to a radius as low as 5 mm. The device demonstrates capacitance of $101.0 \mu\text{F cm}^{-2}$ at a scan rate of 10 mV s^{-1} and $99.4 \mu\text{F cm}^{-2}$ at the current density of $1.8 \mu\text{A cm}^{-2}$ in 1M H_2SO_4 . Lee et al. reported that GQD can chelate graphene effectively enhancing the transmittance of the materials.^[133] As the chelation was formed between

GQDs metal ions, the GQDs binds to the graphene closely. The chelated materials have a transmittance of 92.97 % at 550 nm. With gel electrolyte PVA/H₃PO₄, the specific capacitance is 9.09 $\mu\text{F cm}^{-2}$ at 0.1 $\mu\text{A cm}^{-2}$. A graphene thin film with high electrical conductivity was realized by spin coated over different substrates.^[134] The graphene nanoflakes offer higher ion diffusion channels in the electrode, allows low fabrication temperatures at 150 °C. The electrodes show a transmittance up to 94 %. The special processing methods also lead to a slight amount of amine and carboxylic groups on graphene, which brings capacitance of the final devices up to 68 F g⁻¹ at 10 mV s⁻¹ using 1.0 M H₂SO₄. A freestanding double-layer GO film was fabricated using Langmuir-Blodgett-methods.^[135] The noncovalent interaction between wrinkled GO nanosheets and melamine is confirmed to be as strong as 1 nN. It is attributed to a combination of hydrogen bonding and charge-transfer process. The optical transmittance of double-layer GO film is 84.6% at 550 nm wavelength. The film shows a mechanical strength of 45 MPa at a 3.5% stretch. All these properties contribute to high transparency, high flexibility and long cycling life of the final device. The capacitance of the rGO supercapacitor is 197.3 F cm⁻³ at a current density of 500 mA cm⁻³ using PVA/H₂SO₄. An enhanced EDLC was studied in a Ag nanowire/PET/graphene transparent conductive electrodes.^[136] The graphene layer introduced by a facile electrodeposition process behaves as an oxidation protective layer of silver. Meanwhile, the graphene layers with the co-percolating network of laminated graphene and silver nanowires conduct the electrons with low resistance. The composite electrodes show excellent optical and electrochemical performances in **Figure 2.6**. The maximal transmittance of 90% at 550 nm. The capacitance of final devices coupled with gel PVA/H₂PO₄ is 0.4 mF cm⁻² at the scan rate of 0.1 V s⁻¹.

Graphene-based transparent electrodes also serve as a key component in electrochemical devices. Electrochromic devices can alter light transmission and reflection by employing materials with optical properties under external voltage variation.^[3] These devices are widely used in self-dimming rear mirrors, energy-saving smart windows, information displays, electronic papers and skins, smart sunglasses and many other devices.^[137] A typical electrochromic device takes a multi-layer configuration, consisting of an electrochromic electrode layer, an electrolyte layer, a counter electrode layer, two current collector layers, and optional supporting substrates in **Figure 2.7**.^[138] The charge/discharge process in electrochromic devices resembles that of a supercapacitor or battery depending on where charges accumulate. ^[134,135] Thus, electrochromic devices are generally classified as an ‘electrical thin-film energy storage device’, where a charging state is translated to optical transmittance/absorption. This correlation determines the electrochromic property using the coloration efficiency (*CE*) as the key parameter. At a certain wavelength of observation, λ , *CE* is given by

$$CE(\lambda) = \frac{\Delta OD}{Q} = \frac{\log \left(\frac{T_b}{T_c} \right)}{Q}$$

where Q is the charge state of the material per unit area, ΔOD is the optical density change, T_b is the transmittance at the bleached state, and T_c is the transmittance at the colored state.^[141] Q is positive if the color is induced by a charge insertion at the cathode site, and negative if color is induced by a charge extraction at the anode site.^[3]

However, a single-layer graphene shows limited electrochromic performance arisen from its confined optical absorption. A flexible multilayer graphene (MLG) based electrochromic device was reported.^[142] Ion intercalation in MLG leads to a interband transition between layers, which

generate electro-modulation of the materials. In the visible and near-infrared spectrum, the device yields broadband optical modulation as high as 55%. Another graphene-based electrochromic material was prepared by introducing N-doped few-layer graphene (NFLG) to poly[Ni(3-Mesalen)] film. The electropolymerized composite showed more redox signals at high current intensities compared to pristine polymer. It is attributed to larger active surface area. The NFLG contributes to mitigating polymer degradation. The composite shows yellow at its reduced state, whereas green/russet at its oxidized states. The composite also exhibits increase electrochromic stability by 71%. Furthermore, the switching time of oxidation (from the reduced state) is decreased from 11s to 9s, improved modulation from 22.1% to 35.9% and coloration efficiency from $97.2 \text{ cm}^2 \text{ C}^{-1}$ to $108.9 \text{ cm}^2 \text{ C}^{-1}$. A electrodeposition was used to reduce GO and simultaneously deposit $\text{Co}_{(1-x)}\text{Ni}_x(\text{OH})_2$ on the surface of rGO.^[143] The vertical aligned $\text{Co}_{(1-x)}\text{Ni}_x(\text{OH})_2$ nanosheets homogeneously covered rGO. The redox pseudocapacitance behavior varies by tuning the composition of nickel and cobalt hydroxide. The self-stacked rGO compositing nanosheet material exhibits a coloration coefficient of $14 \text{ cm}^2 \text{ C}^{-1}$. The electrode shows a RC time constant of 22.1 s, which is the time range for the materials to achieve 90% of its electrochromic modulation. The maximal capacitance of the fabricated supercapacitor is 112 mF cm^{-2} at 0.1 mA cm^{-2} with 1M KOH. A long-durable electrochromic supercapacitor fabricated by cellulose nanofiber, silver nanowire, rGO and WO_3 is studied.^[144] The coloration efficiency of the final supercapacitor is $64.8 \text{ cm}^2 \text{ C}^{-1}$ and electrochemical performance. It shows a mass specific capacitance as high as 406.0 F g^{-1} at 1 A g^{-1} using a PVA/ LiClO_4 gel electrolyte. After 10000 charge/discharge cycles, 75.0% of its coloration efficiency and 94.1% of its capacitance is retained. A transparent electrode is prepared based on graphene and CuS on a PET substrate with a high transmittance of over 85 %.^[145] In particular, after the electrodeposition of PANI on the surface, the composite serves as an

electrochromic supercapacitor with an areal capacitance of 17.3 mF cm^{-2} at 0.025 mA cm^{-2} using PVA/H₂SO₄, and a large optical modulation of 40.1% at 620 nm. The coloration of materials indicates a certain charge of the state in supercapacitor as shown in **Figure 2.8**.

2.3.7 DEPRESSED SELF-DISCHARGE RATE

Open circuit self-discharge is a major barrier in the industrialization of supercapacitors as stand-alone or standby energy storage devices.^[146] Electrochemical supercapacitors suffer severe self-discharge where charge storage involves unstable electrostatic interactions rather than stable phase changes that occur in batteries. Since the cell potential linearly depends on the charge accumulated on the electrodes, the self-discharge rate, in time, is determined by the potential decay procedure. In the charged state, supercapacitors are characterized with higher Gibbs free energy (G) than in their discharged state. A decline of G with time is thermodynamically spontaneous due to the increase in entropy driven by ion distribution into the electrolyte upon discharge.^[147] The G decline, manifested as a diminution of the cell voltage (or available charge) of the supercapacitor with respect to time, is determined by the discharge mechanism.^[148] The self-discharge that is predominant in supercapacitors primarily originates from three effects. First, parasitic currents at one or both electrodes lead to self-discharge.^[149] Second, in the case of overcharged cells, the charge tends to be released across the double layer, which leads to a voltage drop. Leakage currents may occur when there are faradaic active impurities in either the electrodes or electrolyte. These redox processes show diffusion-controlled kinetics given that the impurity concentration is small enough. The third effect is ohmic leakage in conductive pathways presents between two electrodes. Furthermore, studies demonstrated that a non-homogenous charging results in a self-discharge which can be attributed to the charge redistribution.^[150,151]

Graphene based supercapacitors are not particularly favorable for low discharge. Yet, graphene holds important advantages including self-discharge suppression, including modifying the electrode surface, porosity and structure engineering, hetero-atom doping and protective coating.^[148] Self-discharge is studied in a rGO symmetric solid-state supercapacitor with gel electrolyte (PVA/Na₂SO₄).^[152] The two-electrode configuration is charged to 1.2 V before the voltage holding test (VHT) and open-circuit discharge test (OCDT). The device demonstrates a high specific capacity of 110.3 mAh g⁻¹ and retains 82.3% of capacity after a 20-hour VHT with the leakage current diminishing from 0.039 mA in the first few seconds to 0.029 mA. The voltage fell to 0.7 V after one hour of OCDT. The degradation is deconvoluted into two parts of self-discharge. The first follows $V \propto t$, which is induced by ohmic leakage. The other follows $V \propto t^{1/2}$ based on a diffusion-controlled model, it results from concentration variation. It is qualitatively demonstrated that the majority of self-discharge is caused by redox active impurities and defects on rGO. A molten-salt method was introduced to prepared rGO with less defects.^[153] The product exhibited a fair amount of nitrogen dopant. Symmetric EDLC devices showed a mass specific capacitance of 130 F g⁻¹ at 1 A g⁻¹ using an ionic liquid electrolyte. In OCDT, it took 0.9 h for the molten-salt derived rGO to decrease to 2 V from its initial voltage (3 V), and another 3.4 h to reach 1.5 V. The self-discharge rate of thermally reduced rGO is higher. It took 0.36 h to drop to 2 V and 1.02 h to reach 1.5 V. The self-discharge characteristics of an rGO and Ppy nanotube composite was also studied.^[154] The areal specific capacitance of the assembled solid-state supercapacitor was determined to be 512 mF cm⁻² at 1 mA cm⁻². The device showed a leakage current at ~32 μ A. It took 24 h for the open circuit voltage of the device to decrease from 1.0 V to ~0.22 V, after charging for 15 min. Comparing the study with previous rGO supercapacitors,

regardless of experimental and characterization set-up differences, it is clear that redox reactions introduced by pseudocapacitance materials increases self-discharge in supercapacitors. A study on CNT-based supercapacitors illustrates the effects of the concentration of oxygen-containing functional groups on the surface of electrodes on self-discharge.^[155] The author contributes the voltage drop in self-discharge into two models,^[156] divided potential driving (DPD, $V \propto V_{final}e^{-t/\tau_f} + V_{initial}e^{-t/\tau_s}$, τ – RC time constant, subscript f and s simply refer to small value and large value) and single potential driving (SPD, $V \propto V_{initial}e^{-t/\tau}$). In the DPD model, the potential field is the dominant driving force. Impurities such as surface functional groups induce interactions at the electrode/electrolyte interface. These interactions lead to an SPD self-discharge. The authors proposed that the CNT electrode self-discharge transits from a DPD to SPD in various time intervals depending on its surface chemistry. By varied treatment on CNT, o-CNT with low C/O ratio and r-CNT with a high C/O ratio are obtained and tested in a two-electrode cell with 1M TEABF₄/PC. It's confirmed that all samples adopt “DPD to SPD” change both at 25 °C and -25 °C. A larger number of functional groups give rise to higher ratio of SPD with respect to the overall discharge process, corresponding to a faster self-discharge rate, as shown in **Figure 2.9**. An effective way to mitigate self-discharge was published recently. Reportedly, self-discharge of supercapacitor originated from leakage current is reduced by electrode coating with insulating materials.^[157] However, this self-discharge improvement is at the expense of the specific capacitance and energy storage density, which is reduced by 56%.

2.4 CONCLUSIONS AND PERSPECTIVES

A major objective in energy storage is to close the energy versus power gap between batteries and supercapacitors which can be seen in a Ragone plot. The development of supercapacitors that exhibit the energy density of a battery without compromising power density and cycling stability remains a fundamental challenge and barrier to make supercapacitors widely utilized as stand-alone power sources. Although approaches such as nanostructuring and chemical doping equip battery-like materials with capacitor-like kinetics, the reversibility of Faradaic reactions is limited by the structural transitions in pseudocapacitance. Furthermore, the chemical stability of pseudocapacitive donors often is limited to a confined voltage window. This is contrary to the qualification of high-voltage (>2.5 V) devices, which are endowed with enhanced energy and power density and are of greater commercial interest. From a present research perspective, graphene materials-enabled hybrid supercapacitor devices hold the best potential to reach an optimal combination of energy, power density and cyclability. **Table 2.2-2** lists the electrochemical attributes of graphene, rGO, GO and CND/GQD measured in most recent studies, compared to critical physicochemical properties that are concerned with respect to their application in supercapacitors.

Graphene has long been considered to be a game-changing material and has been extensively studied in capacitive energy storage research. So far, porosity tuning, nanostructure design and doping methods, etc. have been shown to amplify the specific capacitance of graphene-based supercapacitors on a research scale, although a scalable and cost-efficient materials processing method is still lacking. Moreover, the working potential window has been extended, with the development of solid-state electrolytes like lithium ion conducting polymers for batteries and supercapacitors.^[158] Additionally, researchers have found that graphene nanoribbons are capable

of withstanding voltages as high as 8 V; thus, it is believed that 2D graphene could serve as high-performance electrodes in high-voltage supercapacitors.^[159] High capacitance and an extended voltage window contribute to the high energy density of graphene-based supercapacitors overall. The energy density is believed to be the grand challenge when supercapacitors were first designed.

Nevertheless, a few technical hurdles are left to be overcome before graphene-based supercapacitors are commercialized. The first is the mass production of high-grade graphene with proper quality control. An extensive study on graphene production in the global market indicates that there is almost no high-quality graphene that strictly complies with the International Organization for Standardization (ISO).^[160] ISO defines graphene as containing no more than ten graphene layers.^[161] This standard is based on thermodynamic considerations which suggests that carbon atoms in ten or fewer layer graphene exhibits similar behavior to those in single-layer graphene at room temperature. However, as far as energy storage goes, if you have two layers you lose half the surface area per unit of mass and thus the energy density falls accordingly. Hence, the scaling of single layer graphene is of critical importance.

Additionally, the mechanical strength of graphene materials is proportional to the cube of the layer number. Thus, the flexibility of fewer-layer graphene is vastly different from that of thick graphite flakes. Furthermore, many manufacturers ignore proper removal of contaminants leading to a decrease in sp^2 carbon content in the sheets. Overall, the proper characterization and assessment of graphene quality has hindered applications including coatings and composite technology for existing batteries and supercapacitors that claim they are manufactured based on the numerous

merits of graphene. Thus, the emergence of graphene and other 2D materials calls for standardization of quality control and universal characterization protocols, ranging from particle size, compositional purity, and defect density of the material.

Assembly of graphene-based supercapacitors at an industrial scale is also crucial, especially on the subject of ideal loading mass. As analyzed above, a best combination of energy and power performance is developed from a large active electrochemical area to form EDLCs as well as fast electrolyte-ion diffusion over a short distance for ideal rate capability. This can be realized in thin graphene electrodes with a mass loading less than 1 mg cm^{-2} for the high available surface area. However, the lowest loading mass needed for commercial electrodes is 10 mg cm^{-2} , equal to $200 \text{ }\mu\text{m}$ thickness for sufficient areal energy density and for simple processing at good cost-efficiency.^[162] In graphene electrodes, electrochemical performance is weakened at this loading mass, not only because of decreased specific active surface area, but also due to capacitance degradation caused by insufficient charge transfer and high overpotential. Devices that have been reported to give the highest performances utilized vertical plane graphene which allows for fast ion diffusion along the sheets rather than slow ion diffusion through defects and grain boundaries in basal plane electrodes. A proportional increase of energy and power density of graphene electrodes at the scale of increasing loading mass can be achieved with pore structure design and 3D architecture at an industrial level. In addition, roll coating is the current technology used to manufacture electrodes. This process is cost effective, time-efficient and highly scalable. So far, most graphene-based devices are not compatible with manufacturing techniques in which the coated graphene will not lead to restacking of the layers. Future studies should focus on developing scalable processing techniques.

Overall, graphene has provided a new horizon in the realm of energy storage and will continue to do so until potentially revolutionizing the electronic materials market. Innovative techniques have been developed to fabricate supercapacitors with features that are required for upcoming state-of-the-art technologies. Nevertheless, graphene-based energy-storage has yet to be fully exploited due to difficulties in processing and analysis that remain to be tackled, particularly with regard to feasible production and processing techniques for high-grade graphene, with low contamination and controlled nanostructures at reasonable production costs. Further research into transportation and energy applications to achieve a comprehensive understanding of the interactions among graphene-based supercapacitor components is needed. With improved technologies, graphene-based devices will surely make a great real-life impact.

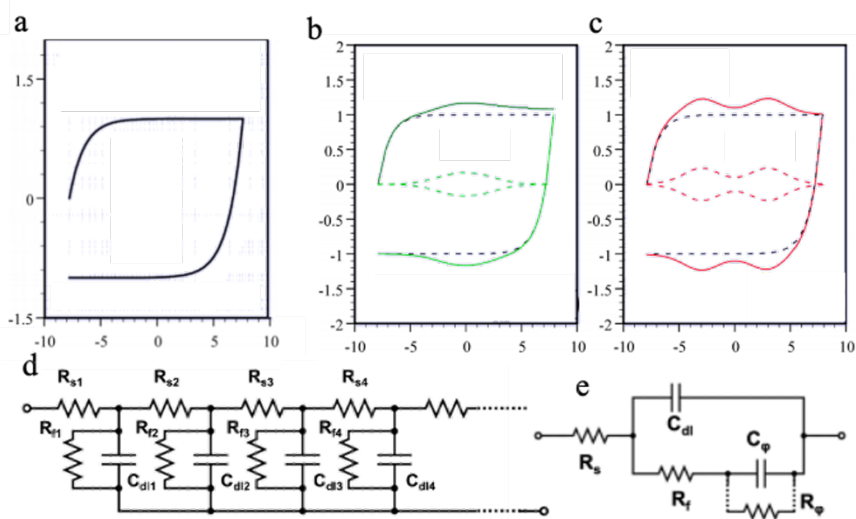
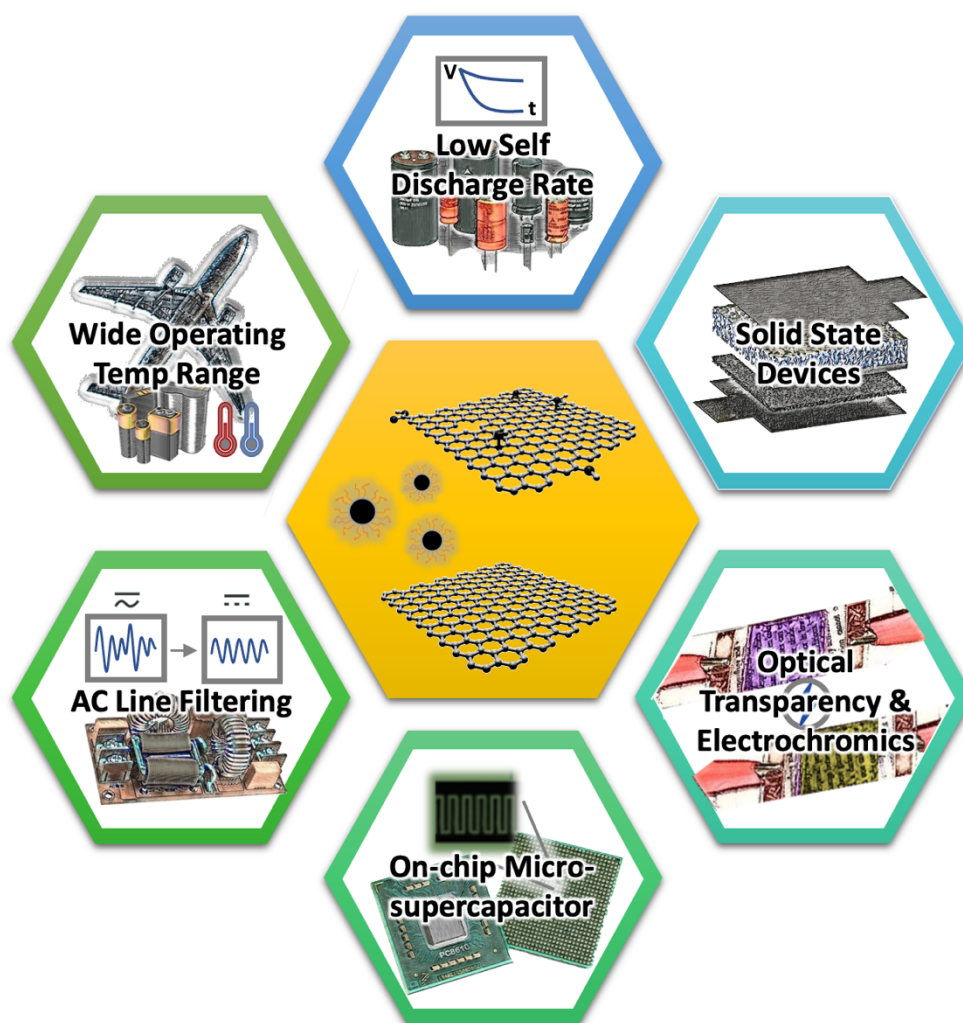


Figure 2.1 (a, b, c) Cyclic voltammetric current potential responses of EDLC, redox pseudocapacitance originated from single Faradaic surface reaction, two successive Faradaic surface reactions.^[7] Copyright 2017, ACS Publications.(d) Equivalent circuit diagram of porous high-area electrical double-layer capacitor, where R_{si} are interparticle contact resistance, R_{fi} are finite resistance of the particles and the electrolyte. (e) Equivalent circuit diagram of

electrochemical pseudocapacitor, where R_s is possible solution resistance, R_F is parallel reaction resistance, C_{dl} is parallel electrical double-layer capacitance, C_ϕ is pseudocapacitance and R_ϕ is charge transfer resistance of the Faradaic reaction.^[8]



Scheme 2.1 Graphene-based materials provide solutions for emerging supercapacitor applications.

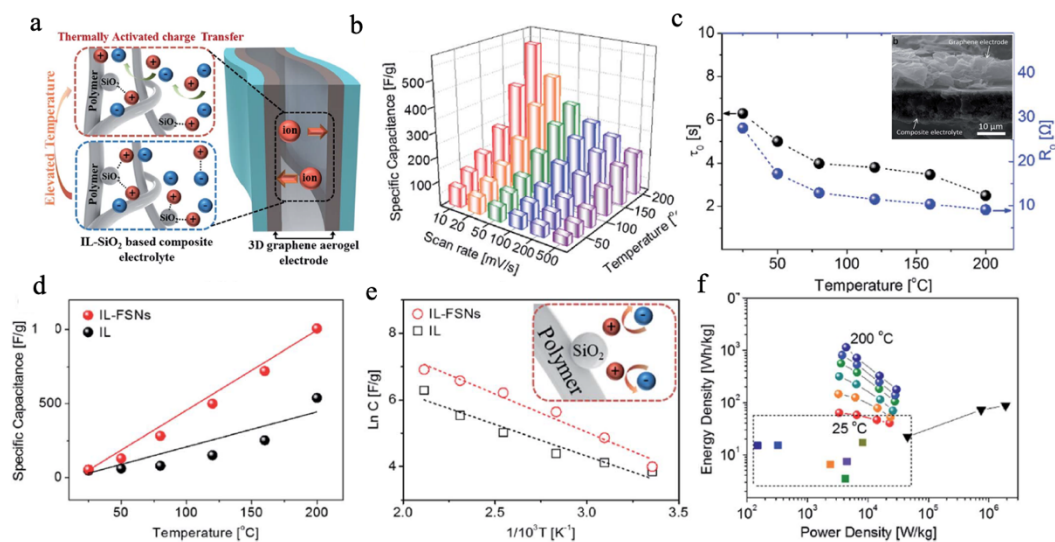


Figure 2.2 (a) Schematic view and ion transfer mechanism at elevated temperature (left) of a high temperature operation, flexible supercapacitor. (b) Specific capacitance calculated from the CV profiles vs. scan rates at each temperature. (c) Plots of resistance and relaxation time vs. temperature. (d) Plots of temperature vs. specific capacitance of the supercapacitor calculated from the CD curves. (e) Arrhenius plot of the specific capacitance calculated from the CD curves vs. inverse temperature for the kinetics of ionic transport. (f) Ragone plot of the energy and power densities according to temperatures and current densities (1, 2, 5, and 10 A g⁻¹). Reproduced with permission.^[76] Copyright 2019, RSC Publications.

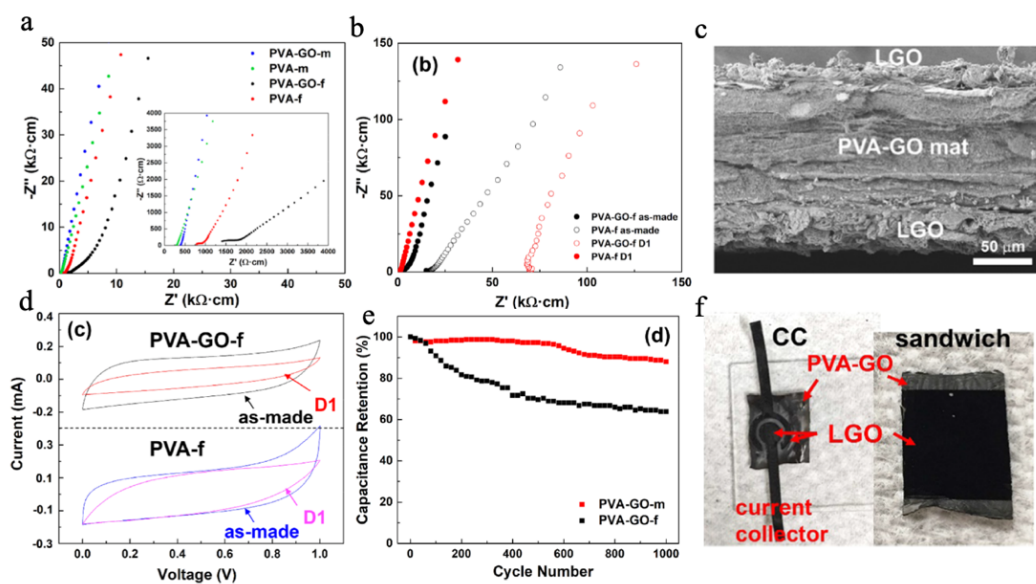


Figure 2.3 (a,b) Nyquist plots from 1 MHz to 0.01 Hz of PVA/GO mat, PVA mat, PVA/GO film, and PVA film upon saturation with 1 M H_2SO_4 ; the inset shows the zoom-in region at the high-frequency domain. Evolution of EIS images. (c) Cross-sectional SEM image of monolithic supercapacitor with sandwich geometry on PVA/GO mat; (d) and CV curves (e) of PVA/GO film and PVA film after 1 day storage. (d) Cycling performance of PVA/GO mat and PVA/GO film at the current density of 1 mA cm^{-2} . (f) photographic images of PVA-GO supercapacitors with concentric circular and sandwich geometries. Reproduced with permission.^[109] Copyright 2018, ACS Publications.

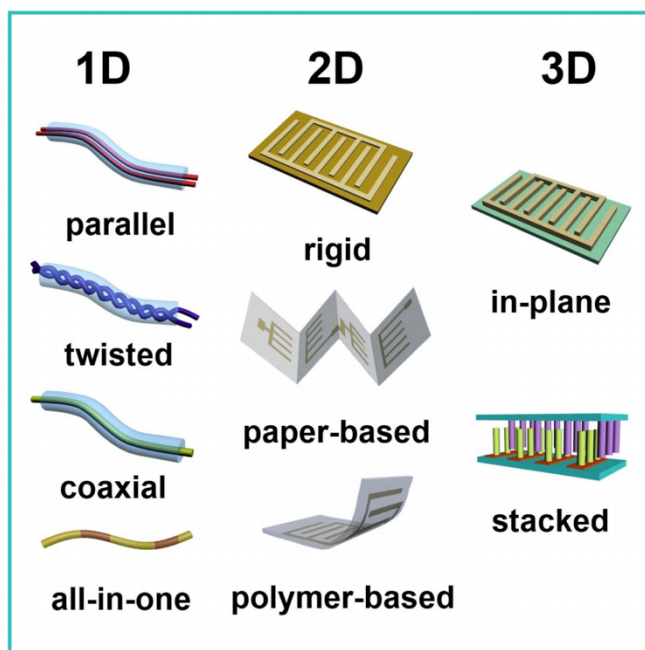


Figure 2.4 Schemes of microsupercapacitor configurations. Reproduced with permission.^[112]

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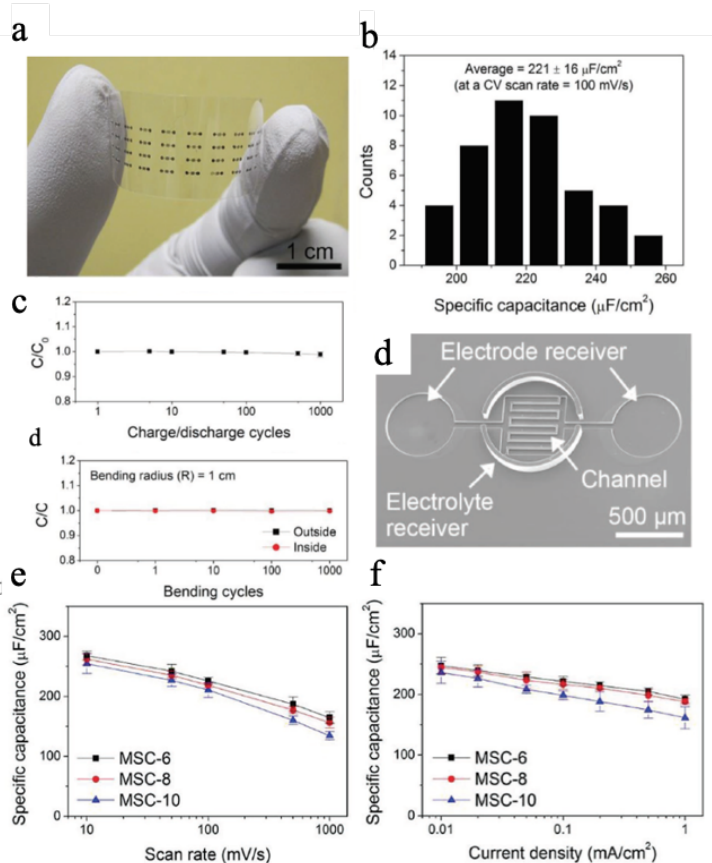


Figure 2.5 (a) Photograph of a 4×11 array of graphene MSCs printed on a flexible PET film. (b) Histogram of the specific capacitance for the 44 devices, measured by CV characterization at a scan rate of 100 mV s^{-1} . (c) Relative specific capacitance over 1000 charge/discharge cycles at a CV scan rate of 1000 mV s^{-1} . C and C_0 are the measured and initial specific capacitance, respectively. (d) Relative specific capacitance over 1000 cycles of bending the devices outside and inside the substrate at a bending radius (R) of 1 cm. (e) Specific capacitance of the devices as a function of the scan rate for the CV characterization. (f) Specific capacitance of the devices as a function of the current density for the GCD characterization. The data points in parts (e) and (f) show the average and standard deviation for five samples. (g) Tilted SEM images for g) the imprinted substrate. Reproduced with permission.^[118] Copyright 2018, Wiley.

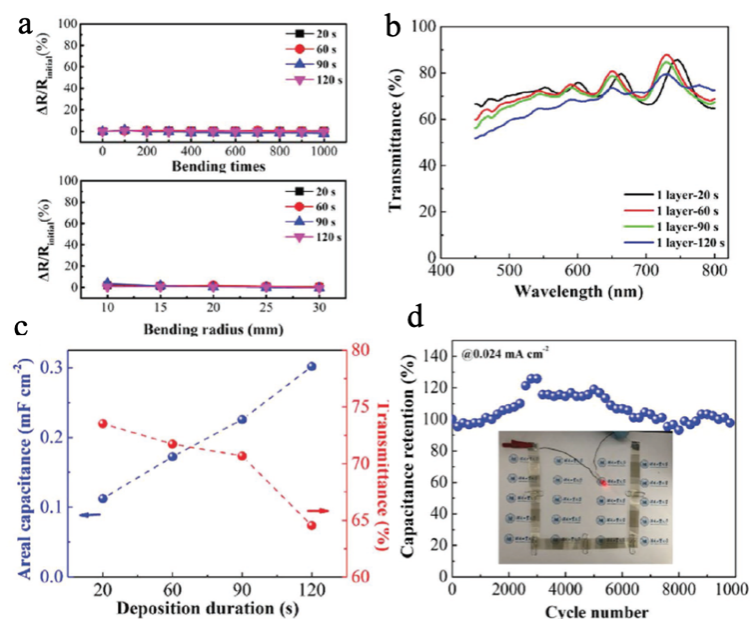


Figure 2.6 (a) Sheet resistance change of graphene@Ag nanowires/PET transparent electrode as a function of bending times and bending radius. b) Transmittance spectra of TFSC device assembled by sandwiching two as-prepared graphene@Ag nanowires/ PET electrodes with PVA/H₃PO₄ gel electrolyte. (c) Areal capacitance and transmittance of TFSC devices under various deposition durations. (d) 10K cyclic test of the supercapacitor at a current density of 0.024 mA cm⁻², and photograph of six supercapacitors in series lighting up an LED (inset). Reproduced with permission.^[136] Copyright 2018, Wiley.

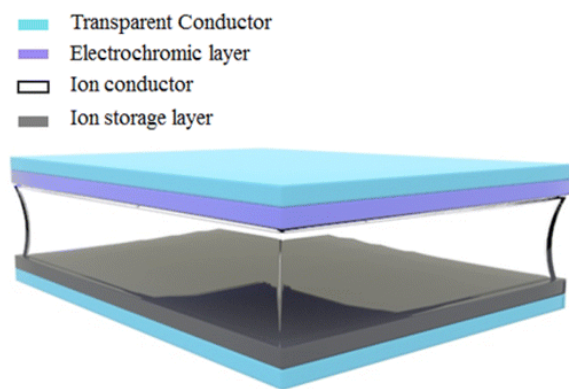


Figure 2.7 Configuration of a typical electrochromic device. Reproduced with permission.^[138]

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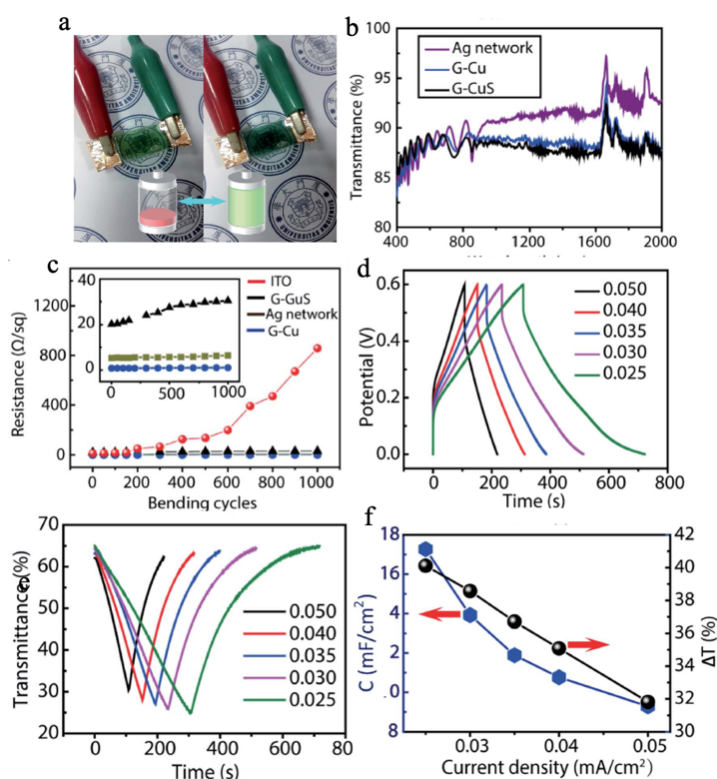


Figure 2.8 (a) The color change of a supercapacitor responds to the level of stored energy during the charge–discharge process. (b) Variations in R_s of the four different transparent electrodes as a function of the number of bending cycles with the bending radius of 0.5 cm. (c) Visible-NIR transmittance spectra of the three different transparent conductive electrodes. (d-f) Galvanostatic

charge–discharge curves (d) in the potential range of 0 to 0.6 V and corresponding in situ optical responses (e) measured at 620 nm under different current densities for the Graphene–CuS/PANI film. (f) The dependence of area capacitance and optical modulation (ΔT) on the current density. Reproduced with permission.^[145] Copyright 2017, RSC Publications.

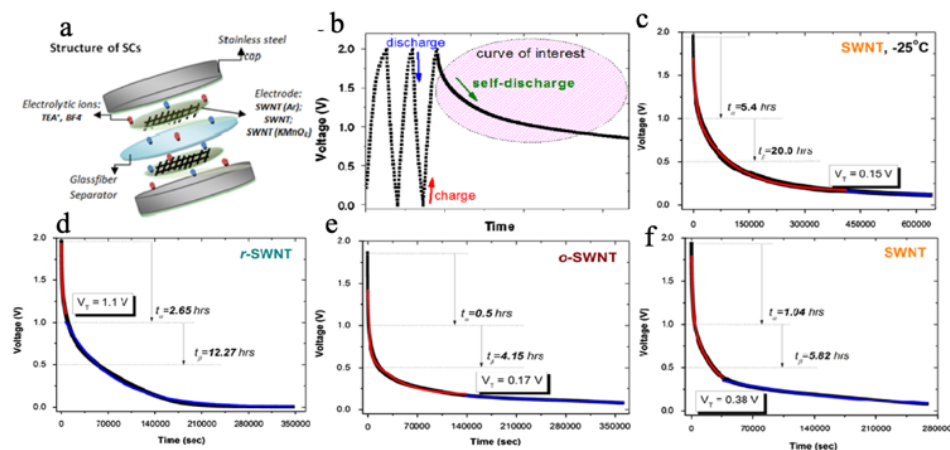


Figure 2.9 (a) Schematic of the built supercapacitors (b) The self-discharge experiments, which are carried out at two different temperatures. Reproduced with permission.^[155] Copyright 2014, Elsevier.

Table 2.1 Comparison between EDLC and pseudocapacitance.

Electrostatic or double-layer capacitance	Pseudocapacitance or supercapacitor
High-voltage operation, high-power operation.	Low-voltage operation, limited by electrochemistry

	and decomposition voltage of solvent
90° phase angle	Phase angle function of frequency, but some embodiments have transmission- line behavior
Low or zero ESR for vacuum or gaseous dielectric. Finite ESR and frequency dependence of phase angle for electrolytic capacitor	Kinetic limitation for high charge/discharge rates: hence power limited by kinetic factors
Indefinitely reversible	Highly reversible
Capacitance constant with voltage	Capacitance not constant with voltage

Has state-of-charge self-indication	Has state-of-charge self-indication
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Table 2.2 Physicochemical and electrochemical properties of graphene-based materials.

Graphene-based materials	Electrical conductivity [S cm ⁻²]	Thermal conductivity [W m ⁻¹ K ⁻¹]	Surface area [m ² g ⁻¹]	Chemical functionality	Specific capacitance	RC time constant [μs] ^{a)}	Preparation methods
Graphene	2359-6000 ^[163–165]	3000-5800 ^[166,167]	2630 ^{b)}	—	550 F g ⁻¹ , 21 μF cm ⁻² c)	200 ^[69]	Graphite exfoliation, chemical vapor deposition, surface lithographic fabrication, etc. ^[168]
rGO	80-2000 ^[169]	300-2000 ^[170]	400-900 ^[171]	-OH, -O-, -COOH, C/O ratio 4-11 ^[172]	100-200 F g ⁻¹ ^[172]	350 ^[173]	Chemical reduction(I ₂ , NaBH ₄ , hydrazine, etc.), thermal annealing(400-1100 °C), photothermal, laser, or microwave-induced pyrolysis ^[172]
GO	0.05-0.1 ^[174]	0.5-1 ^[175,176]	332-890 ^[177,178]	-OH, -O-, -COOH, C/O ratio 1.5-2.5 ^[172]	189 F g ⁻¹ ^[178] 1.5-5.4 μF cm ⁻² ^[179]	—	Brodie, Staudenmaier, or Hummer's method or their modifications ^[180]

CND/GQD	—	0.5-0.3 ^[181]	850- 1502 ^[182]	-NH ₂ , -OH, - O-, -COOH, -SH, etc. ^{d)}	230-290 F g ⁻¹ , 530-670 μF cm ⁻² ^[45]	103.6 ^[183]	Chemical cutting, exfoliation, acid oxidation; water- phase fusion, solid- state synthesis, or hydrothermal, pyrolysis ^[6,45]
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^{a)}The RC time constant reports lowest value among research thus far; ^{b)} The surface area of graphene is the theoretical value; ^{c)} The specific mass and areal capacitance are the theoretical values for single-layer graphene; ^{d)} The types of functional groups on CND/GQD surface is highly dependent on the precursors. The functional groups vary in a wide range of heteroatom containing groups.

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CHAPTER 3. CARBON NANODOTS IN CAPACITORS

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3.1 SUPERCAPACITORS AND CARBON NANODOTS (CNDs)

Electric double-layer capacitors (EDLCs) are energy storage devices in which energy is stored in a capacitive double layer at the interfaces between two high surface area electrodes and an electrolyte. Often, EDLCs are referred to as supercapacitors describing the orders of magnitude higher capacitance and lower voltage limit with respect to conventional capacitors. These are typically composed of carbon electrodes that exhibit high intrinsic conductivity and specific surface area (SSA). Their high power density enables them to complement or even replace batteries in future energy storage systems where high-power input/output is required [1,2]. The energy stored in the electric double-layer is rapidly available with high reversibility, leading to high power density and cycling stability for the overall capacitive storage [3]. Research in the past two decades has focused on tackling the limited energy density by, for example, enlarging the SSA [4] or tuning the pore size into the size regime of desolvated electrolyte ions to minimize the diffusion resistance [5–7]. Meanwhile pseudo-capacitance, where the potential changes non-linearly with respect to the extent of fractional coverage at the interface, has been studied to enhance the overall specific capacitance [8]. Pseudo-capacitive effects includes underpotential deposition of metal ions onto a different metallic electrode surface [9], redox reactions occurring at or near the electrode surface with Faradaic concomitant charge-transfer

[10,11], as well as intercalation of electrolyte ions into tunnels or layers of redox-active electrode materials without crystallographic changes [12]. The energy and power performance of a supercapacitor are evaluated by three metrics: capacitance, voltage window and equivalent series resistance. In addition, the kinetics of charge storage determines cycling life of a device. Current research efforts are targeted to meet these criteria.

Carbon-based materials are the predominant component in EDLC electrodes due to their properties such as low cost, light weight, simple processability, electrochemical inertness, and structural tunability [13]. Besides carbon, considerable progress on newly developed Faradaic active compounds, for example 2D sulfides [14], MXenes [15] and porous organic materials including MOFs [16] and COFs [17] have been reported. The benchmark for carbon-based electrodes is activated carbon (AC) which is widely used in commercially available EDLCs. However, the pore size distribution of ACs often falls into a vast range: some microporous components in ACs contain surfaces that are inaccessible to ions, while macroporous components often lower the mass density and electrical conductivity [18,19]. Besides, the activated surface area often causes electrolyte decomposition [20]. As a result, AC-based supercapacitors show limitations on energy and power density. Therefore, alternative materials such as graphene, metal compounds or conducting polymers have been investigated. Graphene, suggested as a potential alternative with extended surface area and shortened ion diffusion pathways, demonstrates high theoretical gravimetric capacitances (up to 550 F g^{-1}) [21]. However, restacking of individual graphene sheets and low packing density values ($\sim 0.1 \text{ g cm}^{-3}$) has hindered commercial use of graphene EDLCs [22].

More recently, research has begun on using the family of quasi-0D carbon-based materials known as carbon nanodots/carbon dots (CNDs or CDs) or graphene/carbon quantum dots (GQDs

or CQDs) as active components in EDLCs [23–27]. The set of acronyms describe materials with similar properties obtained via different preparation routes. A true picture of the structure of CNDs is still not available, due to the rather complicated structural analysis. A classification with respect to their chemical and electronic structure was suggested by Cayuela and colleagues [28]. For simplicity we use the term CNDs to describe any member of this family. CNDs are carbon-based particles in a size range of 1–10 nm containing a conjugated carbonaceous core and a number of functional groups on the edges. The carbon content ranges from 60 – 90%. Their properties, like high water-solubility, tunable redox activity, and rich functionalities render CNDs interesting candidates as active components in electronic devices. Typically, CNDs are synthesized by either oxidative cutting of larger graphitic carbons – a top-down approach, or carbonization of molecular precursors – a bottom-up approach. In the past few years, several concepts have been introduced to utilize CNDs in supercapacitors. These include the conversion of CNDs into high-surface area carbon electrodes and the improvement of capacitance and electrical conductivity of electrodes based on carbon, metal compounds, and/or conducting polymers. Often, CNDs help to avoid restacking of other components, improve porosity and ion diffusion, and/or enhance electron transport within the electrode materials. Due to their small size, CNDs bear intrinsically high surface areas and the potential to interact with a variety of other electrode materials, for example by increasing surface area and providing pseudocapacitive sites. In this article, we highlight these trends of utilizing CNDs in EDLC electrodes with a focus on the CND preparation methods. The terminology of the original articles has been adopted.

3.2 CONCEPTS OF CND-BASED ELECTRODES

3.2.1 CND-DERIVED 3D CARBON ELECTRODES

CNDs possess a π -conjugated carbonaceous core, often described as a single or few layers of stacked graphene sheets [23–27]. Generally, quantum confinement and edge effects become dominant when reducing the dimensions of graphene nanosheets, particularly for dimensions below 10 nm as present in CNDs [29]. Thus, CNDs usually exhibit nonzero band gaps. As demonstrated by scanning tunneling spectroscopy, downsizing CNDs widens the band gap and subsequently increases the bulk resistance [30,31]. To enable electron transport in CND electrodes, research has focused on the interconnection between CNDs or extending the π -conjugated graphitic domains, for example, by building 3D-graphenes from CNDs. To this end different strategies have been employed such as thermal annealing [32,33] laser-reduction (**Figure 3.1A**) [34,35], or electrophoretic deposition (EPD) (**Figure 3.2A**) [36–38].

In general, 3D-graphenes are desirable structures for EDLC electrodes due to their high intrinsic active surface areas for efficient double layer formation. Recently, a new method to synthesize highly conductive 3D-graphene networks from bottom-up synthesized CNDs was developed [35]. CNDs were obtained using a microwave-assisted hydrothermal reaction of citric acid and urea and subsequent thermalization at 300 °C. Using a CO₂-laser treatment, the films of CNDs are reduced in the hot focus area of the laser beam and react forming C-C bonds to create a foam-like 3D-graphene (**Figure 3.1B**). During the reaction, carboxylates, amides and other functional groups are cleaved and released in the form of gaseous reaction products forming hierarchically arranged channels in the 3D-structure. The degree of carbonization, i.e. the percent conversion into graphene, is influenced by the laser power. The achieved specific surface area

(SSA) of $230 \text{ m}^2 \text{ g}^{-1}$ is rather small compared to GO-based 3D-graphenes [39]. This is due to a high proportion of graphitic domains (multiply stacked layers of graphene) in the 3D-network and a non-negligible amount of remaining unconverted CNDs. On the other hand, the high electrical conductivities and the absence of micropores support a fast and efficient double layer formation during charging and a very good capacitive response in the high-frequency range (1–1000 Hz). The capacitive frequency window can be further widened towards high frequencies by excluding molecular oxygen from the reaction environment [34]. Highly graphitized electrodes with a low density of micropores are beneficial for their high-frequency response. For example, CND-based 3D-carbon electrodes fabricated using a relatively high laser power under argon exhibit excellent capacitive behavior at a frequency of 120 Hz, rendering these electrodes interesting candidates for AC-line filtering applications.

This aspect was pursued in a study from Liu and colleagues [36]. Here, GQDs prepared by oxidation of GO in DMF at 200°C for 8 h, were applied by electrophoretic deposition (**Figure 3.2A**), another possibility to interconnect CNDs to conductive networks, onto interdigitated gold electrodes (**Figure 3.2C**). These few hundred nanometer thick micro-EDLC electrodes showed a significant rate capability with an outstanding capacitive response at high frequencies (**Figure 3.2B**). Remarkably small RC time constants of $104 \mu\text{s}$ were obtained in a $0.5 \text{ M Na}_2\text{SO}_4$ electrolyte and $53.8 \mu\text{s}$ in an ionic liquid electrolyte.

The SSA of carbon monoliths obtained from CQDs is a crucial factor to achieve high capacitances. Using a thermolytic reduction approach, CQDs in the presence of small amounts of KOH were formed into an ultra-microporous carbon matrix [40]. Carbonization of compressed GQD/KOH pellets at 800°C yielded a carbon powder with nearly homogeneous pores of 2.96 nm average diameter, leading to a relatively high surface of $1730 \text{ m}^2 \text{ g}^{-1}$.

3.2.2 CND/CARBON COMPOSITE ELECTRODES

Another effective method to boost the intrinsic conductivity of CNDs is to composite them with other carbon materials. In turn, CNDs are considered a valuable electroactive additive for carbon electrodes. Mechanically dispersing CNDs into 1D or 2D materials helps prevent their potential collapse or restacking with cycling and simultaneously enlarges the SSA. Also, CNDs provide Faradaic reaction sites through insertion of heteroatoms and introduce versatile functionalities that are favorable for their performance in EDLCs. In carbon electrode materials, heteroatom (e.g., B, N, P, S) doping tends to improve the electrochemical activity in EDLCs. It has been demonstrated that heteroatom doping effectively lowers the intrinsic resistance, enhances hydrophilicity (wettability in aqueous electrolytes), and introduces redox active sites for pseudo-capacitance [41]. However, the resulting structural defects attributed to atom size and electron density differences alter the physical properties of the active material [42].

CNDs as additives. GO is widely used as a starting material for graphene electrodes and typically exhibits high SSAs and high gravimetric capacitances. For example, the capacitance of reduced GO (rGO) based electrodes was drastically increased by mixing GO and CDs in a ratio of 1:5 and then applying hydrogen plasma reduction [43]. Notably, the electrochemical parameters such as minimum phase angle, internal resistance, and capacitance were significantly improved with respect to pure rGO electrodes. In a similar manner, the capacitive properties of 3D-graphene from GO was improved by simultaneous hydrothermal reduction with N-CDs, synthesized in a hydrothermal reaction of citric acid and ethylenediamine at 200 °C [44]. Thereby, significant enhancement of the gravimetric and areal capacitance was achieved. Similar results were obtained by Xu and colleagues upon photoreduction of a mixture of graphene oxide (GO) and GQDs in an ammonia atmosphere [45]. Using the abovementioned CO₂ laser reduction

process, it was found that upon reduction of a homogeneous CND/GO precursor mixture, the resulting 3D-graphenes exhibit higher bulk conductivities due to a patching effect of the CNDs during the laser reduction [46]. As a result, the SSAs, and thus, the capacitance, increase. Moreover, upon addition of CNDs, the capacitive frequency window shifted towards higher frequencies and the minimum phase angles were lowered, causing less energy loss during operation of the capacitors.

A similar positive effect was observed by Kumar and colleagues upon adding CDs to AC electrodes. Subsequently, the CDs were introduced into the pores of the AC by further sonication of the AC dispersed in the CD solution [47]. Additional active sites and charges provided by the CDs were likely responsible for the increase in the capacitance of 134%. The same principle applies for GQD/carbon nanotube composite electrodes in EDLCs where the addition of GQD caused a 200% improvement in capacitance [48].

Particularly for flexible micro-EDLCs several examples demonstrate the improvement of the device parameters [49–51]. Due to their intrinsic flexibility, 1D and 2D carbon materials such as carbon nanofibers, carbon nanotubes or graphene are candidates for fabric and wearable EDLCs [52,53]. Li and colleagues integrated CDs and GO into CND-reinforced graphene fibers via a microfluidic strategy and subsequent thermal treatment at 1000 °C [49]. The SSA of the flexible electrode was increased from 245.6 to 435.1 m² g⁻¹ and the CDs contributed 22.1% of the capacitance improvement. CDs also contributed to the improvement of the SSA in graphene hydrogels [51]. In this 3D arrangement, CDs effectively prevented aggregation of the graphene sheets and guaranteed a long cycling life for the final flexible supercapacitor.

3.2.3 CNDS AS PSEUDO-CAPACITIVE REACTION SITES

In a number of studies the positive effects of CNDs on the performance of capacitors has been directly attributed to their potential to serve as pseudo-capacitive reaction sites. In a typical example N-O-GQDs were electrophoretically deposited onto a metal–organic framework (cZIF-8) decorated carbon nanotube (CNT) – N-GQD@cZIF-8/CNT – nanocomposite (**Figure 3.3A**) [55]. In contrast to the pure N-GQD@cZIF-8/CNT electrode, the hybrid electrode containing N-GQD shows two distinct, reversible redox peaks in the cyclic voltammograms attributed to reversible Faradayic charge transfer at the N-GQD (**Figure 3.3B**). The same strategy was utilized to benefit from the synergetic effects of N-doped GQDs (N-GQDs), carbon nanotubes, and a carbon cloth (CC) mesh to obtain a high SSA hierarchical all-carbon structure [54]. These meshes were then fabricated into flexible EDLCs in which energy density and internal resistance were improved by the presence of the GQDs.

Pseudocapacitive reaction sites can also be introduced in the form of redox-active electrolytes. Due to the solubility of some CNDs in polar solvents, they are a well suited material. In a specific study on the influence of GQDs in the electrolyte system, Zhang and colleagues verified a significant increase of the capacitance in the presence of GQDs [56]. Here, GQDs were obtained by harsh chemical oxidation of graphite oxide. Thermally reduced GO (at 1050 °C) was used as a standard electrode material and GQD solutions or GQD films were used as electrolytes. The capacitance was found to be significantly higher in a neutralized aqueous solution which was explained by a full ionization of the oxygen-containing functional groups.

3.2.4 CND/METAL-COMPOUND ELECTRODES

Rich functional groups at the edge of CNDs provide nucleation sites for metal-based nanocrystals. A number of metal-based nano-composites with CNDs for charge-transfer applications have been reported, as described in a recent review [23]. Metal compounds, such as MnO_2 or RuO_2 , have been thoroughly studied as active materials in EDLCs. Although they often facilitate an efficient double layer formation, they contribute mostly in the form of pseudo-capacitance. Often, two or more redox states of the metal centers in the metal compound (e.g., Mn(III) and Mn(IV)) serve as active sites for Faradaic charge transfer.

The use of small CNDs as a starting material for carbon electrodes prompts the exploration of fabrication routes towards homogeneously distributed composite materials with high SSA, high conductivity, and Faradaic reaction sites to increase the overall capacitance. Researchers have developed multiple chemical routes to embedding pseudo-capacitive metal compound nanostructures such as alloys, oxides, or hydroxides to enhance the overall capacitance of CND-based carbon electrodes. On the other hand, CNDs have been used to stabilize metal compound nanoparticles to expose their surfaces to the electrolyte and improve their capacitive performance and lowered the internal resistance. Metal compound/CND nanocomposites include, for example, CND-decorated orthorhombic V_2O_5 nanobelts [57], Ni-Zn phosphates [58], Fe_3O_4 -Hallowsite nanotubes [59], GQD/ CuCo_2S_4 nanocomposites [60], CD-stabilized Fe_3O_4 nanoparticles [64], or GQD decorated NiCo_2S_4 nanowires [61]. A few examples are highlighted in the following sections.

3.2.5 CND-DECORATED METAL COMPOUND STRUCTURES

An early study demonstrated the efficient use of CQDs in a composite with RuO₂ [62]. CQDs were prepared by oxidative cutting of nanographite and subsequent thermal reduction at 250 °C. Amorphous RuO₂, at a weight percentage of 41.9 wt%, was thoroughly mixed with the reduced CQDs. The oxygen containing groups on the CQDs helped to interconnect with the RuO₂ particles and facilitate efficient charge transfer. In comparison to pure RuO₂ electrodes, the hybrid exhibited superior performance in terms of rate capability, capacitance retention, specific capacitance, and frequency response. In a study by Xu and colleagues, δ -MnO₂ nanoflowers were decorated with 10 wt% CQDs by sonochemical mixing (**Figure 3.4**) [63]. The CQDs in the composite caused a higher accessible SSA and helped to improve the specific capacitance, as shown in the cyclic voltammogram in **Figure 3.4C**. Moreover, pseudo-capacitive contributions and a reduction of the internal resistance of the device were observed.

3.2.6 CND-STABILIZED METAL COMPOUND STRUCTURES

This kind of stabilizing effect of CQDs to preserve the surface of metal oxides was also used, for example, during the formation of α -MnO₂ nanowires from a Mn salt mixture [65]. The presence of CQDs on the surfaces of the MnO₂ nanowires increased the SSA, improved the wettability and thus the electrochemical performance. Similarly, CQDs were used to stabilize porous NiCo₂O₄ spheres and other particle morphologies [66,67], where the electrochemical parameters such as rate capability and capacitance were significantly improved with respect to pure NiCo₂O₄.

Aside from metal oxides, metal hydroxides, sulfides, carbides and nitrides also display pseudo-capacitive behavior under rational design. For this class of materials, CQDs were even used as structural directing agents, for example, during the formation of Ni–Al layered double hydroxide (NiAl-LDH) or $\text{Ni}(\text{OH})_2$, highly pseudocapacitive materials [68,69]. In the presence of CQDs, the thermal reaction of a nickel salt yielded $\text{Ni}(\text{OH})_2$ nanoflowers, while nanoplates with significantly lower surface areas were obtained in their absence. The CQDs helped to prevent degradation during cycling and decreased the internal resistance of the CQD/ $\text{Ni}(\text{OH})_2$ electrodes.

Other high SSA metal compound nanoparticles have been demonstrated to be stabilized by CNDs in a core-shell fashion. De and colleagues developed 3D core-shell nanoparticles where a layer of CQDs/carbon stabilized a copper sulfide core [70]. The nanoparticles were prepared in a simultaneous hydrothermal reaction of glucose and ascorbic acid, as precursors for CQDs, and the precursors (Cu salts) for copper sulfide. This arrangement prevented the CuS from aggregation and thus improved the specific capacitance by a factor of 1.5 with respect to pure CuS nanoparticles.

A stabilizing effect of a different kind is the embedding of metal oxide nanoparticles into a carbon network made from CNDs. Again, using the laser-reduction method small size Fe_2O_3 nanoparticles were finely dispersed in a 3D-graphene matrix (**Figure 3.5**) [71]. The accessible SSA of the 3D-graphene was increased with respect to pure CND derived 3D-graphene without Fe_2O_3 nanoparticles. Notably, higher concentrations of Fe_2O_3 nanoparticles led to a decrease of the SSA.

3.3 CND/CONDUCTING POLYMER COMPOSITE ELECTRODES

Conducting polymers, such as polypyrrole (PPy) and polyaniline (PANI) exhibit large charge density and high intrinsic conductivity in the doped state and are obtained by simple processing methods [72]. Faradaic electron transport takes place when the polymers switch between doped states with electrolyte ions. Therefore, higher capacitance can be achieved by increasing the doping level. However, this also leads to large volume changes or swelling during operation often causing mechanical failure after several cycles. Both polypyrrole (PPy) and polyaniline (PANI) have been studied in combination with CNDs as active electrode materials. Because these polymers show low conductivity in the reduced state and a low capacitance under negative potentials, the resulting composites are mostly employed as positive electrodes in asymmetric capacitors. The functional groups on CNDs either form covalent bonds or interact non-covalently with the conducting polymers.

The effects of CDs on conducting polymers in EDLC electrodes were studied by Devadas and colleagues [73]. To this end, composites of both PPy and PANI with CDs were synthesized by *in situ* oxidative polymerization. In both composites the presence of CDs enhanced the conductivity, the capacitance, and most importantly, the cycling durability of the polymers. In an aqueous NaCl electrolyte, the capacitance of PPy@CDs (1:1) and PANI@CDs (1:0.4) were significantly higher compared to pristine PPy and PANI.

3.3.1 POLYPYRROLE

Zhang and colleagues verified a positive contribution of CDs by designing a composite of GO, CDs, and PPy [74]. Mixtures of GO and CDs in equal amounts were simultaneously reduced at

150 °C. The oxidative polymerization of PPy was then carried out in the presence of the reduced GO/CD hybrid. Besides increased capacitance, the CDs were found to enhance the intrinsic conductivity and dielectric properties of the material.

In another approach, Jian and colleagues attached CQDs to PPy nanowires by electrostatic self-assembly [75]. The CQDs in this study were produced by electroablation of graphite rods in water. The open network structure composed of the CQD-coated PPy nanowires was reported to stabilize the polymeric backbone while increasing the SSA. The composite electrode showed higher capacitance and a rate capability increased by 50 times compared with the PPy electrode. Similar composites were obtained in a one-step electrochemical deposition of CQDs/PPy composite films onto a stainless steel wire mesh [76]. Here the polymerization and electrodeposition were carried out simultaneously in one step (**Figure A**). The product was fabricated into an all-solid state flexible EDLC by using stainless steel wire meshes as current collectors and PVA/LiCl as the electrolyte. Thereby, high areal capacitances were achieved with a highly improved rate capability with respect to pure PPy.

3.3.2 POLYANILINE

Zhao and colleagues embedded CQDs, obtained by electrooxidation of nanographite, onto an interconnected network of PANI nanowires [77]. A flexible EDLC was constructed using carbon fiber (CF) paper as the current collector and polyvinyl alcohol gel as the electrolyte, exhibiting a stable capacitive performance in both a planar and a bent state (**Figure B**). The CQDs improve the conductivity of the electrodes and reduce swelling during cycling. Direct addition of GQDs, obtained via oxidative cutting of graphite, to the oxidative polymerization of aniline leads to the formation of a nanofibrous PANI/GQDs composite, as demonstrated by Mondal and colleagues

[78]. Due to high mechanical strength within the conducting polymer chains and the small unit size of CNDs, composites of these two are interesting candidates for flexible supercapacitors.

3.4 CONCLUDING REMARKS AND FUTURE PROSPECTS

CND-based EDLC electrodes, although emerging later than those derived from graphene and activated carbon, are considered significant candidates for commercial applications. Along with recent developments towards miniaturized, flexible, transparent, and/or biocompatible EDLCs for rapid power supplies, CNDs are emerging as versatile building blocks for many other potential applications. In light of studies to push the limits of energy density, power density, and cycling life in EDLCs and to understand the capacitive charge storage mechanism in porous carbon materials, CNDs show great promise for rational electrode design. So far, thermal annealing, electrodeposition and laser-reduction are the predominantly used processing techniques. It is expected that, by smart experimental design and theoretical simulation, CNDs can contribute to understanding capacitive charge storage and ion diffusion on a molecular level because of their distinct domain size and tunable bandgaps and redox potentials. Moreover, due to their small size, CNDs are potential candidates for the preparation of highly uniform carbon/metal compound composites. Coupling small-sized CNDs with well-defined metal compound nanocrystals may support a more effective utilization of redox reactions and psuedo-capacitive effects in composite materials. Noteworthy is that CNDs immobilized on compound structures or used as stabilizers have been found to improve device performances in terms of capacitance (energy density), cycling retention, and/or minimizing charge-transfer or internal resistance. Note that most of these studies were carried out in aqueous electrolytes in which CNDs are often soluble. Therefore, the role of CNDs in the devices should be reconsidered as

they may very well act as solid state electrolytes. Furthermore, particularly interesting is the potential of stabilizing the redox chemistry of conductive polymers with CNDs as additives or in composites. Conducting polymers have been considered in energy storage devices for a long time, however, structural degradation during cycling has hampered their efficient use.

To be utilized in EDLC electrodes, the intrinsic properties of CNDs should be further investigated through chemical and structural design (see **Error! Reference source not found.**).

For example, the potential of increasing capacitance by incorporating pseudo-capacitive CNDs is huge, however, their structural properties are hardly understood. Redox reactions stemming from heteroatom doping is restricted to aqueous electrolytes. In fact, most works investigated CND-based electrodes in aqueous electrolytes due to their high ionic conductivities. However, it is also worth examining interactions between organic electrolytes or ionic liquid electrolytes with CNDs over a wider working potential window. For example, in organic electrolytes intrinsic charges on the CNDs and strong π -stacking interactions lead to vast effects on the active frequency window, which opens possibilities to utilize CND-based electrodes in AC line filtering applications. The mechanism, however, is still poorly understood (see **Error! Reference source not found.**). As often found in the field of supercapacitors, a systematic filtering model to extract survey information is needed to select an energy storage device with the best configuration of energy, power and stability performance.

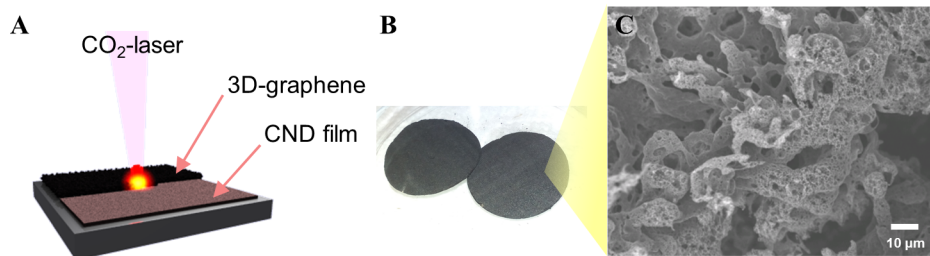


Figure 3.1 Laser-reduced CND electrodes. **A)** Illustration of the CO₂-laser assisted conversion process for converting CND films into 3D-graphene or 3D-carbon; **B)** Photograph of two laser-reduced CND electrodes for assembly in symmetric capacitors; **C)** Scanning electron micrograph of a 3D-graphene obtained from laser conversion of a CND film.

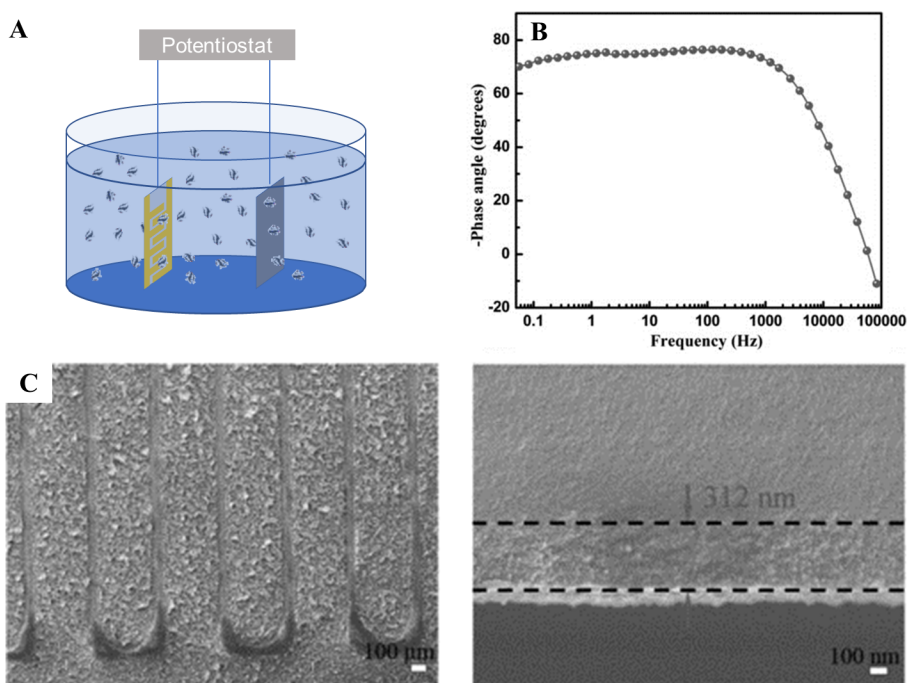


Figure 3.2 Electrophoretically fabricated GQDs electrodes. **A)** Schematic illustration of the electrophoretic deposition of GQDs on interdigitated electrodes to prepare GQDs//GQDs micro-supercapacitors, **B)** SEM images (top view and side view) of the interdigitated electrodes after the deposition of GQDs.

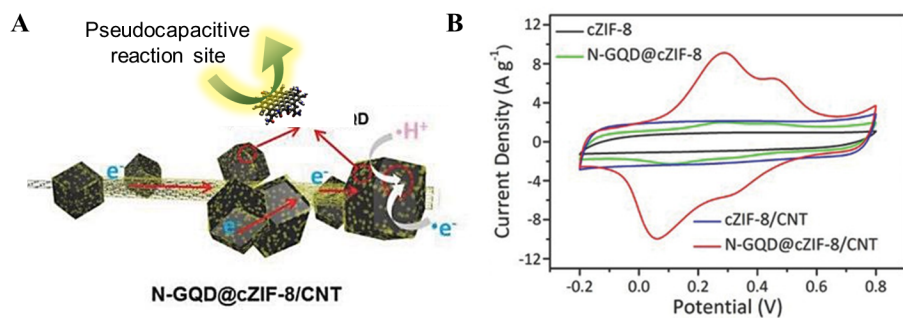


Figure 3.3 Preparation of electrophoretically deposited GQD as pseudocapacitive reaction sites.

A) Schematic illustration of a N-GQD@cZIF-8/CNT composite facilitating electronic transport, and the proton-coupled electron transfer mechanism at the surface of N-GQD; B) Cyclic voltammograms of cZIF-8/CNT and N-GQD@cZIF-8/CNT electrodes. The electrodes containing N-GQD show distinct redox features.

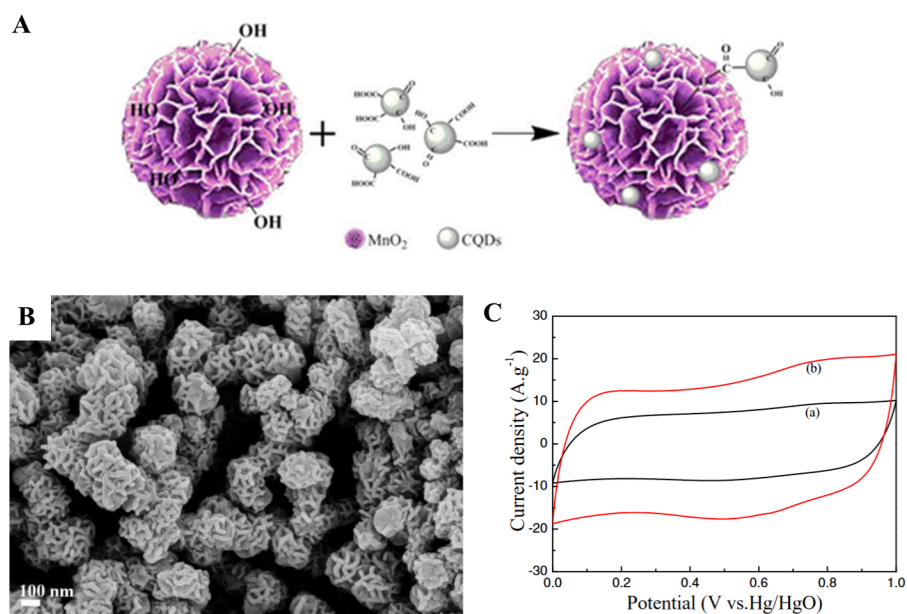


Figure 3.4 Illustration of the GQD decorated nanoparticles. The presence of GQD increases the SSA of the MnO₂-nanoflowers A: Schematic representation of the preparation route for

CQDs/MnO₂ nanoflowers. **B:** Scanning electron micrograph of CQDs/MnO₂ decorated nanoflowers.

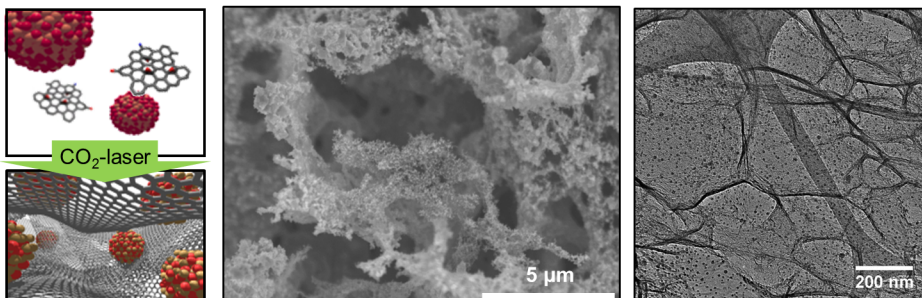


Figure 3.5 A: Illustration of the laser-induced reduction of a precursor slurry containing CNDs and Fe₂O₃-nanoparticles into Fe₂O₃-nanoparticle decorated 3D-graphene. **B:** Scanning electron micrograph of Fe₂O₃-nanoparticle decorated CND-derived 3D-graphene; **C:** Transmission electron micrograph of Fe₂O₃-nanoparticle decorated CND-derived 3D-graphene.

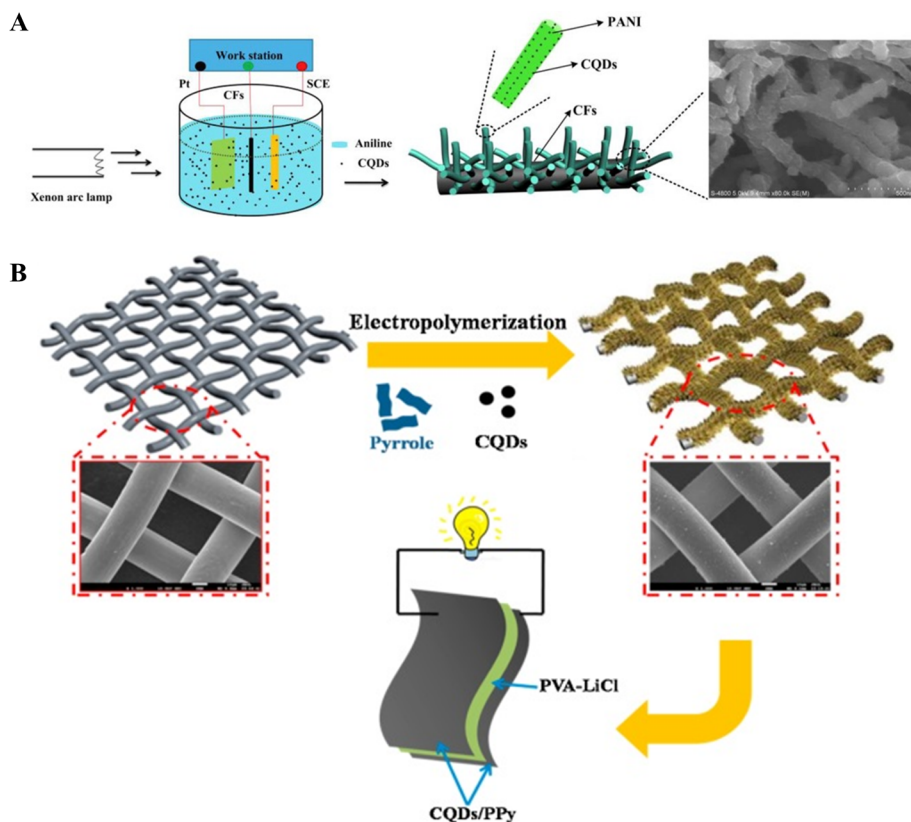


Figure 3.6 Fabrication of CQD decorated PANI or PPy flexible EDLCs. **A:** Schematic illustration of the electrochemical fabrication of CQDs-PANI/CF; **B:** Schematic illustration of the electrochemical fabrication of CQDs-PANI/CF.

GLOSSARY

Asymmetric capacitor: different electrode materials for the two electrodes are used.

3D-graphene: a three-dimensional network of pure carbon sheets.

AC: activated carbon, a highly porous carbon made by oxidative treatment of carbonized organic materials.

Capacitance: the ability to store electrical charge in a capacitive fashion. It is either normalized to the mass of the electrode material (**gravimetric**), or in the case of micro-EDLCs, the volume (**volumetric**), or the area (**areal**) of the electrode.

CNDs or CDs: carbon nanodots, an acronym mainly applied when a bottom-up synthesis is used.

EDLCs: Electric double layer capacitors including supercapacitor or ultracapacitors, which are commonly used names for EDLCs with high energy density.

GQD or CQD: graphene or carbon quantum dots, an acronym mainly applied when a top-down synthesis is used.

GO: graphene oxide.

Internal resistance: is the resistance of an energy storage device specifically when it serves as a power source. When the energy storage device delivers current, the measured voltage output is lower than the no-load voltage caused by the internal resistance.

Micropores: pores with a width of <2 nm; Micropores contribute to the series resistance of the device by diffusion resistance.

Mesopores: pores with a width of ≤ 50 nm.

Macropores: pores with a width of ≥ 50 nm.

Micro-EDLCs: In contrast to a sandwich-type arrangement for conventional EDLCs, micro-EDLC's are mostly arranged in a horizontal fashion in the form of interdigitated electrodes, for application in thin-film electronics.

N-GQD: Nitrogen-doped graphene quantum dots, GQDs with a considerable content of nitrogen containing groups such as pyridinic-N, pyrrolic-N or amines and amides.

Phase angle: In an EDLC, the phase angle is $\geq -90^\circ$ and describes the phase advance of the voltage to the current signal. Phase angles of $> -90^\circ$ are caused by energy dissipation through device resistance and also impact the curve shape in cyclic voltammetry.

Pseudocapacitance: is caused by Faradaic charge-transfer reactions in an electrode of an EDLC [58,59]. Both Faradaic and non-Faradaic charge storage are governed by the correlation that current is proportional to the charge/discharge rate. The total charge stored in a capacitive process should be linear to potential in the working potential window [60].

Rate capability: The energy storage performance in dependence of the charge or discharge speed.

RC time constants: are determined by the product of resistance (R) and the capacitance (C) at a given frequency and relate to the frequency at which the electrical response of a device switches from resistive to capacitive.

Relaxation time: The relaxation time is calculated from the frequency at which the electrical response of a device switches from resistive to capacitive at a phase angle of -45° according to

$$\tau_0 = 1/f_0.$$

Specific surface area (SSA): the surface area of the electrode exposed to the electrolyte.

Typically the SSA is determined using the BET adsorption method. The theoretical SSA of graphene is $2630 \text{ m}^2/\text{g}$.

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CHAPTER 4. A SIMPLE ROUTE TO FUNCTIONALIZED POROUS CARBON FOAMS FROM CARBON NANODOTS FOR METAL-FREE PSEUDOCAPACITORS

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4.1 INTRODUCTION

Supercapacitors are known for their exceptional characteristics: high-power density and extended cycle life. However, their energy density, representing their capacity to store charge, remains relatively poor compared to other energy storage devices. Commercially available supercapacitors have cell-level energy densities of approximately 10 W h kg^{-1} ($5\text{--}8 \text{ mWh cm}^{-3}$), which is only a quarter of that stored in lead-acid batteries ($20\text{--}35 \text{ W h kg}^{-1}$ ($40\text{--}80 \text{ mWh cm}^{-3}$)).¹ Therefore, it is critical to explore electrode materials with much-increased energy densities to make supercapacitors more comparable to batteries. One approach gaining considerable attention is the investigation of non-metal electrodes, such as various forms of carbon and organic molecules. These materials offer advantages, including a positive impact on environmental sustainability and reduced reliance on natural resources.² To further enhance the energy density of supercapacitors, a promising technique involves introducing redox-active moieties into carbon materials. This approach increases the overall capacitance and gives rise to low electrode density, improving cell-level gravimetric energy density.³

However, most redox-active moieties possess electron-withdrawing effects that can impede the electrophilic substitution reaction of aromatic rings.⁴ This leads to sluggish and irreversible redox processes, ultimately resulting in short cycle life and poor Coulombic efficiency.⁵ Among all atom-centred radicals, sulfonyl radicals, which have unpaired electrons delocalized on the S=O bonds, exhibit a remarkable electron transfer rate constant of up to $9.3 \times 10^3 \text{ s}^{-1}$.⁶ This value is seven orders of magnitude greater than that of other organic redox chemicals. Sulfonyl radicals undergo rapid and reversible redox reactions in which they can be converted into oxosulfonium cations or sulfoxide reversibly.⁷ This unique characteristic makes sulfonyl materials the ideal electrode candidates for energy storage devices, as they offer excellent cycling stability and kinetics. Nevertheless, their low electrical conductivity limits the application of sulfonyl-anchored electrodes.⁸ This issue can be resolved by regulating the cross-diffusion rate of the surface-confined redox active species by covalent bonding with well-defined graphitic scaffolds. By accompanying the electron-withdrawing redox species with π -extended conjugated domains, the opposite charges will attract each other electrostatically to reduce electrode localization.⁹ The lowered HOMO-LUMO gap of redox species accelerates the electron migration kinetics of the charge transfer events, leading to improved power densities in the resulting pseudocapacitors¹⁰

Herein, we present a metal-free pseudocapacitor based on sulfonyl porous carbon foams, exhibiting excellent rate capability and extended cycle life. To promote electron coupling between the sulfonyl groups and the conjugated domains, we employ a novel bottom-up approach involving laser irradiation of sulfonated carbon nanodots (SCNDs) in a single rapid step. The resulting pseudocapacitive electrodes demonstrate enhanced redox kinetics and structural stability. The three-dimensional (3D) porous carbon (3D-tsSC) foams with functional groups promise uniform electron and ion diffusion across various loading densities. Notably, these electrodes achieve a

high specific capacitance of 157.6 F g^{-1} at 1 A g^{-1} , that can be attributed to the fast and reversible redox reactions of the sulfonyl groups. The electrodes maintained an impressive 97.4% of their original capacitance after 15,000 cycles at 10 A g^{-1} . The laser-converted turbostratic graphitic domains facilitate seamless interactions with the redox species, resulting in excellent rate capability for the electrode.¹¹ This electrode maintained 78.4% of its maximum capacitance even at a high current density of 20 A g^{-1} . A thorough electrochemical analysis shows that 86.3% of charge is stored via surface-capacitance, while the remaining contribution is due to diffusion-controlled processes. The combined charging mechanisms result in a high energy density of 12.6 mWh cm^{-3} at a high power density of 766.2 W cm^{-3} , in an as-assembled flexible all-solid-state supercapacitor. The integration of these supercapacitors offers higher voltage and energy output, enabling diverse electronic applications. These encouraging findings are a significant step toward the development of more sustainable metal-free pseudocapacitors.

4.2 PREPARATION OF 3D TURBOSTRATIC SULFONYL-FUNCTIONALIZED POROUS CARBON (3D-TSSC) FOAMS THROUGH LASER TREATMENT OF SCNDS

The SCNDs were prepared through a solid-state condensation method involving sulfanilic acid, citric acid, and urea. **Figure S4.1** shows a schematic illustration of the synthetic process. In this bottom-up approach, citric acid, and urea act as the precursors for carbon nanodot formation, while sulfanilic acid ($\text{H}_3\text{NC}_6\text{H}_4\text{SO}_3$) provides the sulfonyl source. The synthesis created SCNDs with a reaction yield of 10.2%.

The characteristic optical properties of SCNDs were examined using UV-vis spectroscopy, as shown in **Figure S4.2**. In agreement with previous reports, the distinctive absorption peak at 286 nm in the UV-Vis can be attributed to the π - π^* transition of C=C bonds within the SCNDs.¹²

Transmission electron microscopy (TEM) and atomic force microscopy (AFM) images reveal spherical or quasi-spherical SCND particles with an average size of 13.0 nm, and uniform atomic arrangements (**Figure S4.3**). After laser irradiation, the TEM of 3D-tsSC shows an interconnected porous structure with identifiable graphitic lattices. Notably, the walls of carbon that divide the pores are composed of just a few layers of graphitic planes. Furthermore, the TEM image in **Figure 4.1a** shows that graphitic layers are stacked into a porous structure, ensuring rapid electron transport in the interconnected porous carbon monoliths.¹³

The X-ray diffraction (XRD) patterns of SCND and 3D-tsSC both show single broad peaks centred at $25^\circ 2\theta$ (**Figure 4.1b**). The peak in the 3D-tsSC appears sharper, confirming the (002) graphitic lattice plane and indicating fewer defects after laser treatment.¹⁴ Furthermore, the peak shift to a lower angle in the 3D-tsSC compared to other graphitic samples suggests an expansion of the d-spacing caused by the presence of dangling sulfonyl moieties on the graphitic planes.¹⁵

The 3D-tsSC exhibits an enhanced specific surface area and optimal porous architecture, making it highly suitable for capacitive energy storage. The surface areas of 3D-tsSC and SCNDs were calculated using nitrogen gas absorption measurements. The nitrogen isotherms of 3D-tsSC show type I isotherm curves with extensively overlapping adsorption and desorption portions, suggesting mechanically strong pore structures with minimal collapse (**Figure 4.1c**).¹⁶ The 3D-tsSC displays a specific surface area of $531 \text{ m}^2 \text{ g}^{-1}$, which is significantly higher than the SCND ($45 \text{ m}^2 \text{ g}^{-1}$) before laser treatment. The macroporosity in the 3D-tsSC was verified by observing a sharp rise along the y-axis in enlarged pictures of the high P/P_0 range (0.8-1) in the isotherm. Mesopores and the majority of macropores were found, according to the Barrett-Joyner-Halenda (BJH) plot, in the 3D-tsBG and 3D-tsSC samples, respectively, with mean pore sizes of 911 nm and total pore volumes of $2.13 \text{ cm}^3 \text{ g}^{-1}$. The high-surface-area porous structure can be further

visualized by scanning electron microscopy (SEM) (**Figure 4.1d**). The SEM images clearly illustrate the multi-layered interconnected network structure of the 3D-tsSC with abundant pores at the micron scale. The macroporous nature of 3D-tsSC plays a critical role in boosting the ion transport kinetics by facilitating rapid electrolyte ion diffusion within the channels.¹⁷

The presence of sulfonyl moieties anchored on the 3D-tsSC was investigated by X-ray photoelectron spectroscopy (XPS). An XPS survey spectra of SCND and 3D-tsSC show shrinking N1s and O1s peaks, indicating a graphitization of SCNDs realized by sub-millisecond laser scribing (**Figure 4.1e**). The S2p peaks are slightly intensified due to the thermal conversion of sulfonates to sulfonyl moieties rather than thermal depletion. The chemical bonding of sulphur motifs is further analysed through the core spectrum of S2p peaks (**Figure 4.1f**). For the SCND, two singlets are detected. The low-binding-energy peak is due to the sulfonated precursors and their chemical binding to the CND surfaces. The S2p_{3/2} contribution is seen at 166.1 eV, in good agreement with the literature.¹⁸ Indeed, typical S2p_{3/2} binding energies for unbound alkyl sulfonates and alkylbenzene sulfonates range between 166 and 166.5.¹⁹ The contribution at the lower binding energy is due to S atoms that are thermally dehydrated. The peak at 167.5 eV can be attributed to S in the +6-oxidation state, i.e., $-\text{SO}_2-$ groups. The S2p_{3/2} contribution of $-\text{SO}_2-$ N₂ bonds (the righthand side group) was reported to be located at 167.6 eV.²⁰ After laser irradiation, the S2p peak is well-fit with one predominant singlet at 167.5 eV, indicating the presence of sulfonyl moieties resulting from the laser reduction of sulfonates. It is important to note that only a small amount of $-\text{SO}_3$ groups are observed at a binding energy of 166.1 eV.²¹ Therefore, laser irradiation excites the lone pair electrons of S-O in the sulfonates, leading to the cleavage of -OH or alkoxide in the form of H₂O or CO₂. A reduction of $-\text{SO}_3$ to $-\text{SO}_2-$ was induced by photothermal effects.^{22–24}

4.3 INVESTIGATION OF THE LASER REDUCTION PROCESS: INFLUENCE OF FORMATION TEMPERATURE ON PHYSICOCHEMICAL PROPERTIES OF 3D-TSSC

To further analyse the laser reduction process, we conducted a comprehensive analysis of the physicochemical properties of 3D-tsSCs obtained from the irradiation of SCNDs at different formation temperatures, namely 220 °C, 300 °C, 350 °C and 400 °C. These variants are labelled SCND220, SCND300, SCND350, and SCND400, respectively. We observed a decrease in the solubility of SCNDs formed at higher temperatures in polar solvents, such as N-methyl-2-pyrrolidone (NMP) (**Figure S4.4**), which is consistent with previous findings.²⁵ This reduced solubility suggests larger particle sizes and less polar oxygen-containing groups for sulfonates formed at higher temperatures. This is supported by the decreased atomic percentages of O1s and S2p and increased C/O ratios observed in the XPS survey spectra for sulfonates formed at higher temperatures (**Figure S4.5 and S4.6**). Furthermore, as the formation temperature was increased, a loss of sulfonic groups from 3.5% remaining in SCND220 to 2.8% remaining in SCND400 was observed. This can be attributed to the decomposition of aromatic sulfonic acid, reported to occur at ~300-350 °C.²⁶ The decomposition products, H₂S and SO₃, have been actively used to dope carbon.^{27,28} Therefore, the number of functional groups in SCNDs can be tuned by adjusting the formation temperature.

Laser irradiation of the previous samples led to the formation of 3D turbostratic porous carbon foams (3D-tsSC), which are denoted as 3D-tsSC220, 3D-tsSC300, 3D-tsSC350, and 3D-tsSC400, respectively. Interconnected porous structures were consistently seen in all products (**Figure S4.7**). As previously concluded, the variation of functional groups (-OH, -O-, -COOH, -SO₃) accounts for the differences in the physicochemical properties of the 3D-tsSC variants. XPS survey spectra

revealed a higher C/O ratio in 3D-tsSC400, which aligns well with the trend observed in SCNDs (**Figures S4.8 and S4.9**). Among the 3D-tsSC variants, 3D-tsSC220 showed the highest sulphur content at 5.4%, while the lowest sulphur content was observed in 3D-tsSC400 (4.25%) (**Figure 2a4**). This observation confirms that the elevated sulphur level in 3D-tsSC220, derived from the highly functionalized SCND220, can be attributed to the conversion of the sulfonic groups present in the SCNDs. The laser irradiation process triggers this conversion by causing coherent heating and rapid cooling, which leads to the trapping of excited sulphur-containing radicals. Consequently, the sulphur atoms collapse and undergo substitutional doping into the graphitic lattices under the influence of photothermal effects.²⁷ At the same time, conventional pyrolysis cleaves sulfonic moieties, generating gaseous products as seen in high-temperature SCNDs.²⁹

FT-IR spectra provide further evidence for the laser conversion from SCNDs to 3D-tsSC (**Figure 4.2b**). For consistency, spectra of 3D-tsSC220, 3D-tsSC300, 3D-tsSC350, and 3D-tsSC400 were normalized using a major absorption peak at 1046 cm^{-1} , corresponding to the C=C stretching vibrations of aromatic carbon. The peak observed at 1353 cm^{-1} may be attributed to S-O out-of-plane vibrations in sulphate or sulphite groups.³⁰ The presence of the C-S stretching signal at 1955 cm^{-1} indicates substitutional sulphur doping.³¹ Notably, an increase in C-S and a decrease in S-O signals are observable at higher formation temperatures. In addition, the S-H stretching vibrations at 2460 cm^{-1} are consistently present in all samples. It is important to highlight that the FT-IR absorptions after laser treatment and the changes of peak intensities observed in 3D-tsSC220, 3D-tsSC300, 3D-tsSC350, and 3D-tsSC400 provide strong evidence for a photothermal cross-linking process. As formation temperatures increase in the SCND precursors, a disappearance of oxygen and nitrogen-related FT-IR absorptions are observed in the resulting 3D-tsSCs, including the predominant peak at 1578 cm^{-1} (aromatic C=C and C-O-C resonant stretching vibrations), two

peaks at 3193 and 3079 cm^{-1} (OH vibrations), a broad peak with a maximum at 3443 cm^{-1} (C=O, amide stretching vibrations), and a series of peaks indicating oxidized functional groups from 1000 to 1700 cm^{-1} , such as 1046 cm^{-1} (C-O-C epoxide vibrations), 1248 cm^{-1} (C-OH out-of-plane vibrations), 1144 cm^{-1} (C(=O)OC out-of-plane vibrations), 1180 cm^{-1} (C=N stretching) and a bimodal peak with maxima at 1478 and 1394 cm^{-1} (C=O stretching in esters, carboxylates, and amides).³² Compared with the predominantly terminal groups present in CNDs,^{25,33,34} such as -OH, -COOH, -NH₂, the strong absorptions observed in 3D-tsSC after laser treatment can be mainly attributed to bridging bonds or fragments of cyclic compounds. The synchronous decline in absorbance of terminal groups in the CNDs and bridging bonds in the 3D-tsSCs suggests that the crosslinking of moieties in CNDs gives rise to the formation of continuous graphitic domains in 3D-tsSC. The laser-induced photothermal amination, esterification, and cyclo-condensation are possibly responsible for the cross-linking.³⁵

The presence of more dopant moieties found in the 3D-tsSCs formed at higher temperatures is also supported by thermogravimetric analysis (TGA). In **Figure 4.2d**, non-plateaued thermal loss exists in all samples from 300 to 800 °C designating a sequence of defunctionalized reactions coupled with a reduction process, including decarboxylation or deoxidation.³⁶ The leaving groups include epoxyl, amides, and hydroxyl groups after the dehydrations reach equilibrium at 250 °C consistent with a previous report.³⁶ After that, 3D-tsSC220 shows a weight loss of 36.1%, whereas 3D-tsSC400 only lost 16.4% of its weight. The larger weight loss in 3D-tsSC220 signifies a higher content of thermally unstable moieties.³⁷

The laser-induced formation of 3D-tsSC was also probed by comparing the Raman spectra of 3D-tsSC220 to that of 3D-tsSC400 (**Figure 4.2e**). Each spectrum was obtained with at least five repetitions to estimate the error in the data and ensure accuracy. All 3D-tsSC variants exhibit

similar defective graphitic patterns, with differences observed in the peak intensities of the D and 2D bands. To assess the defect density, the intensities of the D and 2D bands were normalized by using the intensity of the G band, resulting in I_D/I_G and I_{2D}/I_G ratios, respectively. A higher I_D/I_G ratio typically correlates to a higher defect density (**Figure 4.2f**).³⁸ In 3D-tsSCs formed at higher temperatures, a smaller I_D/I_G signifies fewer defects stemming from oxygen groups and associated vacancies, coupled with an increased C/O ratio in 3D-tsSC400 (**Figure S4.7**). The decline in I_D/I_G is more pronounced from 3D-tsSC220 to 3D-tsSC350, whereas the change in C/O remains relatively constant. This suggests that below 350 °C, substitutional sulfur doping replaced oxygen groups as the primary contributor to the defects. The 2D band corresponds to the double resonance of two close-packed layers. Therefore the I_{2D}/I_G ratio can be used to quantify the turbostratic features.³⁹ A decrease in the I_{2D}/I_G ratio was observed in the 3D-tsSC samples formed at higher temperatures, indicating a stronger turbostratic feature at lower formation temperatures such as 3D-tsSC220. This implies that laser irradiation plays a more significant role in forming turbostratic graphitic domains than high temperature and slow annealing during carbonization. The turbostratic graphitic domains create an electrode with optimal electrical conductivity for charge storage.⁴⁰

Four-probe measurements show a gradual increase in electrical conductivity from 3D-tsSC220 to 3D-tsSC 350, while the 3D-tsSC400 shows the highest conductivity of 872.7 S m⁻¹ (**Figure 4.2c**). This finding is consistent with the increasing C/O ratios at higher formation temperatures. Notably, the 3D-tsSC220 displays a higher sheet electrical conductivity (629.7 S m⁻¹) compared to other carbon or graphene materials with similar C/O ratios reported in the literature.^{41–43} This indicates that the turbostratic nature of the material is responsible for faster anisotropic electron transport between graphitic layers. On the other hand, the much-increased electrical conductivity of 3D-tsSC400 can be attributed to its higher packing density, as indicated by its smaller surface area.

The surface areas of the 3D-tsSC samples were measured using the methylene blue adsorption method and plotted on the same graph as their contact angles (**Figure 4.2c**). The contact angles of electrolyte droplets on both electrodes were examined to assess the wettability of the electrodes by the electrolyte (1.0 M H₂SO₄) (**Figure 4.2c** and S4.10). The contact angles significantly fell from 71.8° in 3D-tsSC220 to 35.3° in 3D-tsSC400. This decrease can be attributed to the strong interaction between the sulfonyl and the aqueous electrolyte, indicating the presence of a higher number of functional groups in the 3D-tsSC electrodes.⁴⁴ It is worth noting that the laser treatment increased the contact angle, As the patterned surfaces created by the laser exhibit higher hydrophilicity due to capillary effects.⁴⁵

4.4 ELECTROCHEMICAL CHARACTERIZATION OF THE PSEUDOCAPACITANCE MECHANISM OF 3D-TSSC ELECTRODES

The acidic aqueous electrolyte, 1.0 M H₂SO₄, was selected to assess the pseudocapacitive performance of the 3D-tsSC electrode. Using a three-electrode testing setup with an Ag/AgCl reference electrode and a graphite sheet as the counter electrode, the 3D-tsSCs were evaluated as working electrodes.

In an acidic electrolyte, cyclic voltammograms (CVs) presented in **Figure 4.3a** compare the performance of unfunctionalized porous carbon (3D-tsC) and 3D-tsSC300 electrodes. The CV profile of 3D-tsC, obtained by laser irradiation of unfunctionalized carbon nanodots, exhibits a rectangular shape at 100 mV s⁻¹, indicative of pure electric double layer capacitance (EDLC) behavior.⁴⁶ However, upon introducing sulfonyl moieties, the CV profiles 3D-tsSC300 reveal prominent redox peaks centred at around 0.62 V and 0.57 V vs. a standard hydrogen electrode (SHE). The enclosed area of the 3D-tsSC300 CV profile is significantly larger than that of the 3D-

tsSC, demonstrating that the 3D-tsSC has a higher capacitive storage capability. Both CV profiles exhibit near 90° angles when the potential is switched from positive to negative, indicating a low resistance for charge storage.⁴⁷ The CV profiles of 3D-tsSC300 were also recorded at scan rates ranging from 20 to 500 mV s⁻¹ (**Figure S4.11**). These profiles gave nearly rectangular and symmetric shapes. The redox peaks and their position remain roughly constant at various scan rates, suggesting fast kinetics and high reversibility of the pseudocapacitive reaction.⁴⁸ Galvanostatic charge-discharge (GCD) curves, shown in **Figure S4.12**, further support the high capacitance of the 3D-tsSC300 electrodes. These electrodes demonstrate a specific capacitance of 157.7 F g⁻¹ at 1 A g⁻¹ and maintain 123.73 F g⁻¹ at 20 A g⁻¹ (**Figure 4.3b**). Notably, the specific capacitance 3D-tsSC300 is consistently higher than those of the 3D-tsC electrode at all current densities, highlighting the pseudocapacitance effect observed in the GCD curves (**Figures S4.12 and S4.13**).

Increasing the areal mass loading of the electrode film is crucial for enhancing the energy and power density of the final device and maximizing its volume fraction in the supercapacitor configuration.⁴⁹ However, it is important to address the challenges of slower ion diffusion that typically occurs in thicker electrodes at high mass loadings, which can compromise the capacitive performance.⁵⁰ To overcome this limitation, a multi-layered approach was employed by depositing repeated layers of SCND followed by laser irradiation. This process successfully increased the mass loading of the 3D-tsSC electrode from 0.76 to 5.7 mg cm⁻². The electrode thickness was captured by cross-sectional SEM images (**Figure S4.14**). At a current density of 5 A g⁻¹, the specific capacitance slightly decreased from a maximum of 134.1 F g⁻¹ to 115.7 F g⁻¹ after 8-layer deposition (**Figure 4.3c**). However, it is worth noting that the areal capacitance significantly increased from 13 mF cm⁻² using 1-layer deposition to 70 mF cm⁻² using 8-layer deposition.

Electrochemical analysis was used to investigate the pseudocapacitive behaviour of the 3D-tsSC formed from SCNDs at different temperatures. **Figure 4.3d** shows the CV profiles of the 3D-tsSC variants. It can be observed that 3D-tsSC220 exhibits more pronounced redox peaks compared to 3D-tsSC400, indicating that a higher concentration of sulfonyl groups induces more substantial pseudocapacitive effects. This finding is further supported by more expansive plateaus in the GCD curves of 3D-tsSC formed by SCNDs at lower temperatures (**Figure S4.15**). The electrochemical impedance spectroscopy (EIS) data were placed in Nyquist plots to better understand the electrochemical performance. The x-intercepts in the Nyquist plot represent the internal resistance of the electrodes.⁵¹ Therefore, the 3D-tsSC220 shows a higher resistance than the 3D-tsSC400, which is consistent with the increased electrical conductivity found in 3D-tsSC220 vs. 3D-tsSC400. A distinct semicircle is observed in the high frequency region in the 3D-tsSC220 electrodes, as shown in **Figure 4.3e**. This semicircle indicates the presence of charge-transfer resistance resulting from the pseudocapacitive process at the interface between the 3D-tsSC220 electrode and the acidic electrolyte. In contrast, the plot for 3D-tsSC350 is more linear than that for 3D-tsSC400, suggesting a predominant electrostatic capacitive charge storage process rather than Faradaic reactions.⁵²

The pseudocapacitance mechanism in the 3D-tsSC electrode is further validated using kinetic analysis of the electrochemical reactions. Theoretically, a power-law Equation (1) governs the measured current (*i*) at varying scan speeds (*v*),

$$i = a v^b \quad (1)$$

where *a* and *b* are obtained by plotting log redox peak current (*i*) vs. log scan rate (*v*). The slope *b* accurately captures the kinetics of the charging and discharging operations.⁵³ A surface capacitive

process is represented by a b value of 1, whereas a diffusion-dominated process is represented by a b value of 0.5. **Figure 4.3e** shows that when H_2SO_4 is employed as the electrolyte, the b value for 3D-tsSC at scan rates from 5 to 500 mV s^{-1} ($\log(v)$ is from 0.7 to 1.3) was calculated for the anodic processes. The b value of 0.987 calculated for 3D-tsSC400 indicates a dominant surface capacitive process. As the synthesis temperature was lowered, the b value becomes smaller. For the 3D-tsSC220 electrode, the b value reaches 0.917 for the anodic and cathodic processes, respectively, reflecting a diffusion-dominated process and surface capacitive behaviour. This variation may be caused by diffusional restrictions and an increase in ohmic contributions (the resistance of the active material and its contact with the electrolyte). In addition, hydronium ions in H_2SO_4 have a smaller radius and a lower charge than other electrolyte ions, which makes it easier for them to diffuse into the deep adsorption sites in the 3D-tsSC electrode. The relatively lower internal resistance and charge-transfer resistance in H_2SO_4 allows for quicker ion transfer.

To better understand the pseudocapacitance in 3D-tsSC, 3D Bode plots were generated by plotting frequency (f) and potential window (V) against the area normalized total capacitance (C') of the variants. These Bode plots, depicted as waterfall plots in **Figures 4.3g-I**, provide a comprehensive 3D representation of the behaviour of the 3D-tsSC electrodes in 1.0 M H_2SO_4 electrolyte. The C' of 3D-tsSC220 reached its highest value at potentials close to 0.59 V (vs. SHE) in the low-frequency region (0.01 Hz) and revealed a pronounced redox-type response.⁵⁴ It was found that the area normalized capacitance was 2.49 F cm^{-2} at $E_{1/2} = (E_{p,a} + E_{p,c})/2$, 0.59 V vs. SHE (where $E_{p,a}$ and $E_{p,c}$ are anodic and cathodic peak potentials determined in slow scan CV profiles and $E_{1/2}$ is half-wave potential), which is nearly ten times greater than values at other potentials. This large real capacitance in 3D-tsSC220 results from sluggish redox processes that engage all sulfonyl groups at low frequencies, aligning with the observed CV profiles. At a frequency of 1 Hz, the 3D-

tsSC electrodes display a reduced capacitance value, indicating that the redox processes in the H₂SO₄ electrolyte are more pronounced over a few minutes and less noticeable at shorter time scales (1 s). The pseudocapacitance in 3D-tsSC was also evaluated regarding the self-discharging process. The 3D-tsSC220 suppressed the charge relaxation at the interface due to ion chemically absorption, confirming the redox nature of sulphonyl ligands (Figure S4.16).

Additionally, the pseudocapacitance in 3D-tsSC was investigated in neutral electrolyte and organic electrolyte.⁵⁵ Rectangular box type cyclic voltammograms (CVs) were seen in the case of neutral electrolytes, specifically 1M Na₂SO₄, as depicted in Figures S4.17a of the Supplementary Information. In comparison to neutral electrolytes, the charge-discharge profiles of 3D-tsSC300 electrodes in 1M H₂SO₄ exhibit a sloping type. The creation of a second layer within the turbostratic graphitic layers by the hydrated Li- and Na-ions is likely the cause of this phenomenon. The presence of a hydration shell effectively hinders the orbital connection between the intercalated ions and the surface functional groups of turbostratic graphitic layers, as stated in previous studies.^{56,57}

In 0.5 M TEABF₄/CAN organic electrolyte, the cyclic voltammograms of the electrodes revealed a capacitance that was 1.25 times greater than that in aqueous electrolyte due to a broadened voltage window (2V), as depicted in Figure S4.18a. Nevertheless, the presence of a less optimal curve shape of CV curves at high scan rates suggests the existence of a greater series resistance. This assertion was substantiated through impedance measurements (Figure S4.18b), which revealed a significant rise in the higher charge transfer resistance and reduced phase angles at all frequencies. The 3D-tsSC300 consists of charged ligands that are bound to the electrode surface, most likely through π - π -stacking interactions (see Figure 4.4d). Hence, the charges are situated at the interface between the electrode and electrolyte, and can be driven by voltage in aqueous

electrolytes.⁵⁸ The diffusion of 3D-tsSC300 in organic electrolytes is impeded by π - π interactions, resulting in a decrease in diffusion resistance. Consequently, coupling with organic electrolytes eliminates these unreacted ligands enhancing the accessibility of the electrode surfaces and micropores to the electrolyte, meanwhile increasing the capacitance by voltage broadening.⁵⁹ However, it also leads to an increase in series resistance.

Furthermore, we compared the frequency responses across electrolytes using the 8-layer thick 3D-tsSC220 electrodes. The 8-layer 3D-tsSC220 electrode significantly impacts the frequencies of redox events (Figure S4.19).⁶⁰ High frequencies (over 10 Hz) cause the capacitive component to gradually lose dominance over the resistive component, resulting in nominal capacitance values. The peak position in the 3D map, consistent with the corresponding CV data (**Figure 4.3g**), shows that 3D-tsSC exhibits strong pseudocapacitance in the voltage range from 0.57 to 0.62 V while displaying capacitive-type response at other potentials. By combining capacitive and redox processes that operate at various potentials, 3D-tsSC350 and 3D-tsSC400 exhibit mixed charge-storage dynamics (**Figures 4.3h and 4.3i**). The high electrical conductivity and the efficient proton transport across the large graphene planes enable 3D-tsSC350 and 3D-tsSC400 to achieve high-rate redox charge storage. Additionally, the 3D Bode plot analysis of 3D-tsSC-300 demonstrates a consistent trend (Figure S4.20). The almost rectangular 3D plot, a hallmark of the EDLC-type response, signifies that the unfunctionalized 3S-tsG electrode stays virtually constant over the potential window (0 to 1.0 V vs. SHE) at any given frequency (Figure S4.21).

4.5 PRACTICAL APPLICATIONS OF A SYMMETRIC 3D-TSSC300 DEVICE AND A FLEXIBLE ALL-SOLID-STATE SUPERCAPACITOR

To leverage the optimal combination of a fast surface capacitive process and high-capacitance diffusion-controlled Faradaic reactions, the 3D-tsSC300 was selected to construct a symmetrical supercapacitor (3D-tsSC300||3D-tsSC300). This configuration was tested on an electrochemical workstation to assess its potential 3D-tsSC as a practical energy storage device. The CV profile of the supercapacitor exhibited a quasi-rectangular shape in the voltage window 0-1 V across various scan rates, demonstrating its potent ion and charge transfer capabilities (**Figure 4.4a**). The device demonstrates excellent rate performance retaining 51.4% of its capacitance when the current density was increased by 50-fold from 1 to 50 A g⁻¹ (**Figure 4.4b** and S4.22 and S4.23). This exceptional performance can be attributed to the hierarchical interconnected porous structures of turbostratic graphene in 3D-tsSC300. The high specific surface area of these graphene films enables enhanced electroactivity, accessibility to electrolyte, and faster ion diffusion. This symmetric supercapacitor achieved a high energy density of 20.9 Wh kg⁻¹ at a current density of 1 A g⁻¹. These findings demonstrate the significant potential of 3D-tsSC300 as a promising candidate for advanced energy storage applications.

To quantify the contribution of capacitive and diffusion-controlled processes to the overall charge in the symmetric supercapacitor, the relationship between the potentiostatic scan rate and current responsiveness was examined.⁶¹ The entire charge transfer process for any material can be expressed as Equation (2),

$$i = k_1 v + k_2 v^{\frac{1}{2}} \quad (2)$$

Equation (2) can be rewritten as Equation (3) for analytical purposes,

$$i / v^{\frac{1}{2}} = k_1 v^{\frac{1}{2}} + k_2 \quad (3)$$

where i is the response current that is taken to be a combination of diffusion-controlled currents (which vary as $k_2 v^{\frac{1}{2}}$) and surface capacitive currents (which vary as $k_1 v$). Therefore, it is feasible to deconvolute the portion of the current resulting from capacitive processes and that from diffusion in the examined voltage window by computing both k_1 and k_2 from plotting $i / \frac{1}{v^2}$ vs. $v^{\frac{1}{2}}$.

Figure 4.4c compares the overall measured current obtained at a sweep rate of 10 mV s^{-1} for the 3D-tsSC300 electrode with the voltage profile for the surface capacitive current (the shaded region). The slow CV scan was adopted to comprehensively analyse the contribution from non-capacitive Faradaic processes at various potentials. The capacitive charge storage ratio to the overall charge storage is 85.3%, which shows the system's capacity to operate at high rates. The percentages of surface capacitive contribution were also reported at various scan rates from 5 to 100 mV s^{-1} (**Figure 4.4e**). All the values are comparably high among all published data, suggesting that the non-metal 3D-tsSC electrodes can provide a high-density pseudocapacitance realized at fast kinetics, a characteristic rarely achieved with metal-based pseudocapacitive electrodes.

In **Figure 4.4d**, the cycling stability of the 3D-tsSC300 electrodes was investigated under charge/discharge cycling at 10 A g^{-1} . Remarkably, the thin electrodes, formed by 1-layer deposition, exhibit a capacitance retention of 97.4% after ultralong testing for 15,000 cycles, demonstrating the strong electrochemical stability of the 3D-tsSC300 electrode. This excellent stability can be attributed to the strong bonding of the redox active sulfonyl groups to the turbostratic graphene domains, ensuring steady electrical contact and fast redox kinetics. Furthermore, the thick electrodes, created through an 8-layer laser deposition process, demonstrated an impressive capacitance retention of 95.6%. The insets in **Figure 4.4d** show the GCD curves at 10 A g^{-1} and the EIS spectra of 3D-tsSC300||3D-tsSC300 in both thin and thick

electrode configurations before and after 15,000 GCD cycles. The GCD curves are linear and overlap more in the thin 3D-tsSC300 electrode, indicating the extended charge-discharge cycles. The thick 3D-tsSC300 displays charging and discharging curves with a hump-like shape, as shown in the middle inset in **Figure 4.4d**. Notably, the curves in the thick electrode display a slightly shorter discharge time after prolonged cycling while maintaining a symmetrical shape. The EIS diagrams of the symmetrical supercapacitor 3D-tsSC300||3D-tsSC300 were recorded before and after cycling under identical conditions. The impedance analysis reveals a noticeable decrease in series resistance (R_s) and charge transfer resistance (R_{ct}) during cycling, as determined by the smaller variations in x-intercepts and semicircle diameters in the Nyquist plots before and after cycling (**Figure 4.d**). This signifies the high electrical conductivity and reliable charge-transfer kinetics of the pseudocapacitive 3D-tsSC300 electrodes. These phenomena were observed in thin and thick electrode configurations, emphasizing the uniform distribution of the active sites on the porous graphene sheets.

To respond to the growing demand for compact and flexible electronics, we fabricated thick 3D-tsSC electrodes (8-layer) into flexible all-solid-state supercapacitors (FSSCs). FSSCs offer several advantages including metal-free electrodes and interconnected porous structure, which ensures excellent contact between the electrode material and electrolyte. The design promotes better performance and enhances the recyclability of the devices. **Figure 4.5a** illustrates an FSSC configuration with two devices connected in series to power a red LED device. In **Figure 4.5c**, the CV profile of the FSSC demonstrates a well-defined rectangular shape even at a relatively fast scan rate of 100 mV s^{-1} . Under this condition, the specific capacitance of the sul-pG300 electrode was determined to be 12.5 mF cm^{-2} . The GCD curves further verified the high capacitance, displaying a nearly perfect triangular response, indicative of efficient energy storage and release

in the FSSC. At a current density of 2 mA cm^{-2} , a specific capacitance of 17.7 mF cm^{-2} was achieved, indicating a high energy storage capacity. Additionally, even at a significantly higher current density of 50 mA cm^{-2} (25-fold increase), the FSSC still retained 55.6% of its capacitance, demonstrating its ability to maintain a considerable amount of charge storage under demanding conditions, as shown in **Figure 4.5d** and **Figure S4.24**. Furthermore, both CV and GCD analysis were obtained for serial-connected and parallel-connected two-FSSC circuits to fulfil different output requirements. The series FSSCs operated in a 2 V potential window (twice that of a single FSSC), while the parallel FSSCs provided twice the current of a single FSSC and showed an increased capacitance of up to 31.2 mF cm^{-2} at 2 mA cm^{-2} . Electrochemical impedance spectroscopy was acquired to assess the electrical and ionic resistance in the FSSCs (**Figure S4.25**). Due to the comparatively poor ionic conductivity in the polyvinyl alcohol (PVA)/ H_2SO_4 gel electrolyte, the charge-transfer resistance is higher in these FSSCs than in the 1.0 M H_2SO_4 aqueous solution. To examine the flexibility and stability of the 3D-tsSC300-based FSSCs, a folding test was conducted to assess their mechanical performance during the galvanostatic charge and discharge cycling at 100 mA cm^{-2} . Remarkably, the FSSCs exhibited a capacitance retention of 91.6% in the initial cycle. Even after undergoing 90° bending cycles five times, only a slight capacitance decay was observed in the following cycles. Compared to other publications (**Figure 4.5e**), the 3D-tsSC300-based FSSCs demonstrate a comparable energy and power density, even when compared to state-of-the-art metal compound-based pseudocapacitors.^{62–70} The 3D-tsSC electrodes stand out due to their wide operating voltage window, high mechanical flexibility and durability, safe operation (free of electrolyte leakage), cost-effectiveness, and excellent recyclability (free of metal compounds).⁷¹ These features position 3D-tsSC electrodes as promising candidates to provide power for flexible electronics.

4.6 CONCLUSIONS

Here we have presented a unique approach to constructing metal-free pseudocapacitive energy storage devices. Laser-converted SCNDs have been created for scalable and rapid construction of high-performance porous graphene pseudocapacitive electrodes. In an acidic electrolyte, a high specific capacitance of 157.6 F g^{-1} was attained at a current density of 1 A g^{-1} . Remarkably, even after 15,000 cycles at 10 A g^{-1} , the electrodes demonstrate exceptional stability retaining 97.4% of their initial capacitance. Moreover, the electrodes exhibit high-rate capability due to their good electronic conductivity and interconnected porous structure, maintaining 78.4% of their capacitance at a high current density of 20 A g^{-1} . Thorough electrochemical analysis reveals that the sulfonyl groups substantially contribute to the electrode's pseudocapacitance, which enables diffusion-capacitive dual-model energy storage. Our research underscores the potential of sulfonyl groups for fast reaction kinetics and extended durability. These features enable them to effectively contribute to the pseudocapacitive reaction in supercapacitors, rivalling or even surpassing the performance of traditional metal oxide and conducting polymer materials.⁷² By offering a metal-free electrode with manufacturing cost advantages and environmental friendliness, our findings should inspire further exploration of innovative nanomaterials, particularly those based on sulphur for energy storage applications.

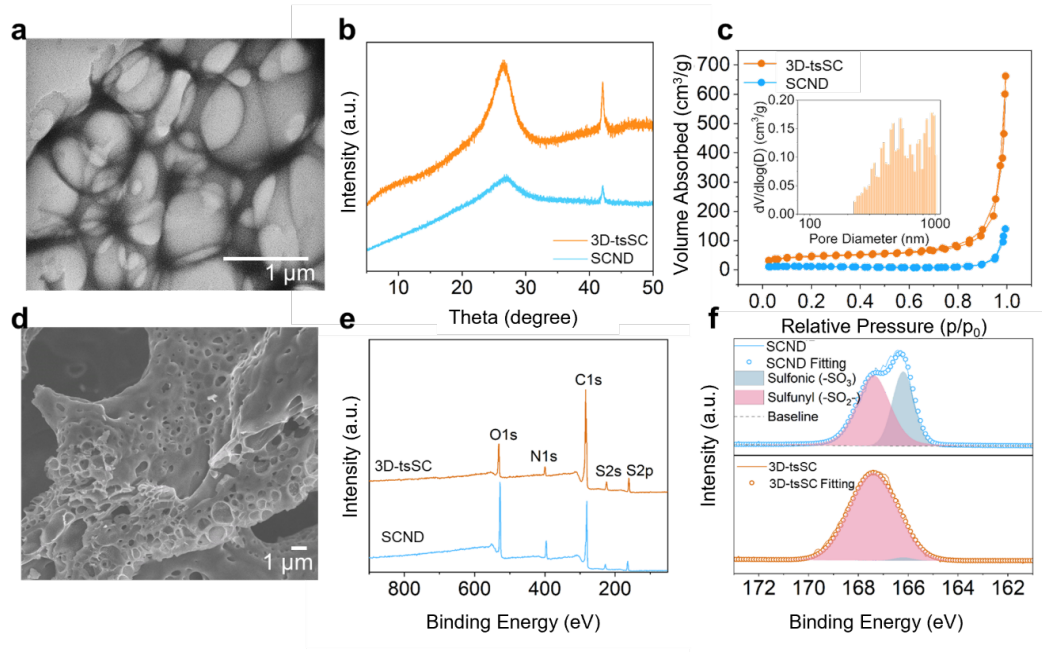


Figure 4.1 a) Typical TEM (left) and HRTEM (right) images of SCND (top) and 3D-tsSC (bottom). The scale bars are as indicated. b) XRD patterns of 3D-tsSC and SCND. c) The nitrogen adsorption-desorption isotherms and pore size distribution curves of SCND and 3D-tsSC. d) Typical SEM images of 3D-tsSC. e) XPS survey spectra of SCND and 3D-tsSC. f) Peak fitting of S2p core spectra of SCND and 3D-tsSC.

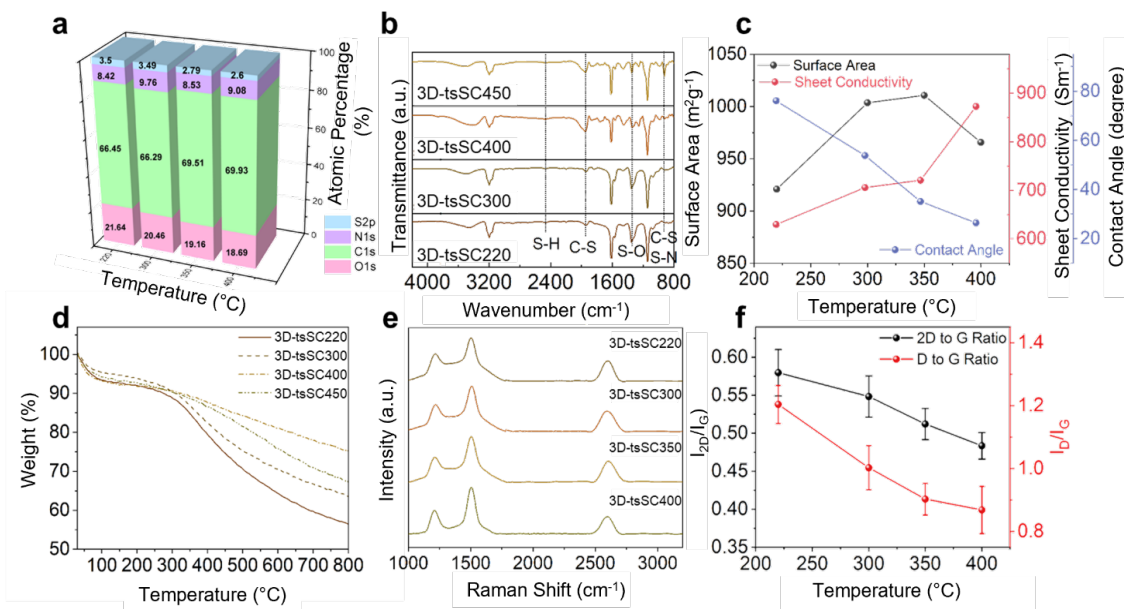


Figure 4.2. a) The elemental composition percentages of 3D-tsSC220, 3D-tsSC300, 3D-tsSC350, and 3D-tsSC400, derived from the integrated peak areas using the XPS survey spectra. b) FT-IR spectra of 3D-tsSC220, 3D-tsSC300, 3D-tsSC350, and 3D-tsSC400. c) The variation of the surface area measured using methylene blue adsorption (black), the sheet electrical conductivity obtained using four-probe measurements (red), and water contact angles (blue) of 3D-tsSC220, 3D-tsSC300, 3D-tsSC350, and 3D-tsSC400. d) TGA curves, e) Raman spectra of 3D-tsSC220, 3D-tsSC300, 3D-tsSC350, and 3D-tsSC400. f) The variation of the peak intensity ratio of D to G peaks (black) and 2D to G peaks (red) of 3D-tsSC220, 3D-tsSC300, 3D-tsSC350, and 3D-tsSC400.

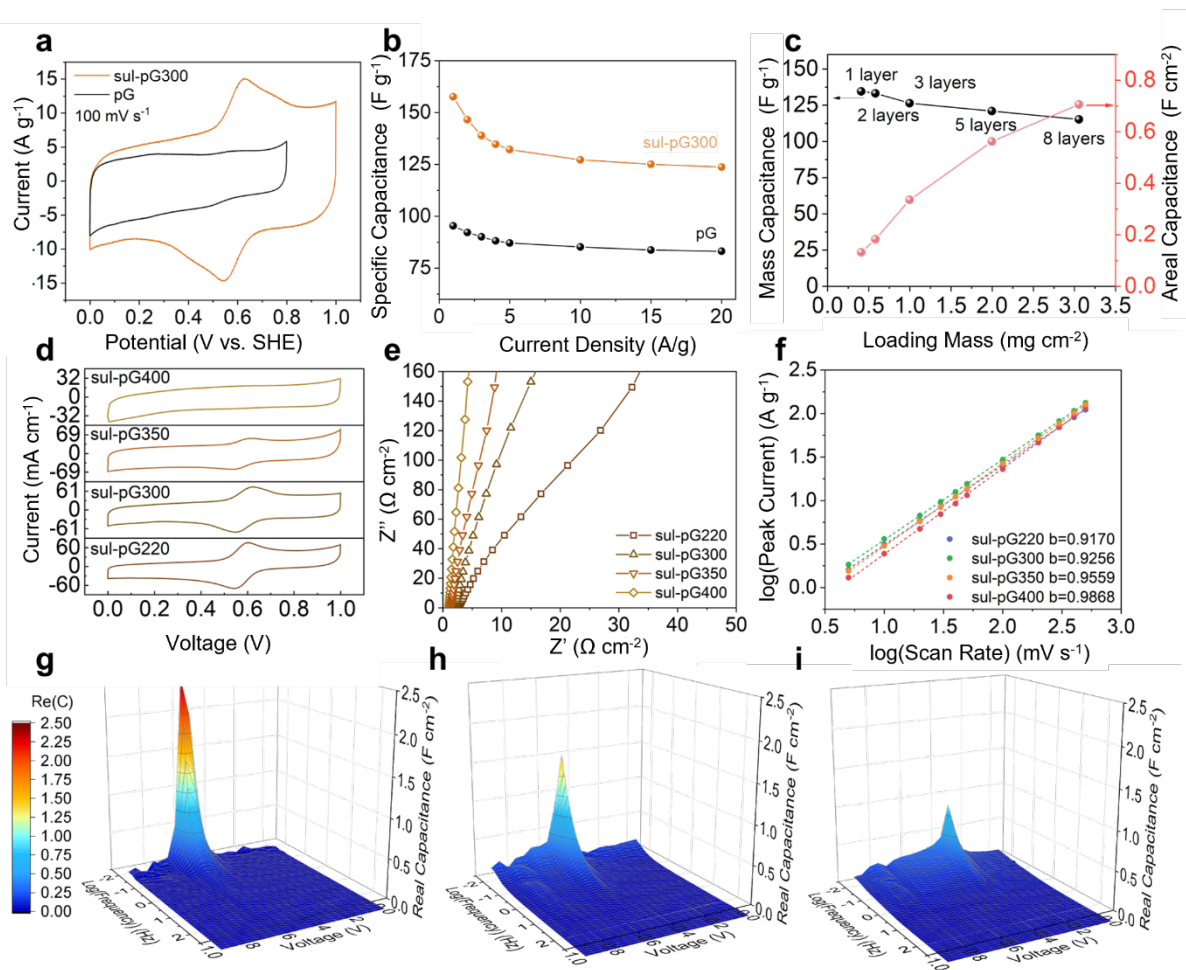


Figure 4.3 a) CV profiles at 100 mV s^{-1} , b) rate performance from 1 A g^{-1} to 20 A g^{-1} of 3D-tsG and 3D-tsSC300 electrodes. c) The variation of mass specific capacitance (black) and areal specific capacitance (red) with respect to the number of laser-converted layers of 3D-tsSC300 at 5 A g^{-1} . d) CV profiles at 10 mV s^{-1} , e) Nyquist plots, f) b value determination of normalized anodic peak currents of 3D-tsSC220, 3D-tsSC300, 3D-tsSC350, and 3D-tsSC400. 3D Bode maps of capacitance-potential-frequency of (g) a 3D-tsSC220 electrode, (h) a 3D-tsSC300 electrode, and (i) a 3D-tsSC350 electrode. Potentials and voltages were measured vs. Ag/AgCl in $1.0 \text{ M H}_2\text{SO}_4$.

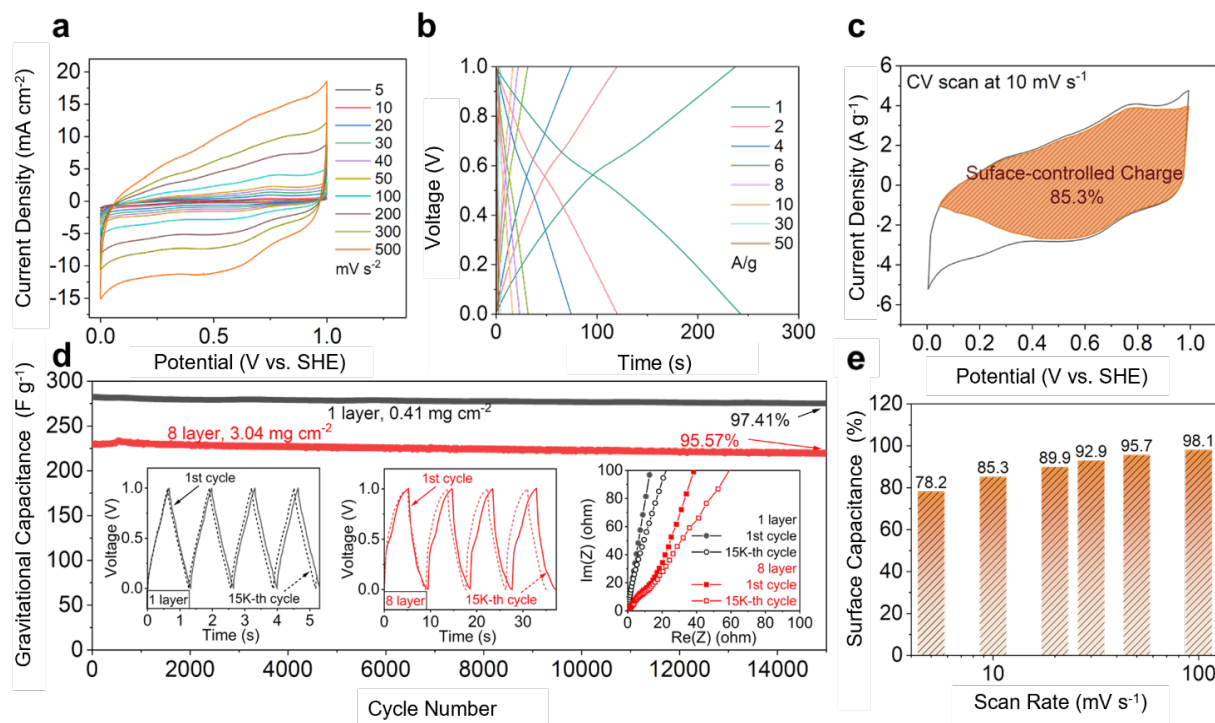


Figure 4.4 In a 3D-tsSC300 symmetric supercapacitor a) CV profiles at scan rates ranging from 5 mV s⁻¹ to 500 mV s⁻¹, b) GCD profiles at current densities ranging from 1 to 50 A g⁻¹. Rate performance from 1 A g⁻¹ to 20 A g⁻¹ of pG and 3D-tsSC300 electrodes. c) Total current response and surface-controlled current in a 1 V voltage window. d) The cycling performance of mass specific capacitance of the symmetric supercapacitor using 1-layer and 8-layer electrodes. The left inset is GCD profiles of the 1st to 4th cycles compared with the 14997th to 15000th cycles. The middle inset is GCD profiles of the 1st to 4th cycles compared with the 14997th to 15000th cycles in a symmetric supercapacitor using a 1-layer 3D-tsSC300 electrode. The right inset is GCD profiles of the 1st to 4th cycles compared with the 14997th to 15000th cycles in a symmetric supercapacitor using an 8-layer 3D-tsSC300 electrode. f) Surface-controlled capacitance contributions at different scan rates.

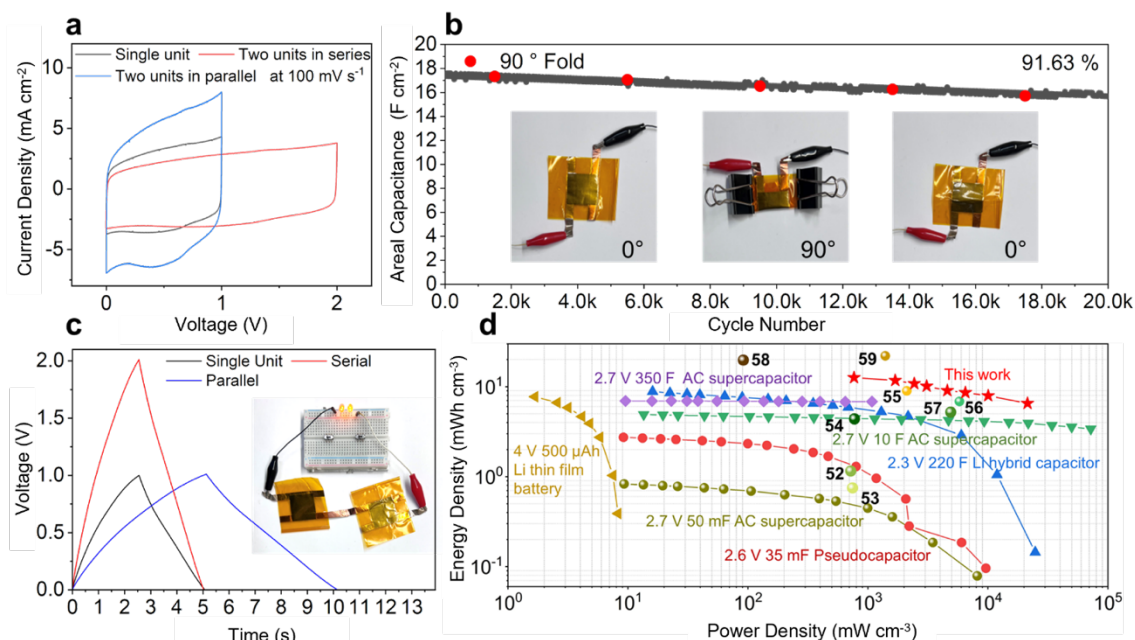


Figure 4.5 Fabrication of the FSSCs using a gel electrolyte. a) CV curves at a scan rate of 100 mV s^{-1} . b) The cycling performance of the fabricated FSSC. The cycling test was coupled with folding the device five times, labelled by the red cycles. The insets are photographs of FSSCs under various bending angles. c) GCD curves of FSSCs at 2 A cm^{-2} . Insets are photographs of two parallel-connected 2 V LEDs being powered by the assembled FSSCs. d) Ragone plots of the 3D-tsSC FSSCs (solid red stars are this work) compared with previously reported values and state-of-the-art energy storage devices. Note that all the presented energy density and power density values were calculated based on the entire device volumes.

4.7 EXPERIMENTAL SECTION

Solid-state synthesis of CNDs and SCNDs: All chemicals mentioned were incorporated in the procedure as purchased (i.e. without processing or purification). Carbon nanodots (CNDs) were synthesized by means of solid-state pyrolysis of urea and citric acid in argon flow. Preparation of SCND precursor solution involved dissolving 18 mmol citric acid (Fisher Scientific, ACS grade), 3.6 mmol urea (Aldrich, 99%), and 1.6 mmol sulfanilic acid (4-aminobenzenesulfonic acid, Fisher Scientific, ACS grade) in 300 mL deionized water. To acquire a homogeneous precursor for the solid-state reaction, this solution went through freeze-drying at -40 °C. The freeze-dried precursor was then moderately ground down to grains ready for pyrolysis using a pestle and a mortar. Under a 250 mL min⁻¹ Ar flow, a tube furnace heated the precursor to 300 °C at 10 K min⁻¹. The sample was held at this temperature for 2 hours and then cooled to room temperature. Following this, the product was collected, dispersed in 100 mL deionized water under ultrasonication, and centrifuged at 4750 rpm for 30 min. To remove unreacted reactants, the supernatant went through dialysis in regenerated cellulose dialysis tubing with MWCO 1k Da for 48 h to remove unreacted reactants. Once more, the remaining aqueous solution was freeze-dried for later characterization and application steps. Pyrolysis at a temperature gradient was carried out in a range from 220 to 400 °C. The SCNDs with different graphitization degrees were obtained.

Laser Formation of 3D-tsSC electrodes: The dried SCND powder (formed at temperature gradient) was dispersed in ethylene glycol at 10 mg/mL and drop-casted on stainless steel. Hydrophilic tapes were used to help control and enclose the drop cast area. A film, upon baking at 70 °C, was formed at a density of 0.5 mL/cm² at the pyrolytic graphite sheet (Digi-Key Corporation, 0.07 mm). The baked film was irradiated with a CO₂ laser (Full Spectrum FSL laser engraver, 10.6 μm). The laser was set to 30% of its 45W full power and 30% of its max scan speed (~ 9 cm s⁻¹). The Z height was adjusted to focus on the top surface of the coating film.

A 50 mm diameter zinc selenide window was incorporated into the reaction chamber lid, allowing the CO₂ laser (10.6 μm) to pass into the gas-reaction chamber. The sample was placed in the center of the chamber. A continuous airflow of 0.1 L s⁻¹ during the reaction was used to ensure a good mass transfer. The substrate-supported films were washed by immersing them into either NMP or 1 M KOH. After the unreacted SCND was dissolved, the electrodes were thoroughly rinsed with deionized water and methanol. The resulting film was used as the electrodes for the electrochemical characterizations.

Fabrication of high-mass loading 3D-tsSC electrodes: Electrodes were fabricated through repeated drop-cast and laser conversion processes. On the top of the first layer of 3D-tsSC laser formation, a certain number of sequential drop casts was done at the same loading density. Each drop cast was followed by a laser conversion at the same power and speed settings. The thickness was determined by averaging the distance in cross-sectional SEM images at three spots. The electrode loading mass was determined by the final mass subtracting the mass of graphite paper.

The average mass loadings were measured by averaging five electrodes (1 cm²). 0.39 mg cm⁻² was obtained after a single 1-layer deposition-laser. 0.76 mg cm⁻² was obtained after a 2-layer deposition-laser. 1.05 mg cm⁻² was obtained after a 3-layer deposition-laser. 2.21 mg cm⁻² was obtained after a 5-layer deposition-laser. 5.7 mg cm⁻² was obtained after a 5-layer deposition-laser.

Assembly of Flexible all-solid-state 3D-tsSC Supercapacitors (3D-tsSC FSSCs): The symmetric device contains a 1.0 M H₂SO₄ gel electrolyte. The preparation of which involved dissolving 1.0 g PVA in 10 mL water, stirred vigorously for 30 min at 90 °C, to which 0.56 mL of stock H₂SO₄ was added. The electrolyte was then deposited at the surfaces of two 3D-tsSC electrodes (2 cm x 2 cm) and left to rest for 1 h to ensure surface wetting. A cellulose separator (NKK TF4030) was next placed between the two electrodes to assemble the device. The device was dried for 12 h at room temperature until the gel solidified. After drying the FSSC was sealed with Kapton tape on both sides to prevent the electrolyte loss during the electrochemical characterizations.

Electrochemical characterization: The electrochemical characterizations were performed on a Biologic VMP3 electrochemical workstation. The three-electrode characterization was performed using 3D-tsSC as the working electrode, graphite sheet as the counter electrode, and a standard Ag⁺/AgCl (1M KCl) as the reference electrode. The two-electrode characterization was performed using 3D-tsSC as both working and counter electrodes. For CV and GCD studies, the window voltages were set from 0 to 1.0 V. Specifically in three-electrode configuration, the potential was set as -0.2 to 0.8 V vs. Ag⁺/AgCl reference electrode, which can be converted to 0

to 1.0 V vs. standard hydrogen electrode (SHE). The cycling stability test was carried out using a GCD method. EIS tests were performed at 10 mV amplitude in the frequency range from 10 mHz to 100 000 Hz. The OCV self-discharge processes were evaluated by the Biologic VMP3 electrochemical workstation. Specifically, the OCV self-discharge was measured via charging to the working voltage of 1.0 V with 0.1 A g⁻¹ constant current density and maintaining constant voltage for 120 min. Once the supercapacitor was fully charged, disconnected the circuit and recorded the change of open circuit voltage with time to determine the self-discharge. In order to ensure the stability of the equipment and reduce the influence of charge redistribution on the self-discharge, 50 cycles of cyclic voltammetry were scanned at 200 mV s⁻¹ before the leakage current and self-discharge test.

General characterization: A Jasco FT/IR-4100 with a single reflection ATR unit was used for FT-IR spectroscopy. Bruker's D8 Discover powder X-ray diffractometer recorded CuK α radiation (λ = 1.5406 Å) XRD patterns. A Renishaw InVia Raman Microscope with a 633 nm laser captured Raman spectra in individual spectral or mapping mode. Single Lorentzian functions with R²-values of 0.99 fit Raman spectra peak fitting. Fluorescence baseline subtraction and Lorentz peak centers deconvolved the powder Raman spectra. Peak positions were determined via Raman spectra of several materials. A 3 or 5 kV FEI Nova 230 Nano SEM was used for SEM. Al or Cu foil substrates were used to support samples. A 120 kV FEI T12 TEM performed TEM. A 5 μ L ethanol-diluted powder dispersions were drop casted over Lacey-carbon supported TEM grids to produce TEM samples. A Kratos Axis Ultra DLD spectrometer with a monochromatic Al K α X-ray source ($h\nu$ = 1486.6 eV) produced XPS spectra. Carbon tape (Ted Pella) was used to calibrate high-resolution spectra. CasaXPS processed raw data (version

2.3.16). C 1s spectra were fit using Gaussian–Lorentzian line-shapes for all spectral components except the sp² C component, which was fitted with an asymmetric line shape to reflect the metallic nature of the samples. All samples used FWHM and position limitations for consistency. UPS measurements were performed on the same instrument with an unfiltered HeI (21.22 eV) gas discharge lamp and a total instrumental energy resolution of 100 meV. The electrical sheet conductivity of the 3D-tsSC electrodes was measured using the four-point conductivity probe (Veeco; Plainview, NY). The contact angles were measured using the First Ten Angstroms contact angle analyzer Model FTA 125. The droplets were formed by 0.05 mL 1M H₂SO₄ water solution.

Methylene blue surface area determination: The surface area is determined using the powder collected and washed from the laser formation step. 50 mg of the powder is displaced in an aqueous solution of methylene blue with a concentration of 0.1 M. Note that polypropylene beakers and vials were used to handle methylene blue. The mixture is stirred vigorously for 24 h and is then centrifuged at 16,000 rpm to isolate any suspended material. The supernatant is measured in its absorption at 665 nm against a reference of the stock solution of 0.1 M aqueous methylene blue. The measurement also relied on the assumption that every methylene blue molecule occupies 1.35 nm² of active surface area.

Calculation of specific capacitance: Gravimetric specific capacitance (CS) of electrodes tested in a two-electrode cell setup and areal capacitance (CA) of FSSC symmetric devices were calculated from GCD profiles using the following relations:

$$C_S = 4 \times \frac{I \times \Delta t}{m \times \Delta V} (F g^{-1}) \quad (1)$$

$$C_A = 2 \times \frac{I \times \Delta t}{A \times \Delta V} (F cm^{-2}) \quad (2)$$

where I is the discharge current (mA), Δt the duration of discharge (s), m the active material mass loading (mg), A the surface area of the electrode (cm^2), and ΔV the voltage window (V).

Calculation of Coulombic efficiency based on GCD: Charge and discharge curves of the GCD profiles are integrated to yield total capacity charged and total capacity discharged, and the ratio of discharged capacity to charged capacity grants the Coulombic efficiency of particular electrodes/devices.

Energy density E and power density P follow the equations below:

$$E = \frac{1}{2} C_x \Delta V^2 \times \frac{1000}{3600} (Wh/kg) \quad (3)$$

$$P = \frac{E}{\Delta t} (Wh/kg) \quad (4)$$

where $C_x = C_S$ for the energy density of electrodes in the two electrode-configuration, outputting gravimetric energy density.

Calculation of Capacitance from Impedance: The electrode-electrolyte interface is approximated with a Randles circuit within the frequency range of 10 mHz to 100 Hz to estimate the real component of capacitance (C'). Electrochemical impedance spectroscopy provided impedance readings from which real and imaginary components of capacitance can be derived as follows:

$$C' = -Z'' / 2\pi f |Z|^2 \quad (5)$$

$$C'' = -Z' / 2\pi f |Z|^2 \quad (6)$$

where f represents the frequency (Hz), $|Z|$ represents the absolute value of impedance, and Z' and Z'' represent, respectively, the real and imaginary impedance components.

With the real and imaginary impedance components, the phase angle may be calculated with the following equation:

$$\phi = -\arctan(Z'(\omega)/Z''(\omega))$$

4.8 SUPPORTING INFORMATION AND FIGURES

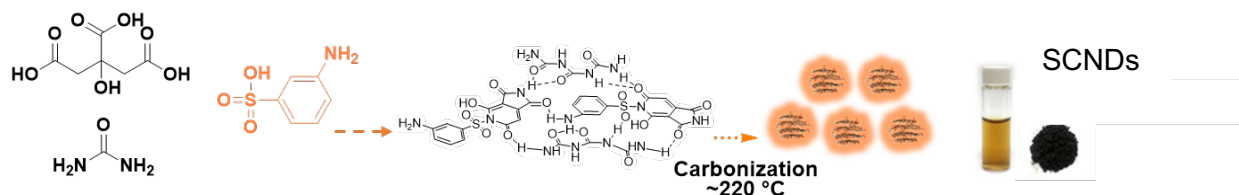


Figure S4.1 Reaction diagram of SCNDs formation.

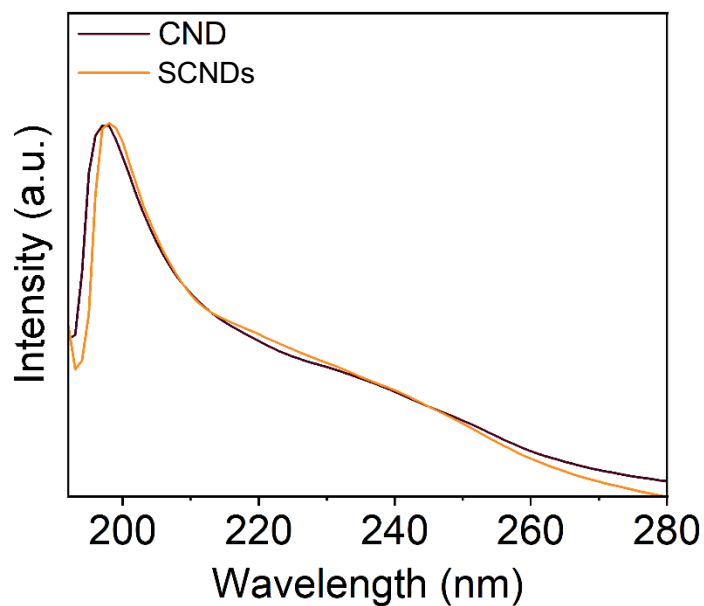


Figure S4.2 UV-vis spectrum of SCNDs and non-functionalized CNDs in ethanol solutions.

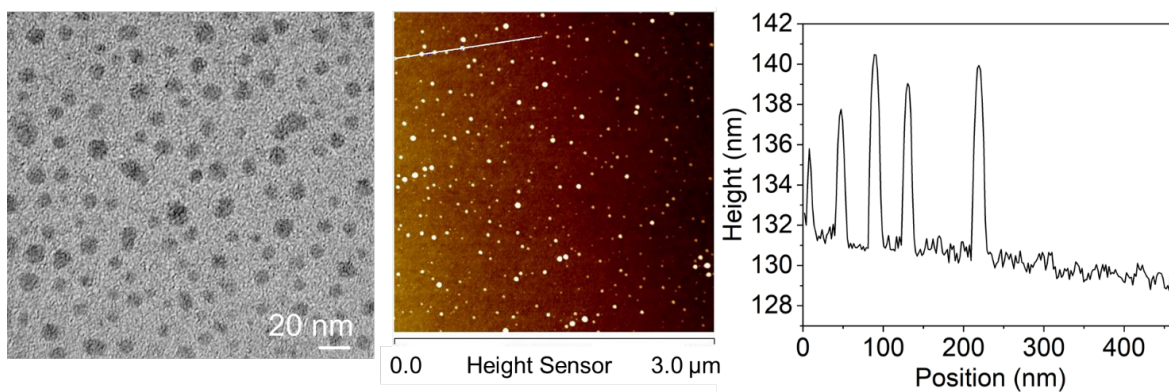


Figure S4.3 TEM (left) and AFM (middle) images of SCNDs. The height profile diagram indicates the sizes of five carbon SCNDs shown on the white line in the AFM image.

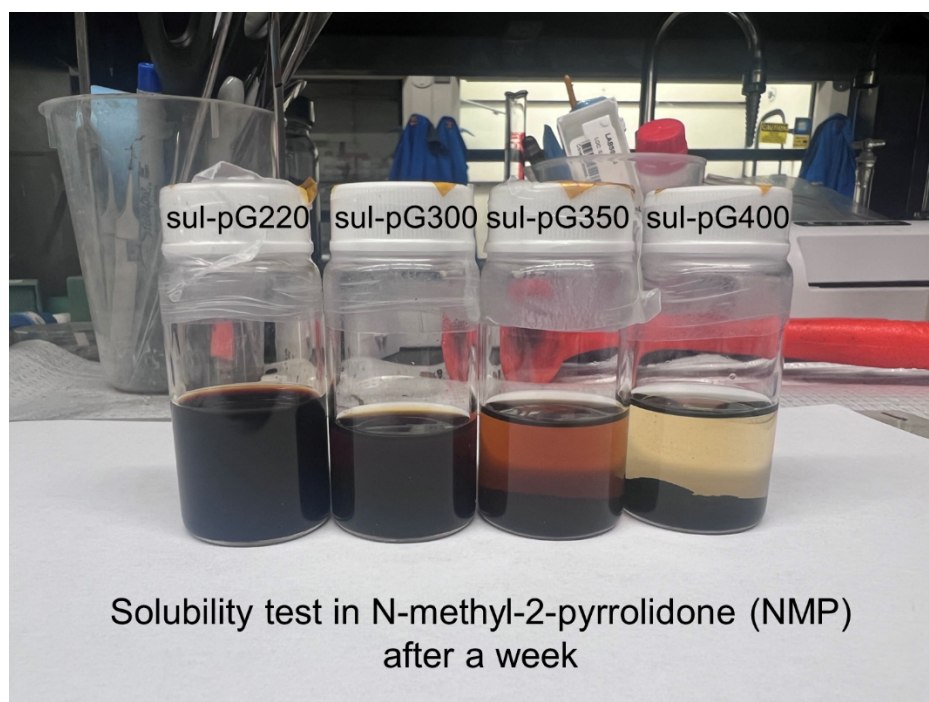


Figure S4.4 The dispersion of 3D-tsSC220, 3D-tsSC300, 3D-tsSC350, and 3D-tsSC400 in NMP after one week.

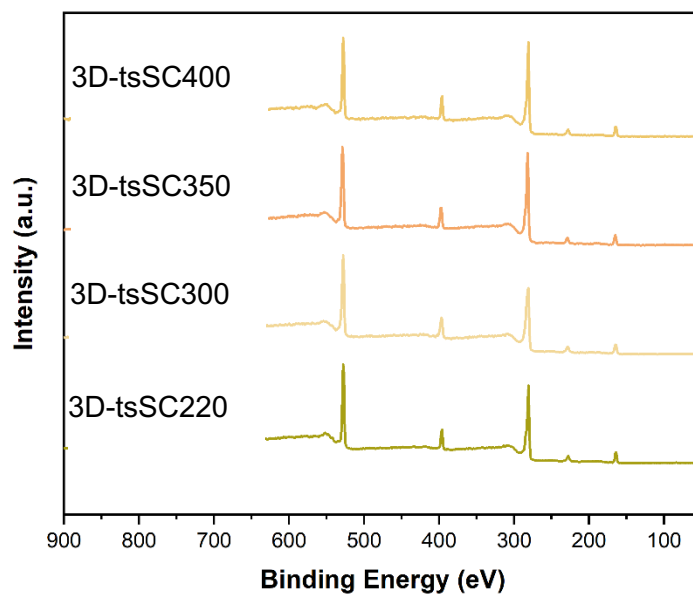


Figure S4.5 XPS survey spectrum of SCND220, SCND300, SCND350, and SCND400.

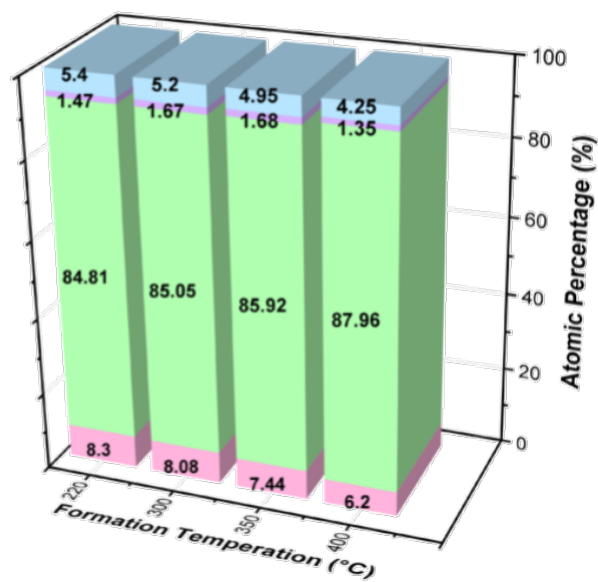


Figure S4.6 Compositional percentages of S2p, O1s, N1s, and C1s of SCND220, SCND300, SCND350, and SCND400 derived from their XPS survey spectra, respectively.

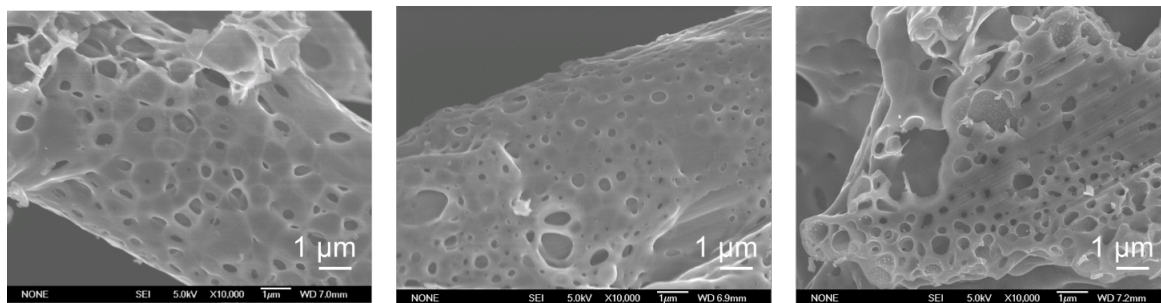


Figure S4.7 Typical SEM images of 3D-tsSC220 (left), 3D-tsSC350 (middle), and 3D-tsSC400 (right).

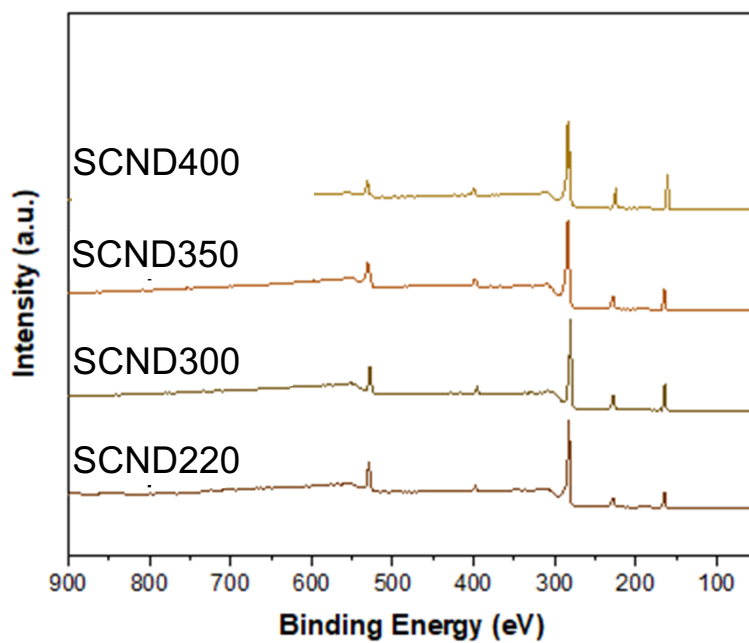


Figure S4.8 XPS survey spectrum of 3D-tsSC220, 3D-tsSC300, 3D-tsSC350, and 3D-tsSC400.

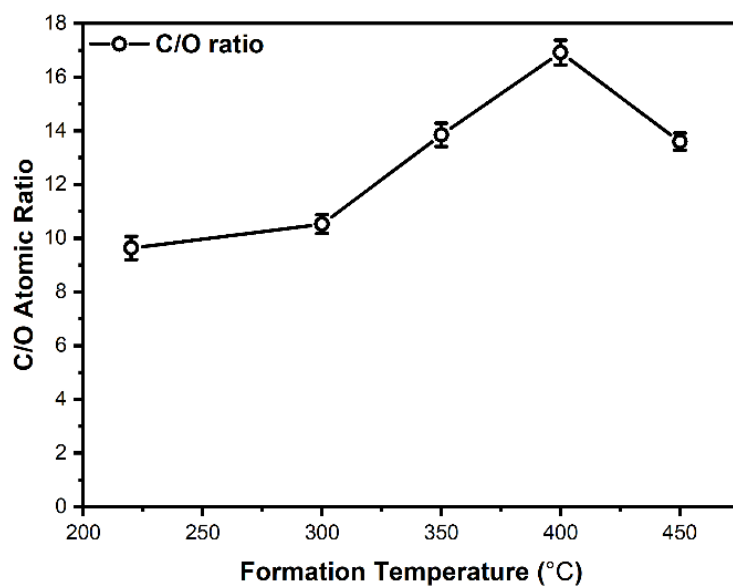


Figure S4.9 Variation of C/O ratios of 3D-tsSC220, 3D-tsSC300, 3D-tsSC350, 3D-tsSC400, and 3D-tsSC450.

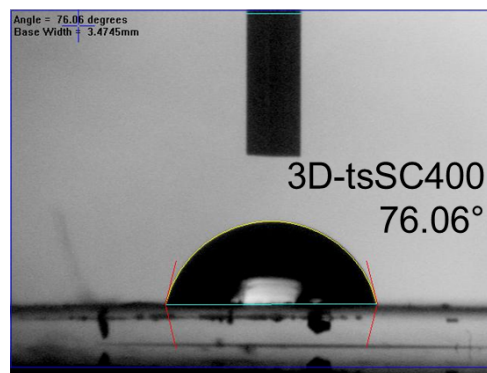
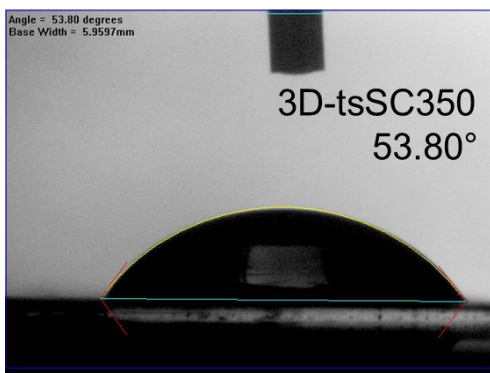
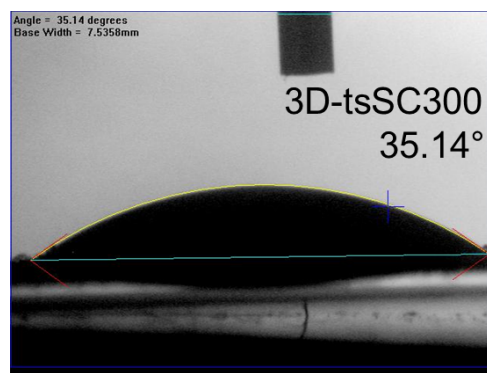
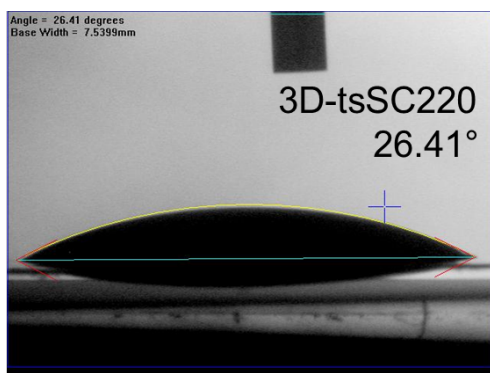


Figure S4.10 1M H₂SO₄ contact angles of 3D-tsSC220, 3D-tsSC300, 3D-tsSC350, and 3D-tsSC400.

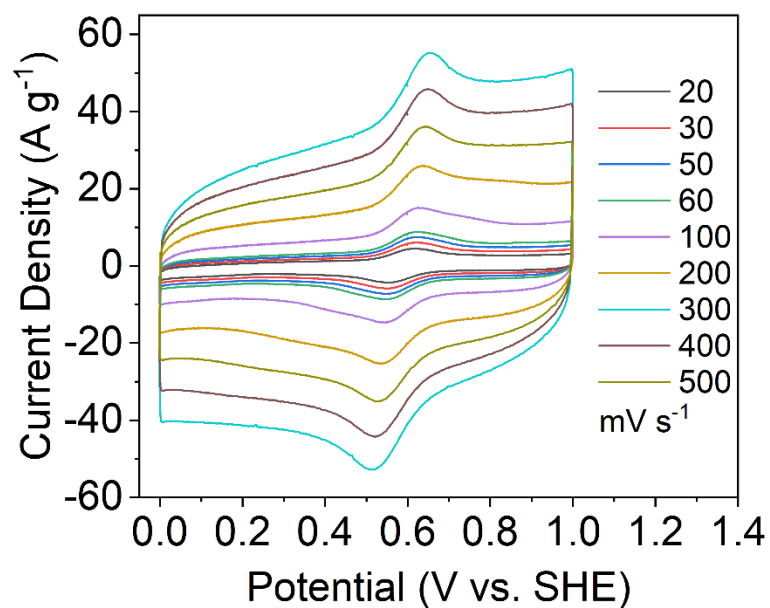


Figure S4.11 CV scans of 3D-tsSC300 at various scan rates in 1M H₂SO₄ measured by three-electrode configuration.

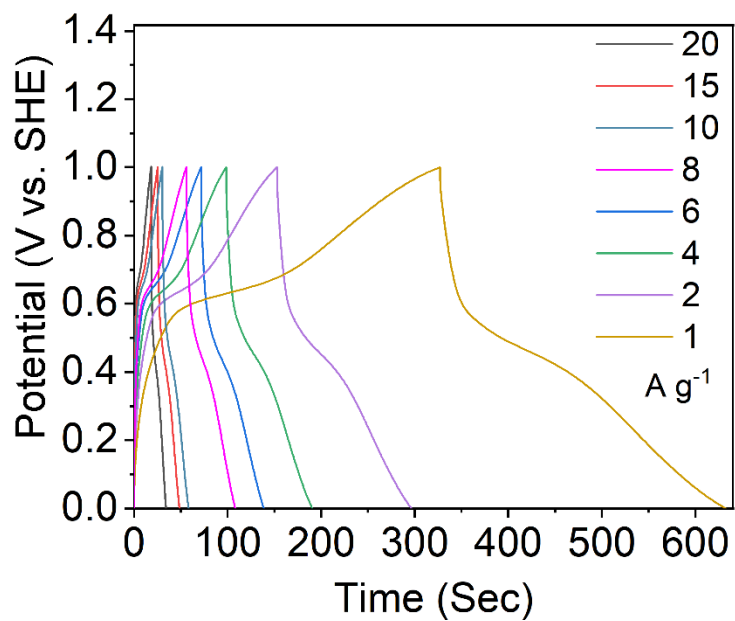


Figure S4.12 GCD profiles of 3D-tsSC300 at various current densities in 1M H₂SO₄ measured by three-electrode configuration.

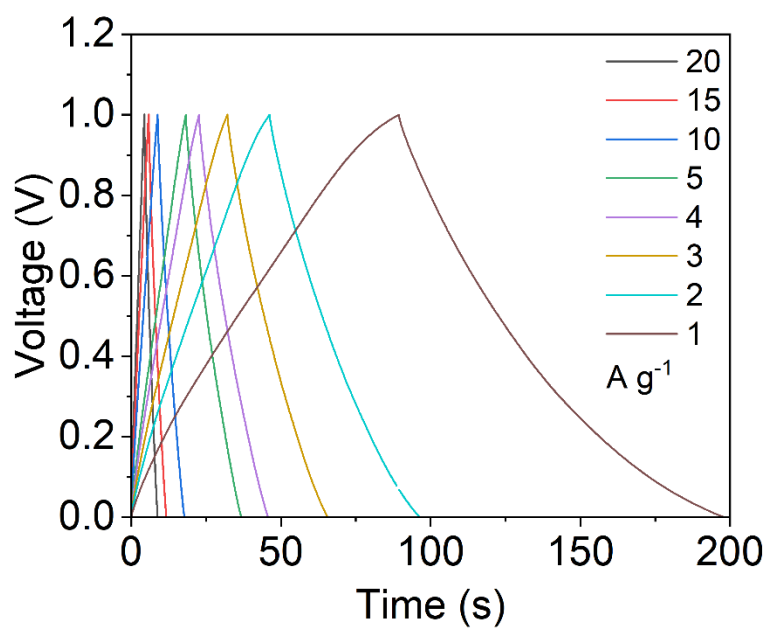


Figure S4.13 GCD profiles of tsSC at various current densities in 1M H₂SO₄ measured by three-electrode configuration.

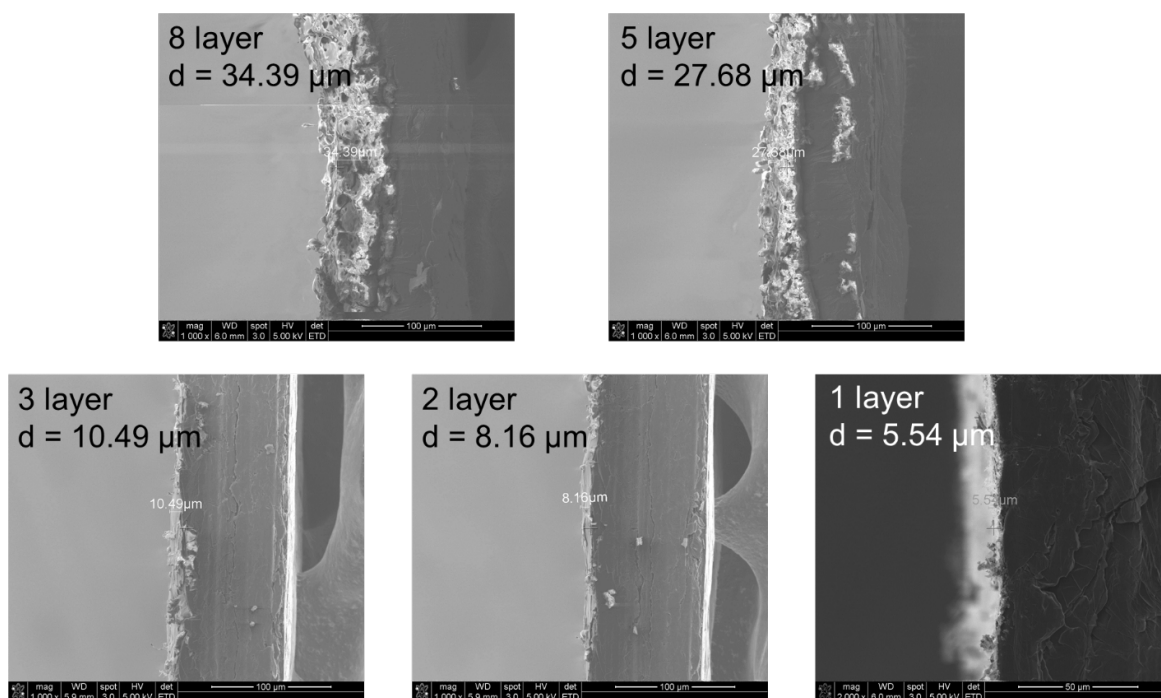


Figure S4.14 Cross-sectional SEM images and electrode thickness measurement of different loading masses.

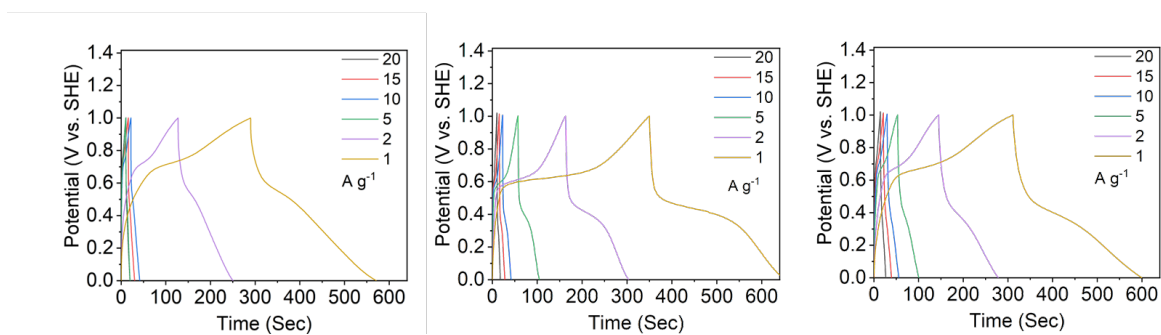


Figure S4.15 GCD profiles of 3D-tsSC220, 3D-tsSC350, and 3D-tsSC400 at various current densities in 1M H₂SO₄ measured by three-electrode configuration.

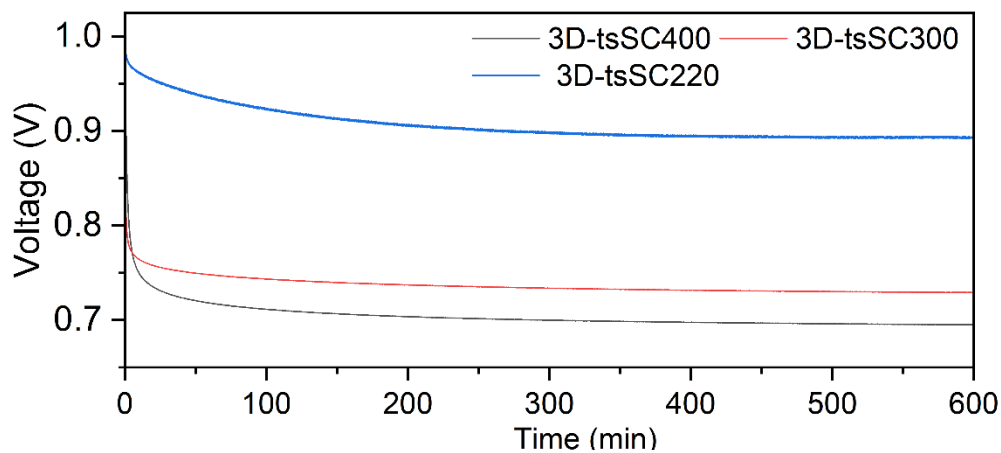


Figure S4.16 OCV self-discharge curve after charging at 1.0 V for 120 min.

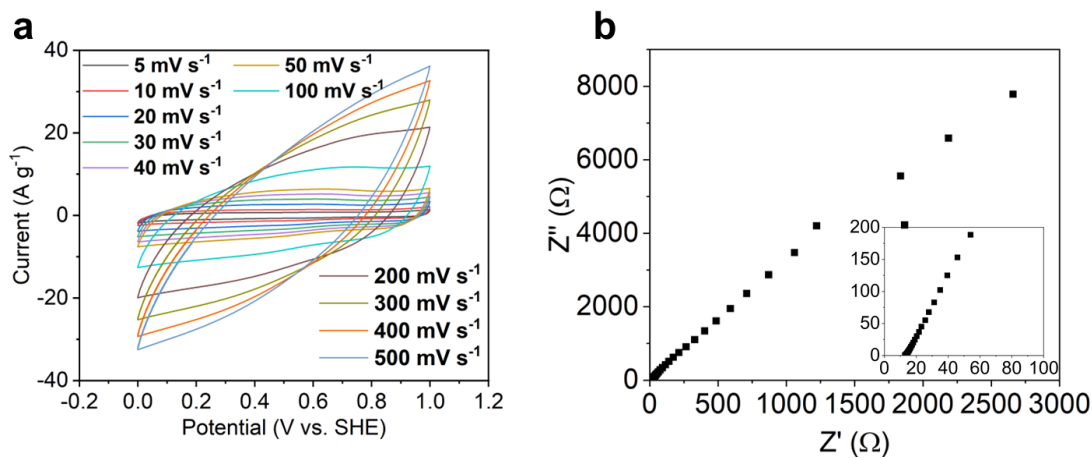


Figure S4.17 a) the CV profiles at various scan rates, b) the Nyquist plot (inset is a zoom-in plot in high frequency region) of 3D-tsSC300 in 1 M Na₂SO₄ aqueous electrolyte.

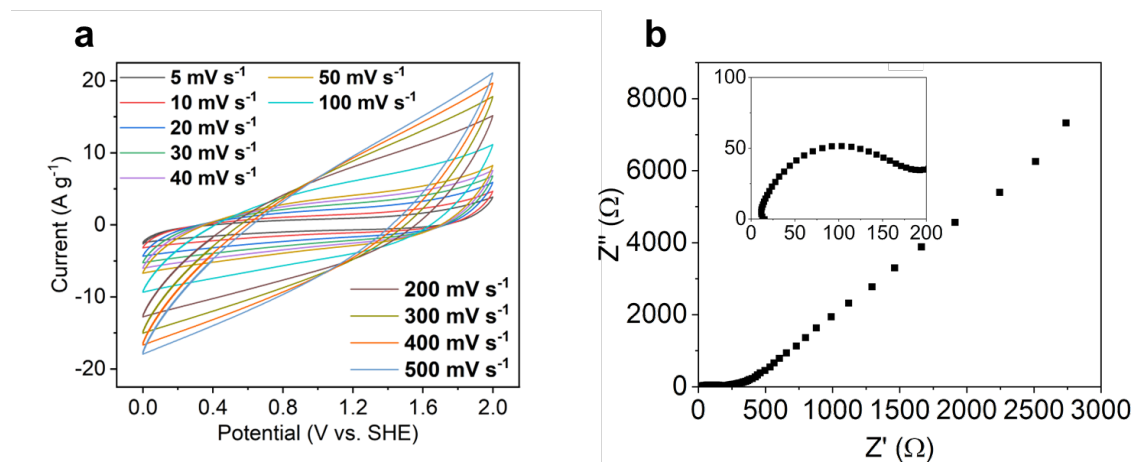


Figure S4.18 a) the CV profiles at various scan rates, b) the Nyquist plot (inset is a zoom-in plot in high frequency region) of 3D-tsSC300 in 0.5 M TEABF₄/ACN organic electrolyte.

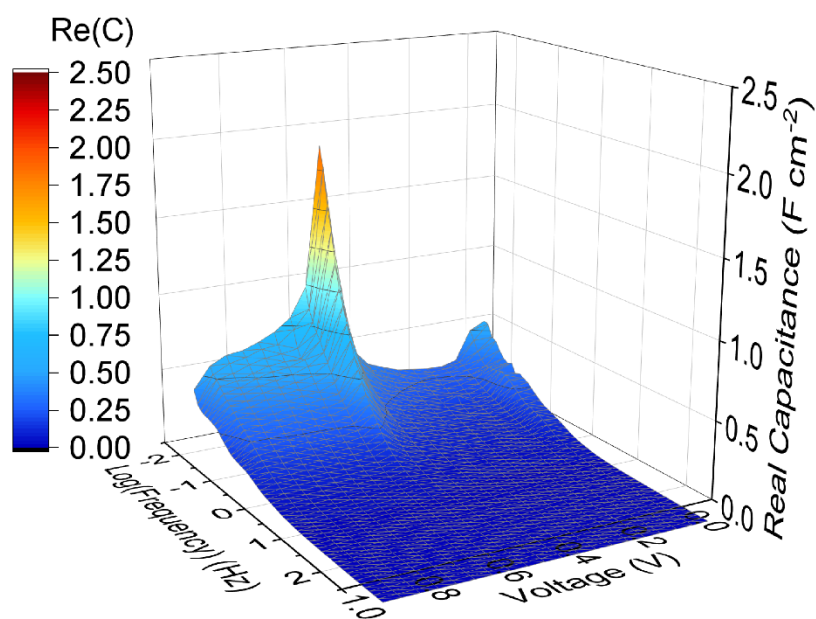


Figure S4.19 3D Bode plot of 8-layer 3D-tsSC220 electrode.

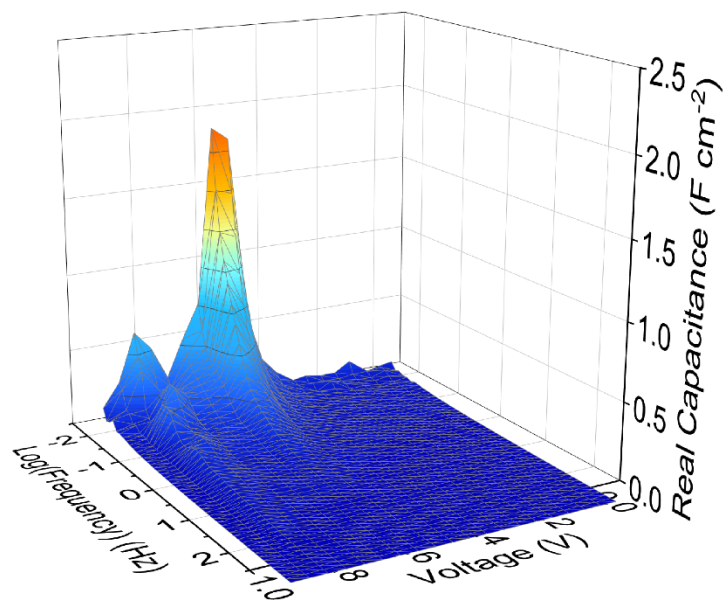


Figure S4.20 3D Bode plot of single layer 3D-tsSC300 electrode.

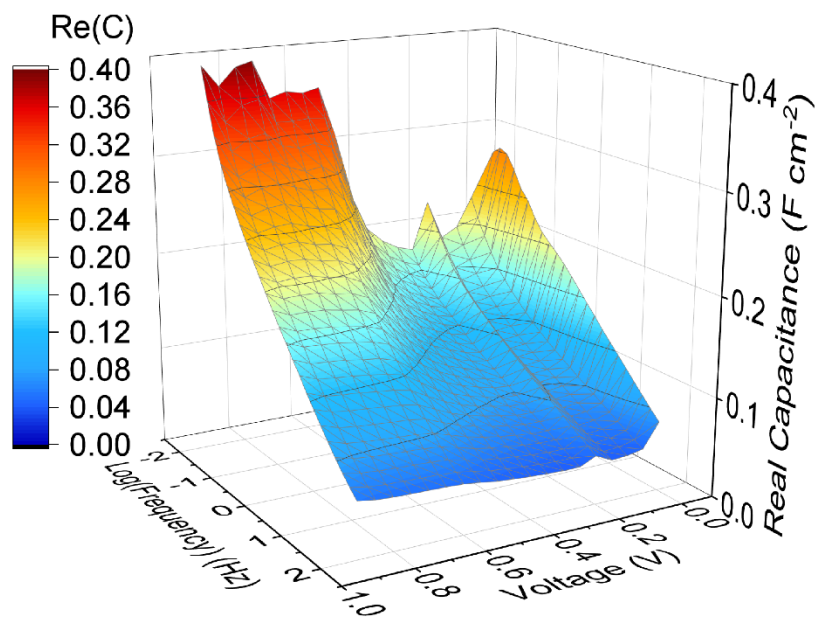


Figure S4.21 3D Bode plot of single layer unfunctionalized CND laser-converted tsSC electrode.

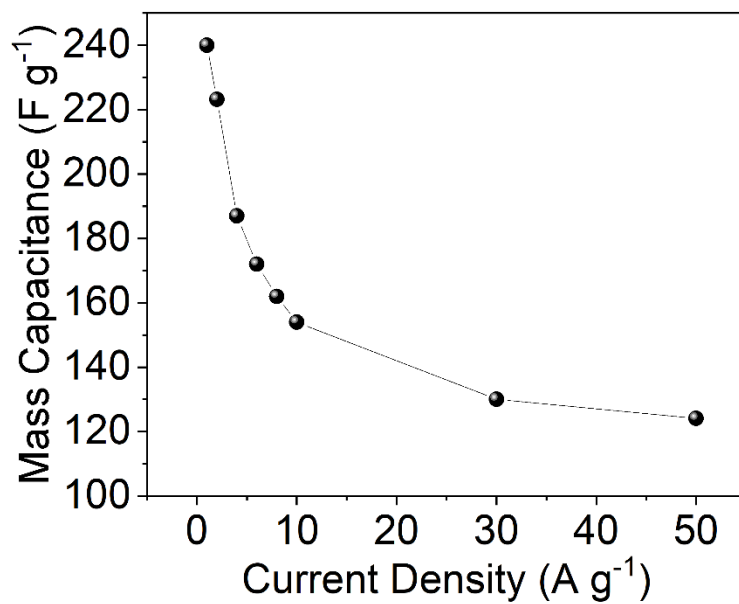


Figure S4.22 Mass capacitances of symmetric 3D-tsSC300 at various current densities.

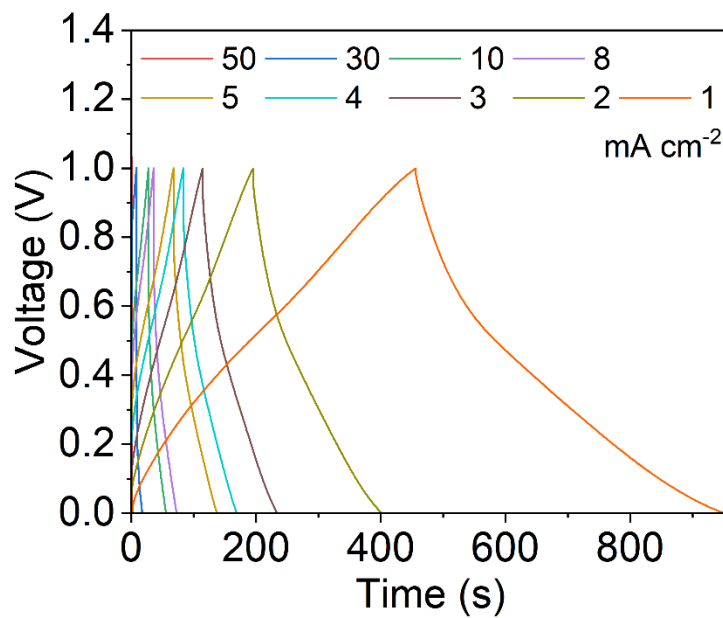


Figure S4.23 GCD plot of 3D-tsSC300 symmetric supercapacitor at various current densities.

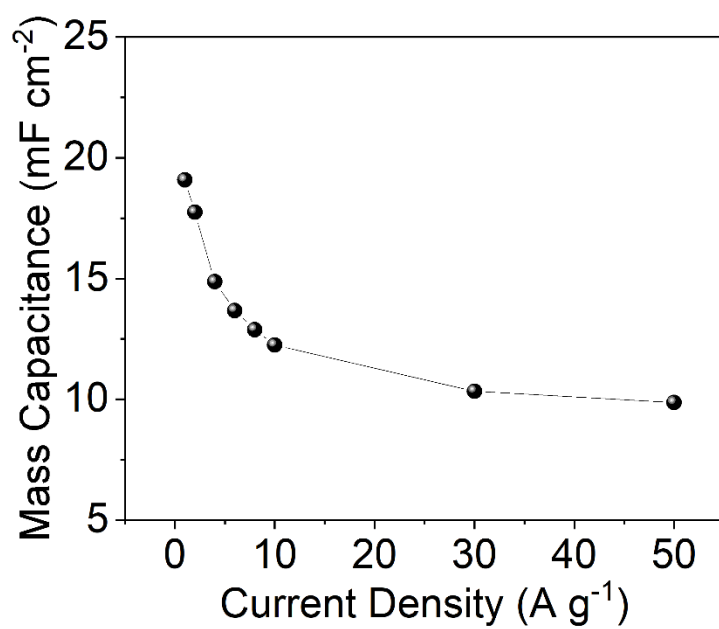


Figure S4.24 Rate performance of sup-pG300 FSSC at various current densities.

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CHAPTER 5. DESIGN EFFICIENT, RELIABLE, AND WIDE-BAND FILTER ELECTROCHEMICAL CAPACITORS VIA MATCHING POSITIVE WITH NEGATIVE ELECTRODES

"Adapted from a manuscript written by Wang C, Sung K, Zhu JZ, Qu S, Bao J, Chang X, Katsuyama Y, Yang Z, Zhang, El-kady MF, Kaner RB.

5.1 INTRODUCTION

Using intermittent renewable energy to power our lives poses a major challenge. Despite significant advances,¹ energy generation and storage systems create a frequency gap when renewable electricity enters stationary storage. Wind and hydropower (~77.5% of renewable energy) generate bidirectional alternating current (AC) with fluctuating frequencies.² However, stationary storage, like electrochemical batteries, only stores direct current (DC) power.¹ AC line filter capacitors offer interlinkage, converting AC power into DC. Additionally, filter capacitors modulate multifrequency signals in integrated circuits (ICs) for emerging automation technologies.³ Recent studies have indicated that electrochemical capacitors (ECs) can achieve efficient AC filtering.^{4,5} Due to interfacial charge exchange, ECs show much higher capacitance than electrolytic capacitors,⁶ benefiting optimized filter output at small device sizes. Therefore, engineering ECs for line filtering makes possible key technologies from grid-level renewable storage to advanced electronic miniaturization.

For practical EC-based filter capacitors, electrochemical and kinetic issues must be tackled. 1) Transmission line specifications require high-voltage filter capacitors. Typical line filtering uses bulky electrolytic capacitors with rated voltages of 10-1000 V,⁷ whereas ECs generally display voltages of <4 V.⁸ Although ECs in series enhance the voltage limit, serial resistive and capacitive

losses still reduce filter efficiency. Thus, high-voltage ECs should be designed for line filtering. 2) ECs must have a high capacitance and a near-90° phase angle throughout their lifespan. Thus, fast ion/electron transport and reversible charging electrodes are favored.⁹ Additionally, charge-exchange between the two electrodes should align in infinitesimal periods to suppress cell polarization.¹⁰ Conventional electrolytic capacitors charge via free electron separations, where fast frequency-response keeps electrons balanced on the two electrodes. However, ECs experience different ionic environments between negative and positive electrodes, leading to contrasting interfacial charge-exchange kinetics.¹¹ This discrepancy overcharges the electrode, which responds slower to charging, resulting in capacitor failure and irreversibility within less than million cycles.^{12,13} The compromised lifespans are uncompetitive with commercial aluminum filter capacitors (typically 1000-hour lifespans, equivalent to 12.8 million cycles for a capacitor with a time constant of 8.3 ms).¹⁰ Therefore, single-electrode reversibility and fast rate capabilities should be engineered for durable filter electrochemical capacitors (FECs).¹⁴

This study examines the coupling effects of individual electrodes on device-level EC performance, such as electrochemical storage and line filtering. We observe that complementary potentials of single electrodes create voltage separation at each state-of-charge (SoC), increasing the full-capacitor voltage. Cycling studies show that electrode pairs with distinct charge-exchange kinetics undergo severe cycling degradation due to frequency-response discrepancies between negative and positive electrodes. Mismatched negative and positive electrodes have been found experimentally to induce instantaneous charge imbalance and shifted electrode potentials, leading to cracked pores and agglomerated electrode surfaces, deteriorating EC reversibility. An analytical approach employing Coulombic efficiency (CE) at ultraslow scans, resistor-capacitor (RC) capacitances, and time constants at 120-Hz perturbations have been developed to quantify electrode stable

potentials and frequency-response time. Applying this approach to match negative and positive electrodes, a 1.8 V durable FEC is demonstrated. The resultant FEC show integrated filtering accuracy and longevity comparable to commercial electrolytic capacitors. This paper advances ECs for line filtering, illustrating how individual electrodes balance interfacial interactions and mitigate EC reversibility deterioration during ultra-fast charging.

4.2 RESULTS AND DISCUSSIONS

4.2.1 DESIGN HIGH VOLTAGE BY MATCHING SINGLE-ELECTRODE POTENTIALS

Single-electrode stable potentials were studied using ultraslow CV scans at 0.2 mV s^{-1} . Slow scans allow for discrete observation of irreversible electrode reactions at each potential, such as hydrogen/oxygen evolution and carbonations.¹⁵ The stable potential ranges were identified by extending the measurement boundaries by $\pm 0.1 \text{ V}$ until an irreversible scan was detected. Average Coulombic efficiency (CE) below 99% in ten scans defines irreversibility.¹⁶ Two heteroatom-rich activated carbon materials (boron and sulfur-doped activated carbon, denoted as 3D-tsBC and 3D-tsSC) were prepared and tested.^{17,18} Derived from the same activation process, they showed comparable degrees of graphitization, electrochemical surface areas, and macroporous morphologies (**Figure S5.1**).^{19,20} The 3D-tsBC displays a stable potential from -0.8V to 0.4V vs. a standard hydrogen electrode (SHE), with CEs of 99.8% or higher observed (**Figure 5.1a**). At -0.9 or -1.0 V, a non-rectangular CV curve with a current leap was observed, indicating the occurrence of irreversible electrochemical reductions of the electrode or oxidations of the electrolyte.²¹ For 3D-tsSC, CEs are over 99.0% were observed until the potential exceeds 1.0 V, suggesting that it is stable from 0 to 1.0 V. The surface terminations and chemical doping in carbon

electrodes tune charge transport processes such as surface molecular absorption and electron transfer,^{22,23} affecting CV background current and potential window (**Figure S5.2-4**).²⁴⁻²⁶

The full-capacitor stable voltage was evaluated at 0.2 mV s⁻¹ using 3D-tsBC as the negative electrode and 3D-tsSC as the positive electrode. The 3D-tsBC and 3D-tsSC350 pair at a 1.27:1 mass ratio provides well-aligned output currents at ultrafast charging (**Figures 5.1b and 5.1c**). This suggests maximized energy and power collection from the two electrodes in a well-coordinated asymmetric design due to the charge balance between the negative and positive electrodes (**Figure S5.7**).²⁷ The full-capacitor showed reversible CV scans at 1.6 - 1.8 V (**Figure 5.1d**). We coupled a parallel three-electrode chronopotentiometry to monitor the in-operando working potential of each electrode at varied voltages. Both single electrodes showed reversible cycling with near-ideal rectangular curves within their stable potential range when the full capacitor was operated at 1.6-1.8 V (**Figure 5.1e and 5.1f**). The suppressed side reactions of each electrode at vastly separated potentials stabilizes the full capacitor at high voltages.¹ Irreversible redox peaks were identified as the current was increased to raise the full-capacitor voltage beyond 1.85 V (**Figure 5.1g**).² This irreversible process was caused by electrolyte decomposition on the positive electrode above 0.65 V and on the negative electrode below -1.0 V (**Figure 5.1h**). The response altered the electrode, expanding the positive electrode's working potential to an unstable regime (**Figure 5.1i**).

The CV scans illustrate ultrafast capacitive charging processes. Because both electrodes display near-constant current in response to fast-sweeping potentials, the full capacitor shows a linear charge density with increasing voltage up to 1.8 V. In **Figure 5.1j**, the CV profiles of the full capacitor pairing by 3D-tsBC and 3D-tsSC350 exhibit near rectangular shapes and a linear relationship of discharge current to scan rate to 1000 V s⁻¹, which demonstrated fast charge transport within the asymmetric configuration. **Figures 5.1k and 5.1l** present the in-operando

current response of 3D-tsBC negative electrode and 3D-tsSC350 positive electrode, respectively. Both reveal non-distorted and rectangular CV curves, indicating synchronized charging between negative and positive electrodes even during ultra-fast charging, leading to high-power capability in full capacitors at 1.8 V. The discharge current density vs. scan rate plot in both electrodes exhibits strong linearity, with R^2 values over 0.995 throughout 1–1000 $V\ s^{-1}$ (**Figure 5.1b**), confirming ideal capacitive charge/discharge kinetics.²⁸ This is further supported by GCD profiles, which are symmetric triangular with little IR drop at current densities of 1–50 mA/cm^2 (**Figure S5.6**).

4.2.2. DESIGN LONG LIFESPANS BY MATCHING FREQUENCY-RESPONSE OF INDIVIDUAL ELECTRODES

Frequency-dependent impedance analysis of symmetric coin-cell ECs was used to characterize the frequency-response of carbon electrodes. For quantitative analysis, we studied key parameters, including phase angle at 120 Hz (Φ_{120Hz}), cutoff frequency (f_0), time constant (τ_0), and RC time constants (τ_{RC}) of 3D-tsBC and four sulfur-doped activated carbon species (3D-tsSC220, 3D-tsSC300, 3D-tsSC350, and 3D-tsSC400, the ending numbers indicate the different carbonization temperatures) (**Figure 5.2a-d**, S5.8-11). All four parameters show reasonable variations, suggesting that the frequency-response is fastest in 3D-tsSC400 and slowest in 3D-tsSC220. Varied carbonization temperatures effectively tuned doping levels and functional group densities.^{29,30} At high carbonization temperatures, diminished charge-localizing ligands promote rapid ion diffusion by reducing polarization; additionally, large graphitic domains reduce ohmic loss at high-frequency voltages. Both lead to faster frequency-response in high-temperature products. Compared to 3D-tsBC, 3D-tsSC350 shows a matched frequency-response considering

that all four parameters are identical within the standard deviation. This stems from comparable electrical conductivities and surface properties such as hydrophilicity (**Figure S5.12**).³¹ Other sulfur-doped carbon species deviate further from 3D-tsBC, whereas 3D-tsSC220 contrasts the most.

The frequency-response discrepancies between positive and negative electrodes can over-polarize capacitor electrodes and deteriorate cycling reversibility.³² To investigate the effect of frequency-response matching on ECs reversibility, two prototype full-capacitors were studied, 3D-tsBC||3D-tsSC350 with a matched electrode pair and 3D-tsBC||3D-SC220 with a mismatched electrode pair. In-operando frequency-response studies at successive SoCs explicitly revealed potential-dependent kinetics of interfacial charge exchange. We investigated single-electrode frequency-response using a three-electrode Swagelok cell to reduce diffusion distance-induced spectrum distortion (**Figure S5.13**). **Figure 5.2e** shows the 3D-tsBC Nyquist plots at 0, 0.6, 1.2, and 1.8 V. All the curves display straight, near-perpendicular plots. A decreasing slope as the potential rises indicates increasing resistive loss to HSO_4^- , SO_4^{2-} , and OH^- anionic polarizations. In addition, 3D-tsBC's Nyquist plot strongly overlaps with 3D-tsSC350 at 1.8 V, indicating the coinciding charge exchange when fully charged. By circuit simulation modelling (**Figure 5.2g**), the Nyquist plots of 3D-tsBC negative and 3D-tsSC350 positive electrodes were quantitatively deconvoluted at each SoC.³³ (**Figure 5.2f**). Less than $\pm 5\%$ across all elementary components indicates consistent charge-exchange mechanisms (**Table S5.2**). The close impedance characteristics can be ascribed to similar spectroscopic features of the two electrodes during charging/discharging, for instance, I_D/I_G and I_{2D}/I_G ratios in *in situ* Raman (**Figure 5.2h-j**) and carbon-oxygen ratios in *ex situ* XPS of 3D-tsBC and 3D-SC350 (**Figure 5.S3, 14**). The Raman shifts of the D and G bands were noted from 0.0 to 1.0 V. In 3D-tsSC and 3D-tsBC, the D bands redshift with potential due to altered

work function stemming from ionic polarization at high potentials. The redshift of the G band is attributed to a strengthened $E_{2g2}(b)$ mode (1615 cm^{-1}) and weakened $E_{2g2}(i)$ mode at 1584 cm^{-1} in the G-band envelope.^{3,4} The $E_{2g2}(b)$ mode is more associated with graphite domains near the ion adsorption layer, including the ion surface excess at high potentials. Briefly, the G-band redshifts indicate a close binding of ions to graphitic domains. Besides, the D bands intensify as electrolyte ion intercalation, resulting in a D/G ratio larger than unity, in agreement with observations of in-situ Raman spectroscopy in graphitic electrodes.^{5,6} 3D-tsSC220 (D/G = 1.76 averaged in the range of 0-1.0 V) still exhibits a higher D/G ratio than 3D-tsSC350 (D/G = 1.54) in in-situ Raman spectra.

Potential-dependent frequency-response was further investigated using 3D impedance mapping, which projected resistor-capacitor (RC) capacitance (**Figure 5.3a-c**) and phase angles (**Figure 5.3e-g**) against working frequencies and potentials.³⁴ The capacitance mappings of 3D-tsBC and 3D-tsSC350 in Figure 5.3a and 5.3b both exhibit high magnitude ($>900\text{ }\mu\text{F}/\text{cm}^2$) at frequencies of $<5\text{ Hz}$ due to the slow interfacial charge separations such as surface redox and interlayer intercalation. High potentials accelerate interfacial charge separations, reducing local charge densities on polarized pendent functional groups. Thus, the capacitance decreases slightly against the potential. Specially, the 3D-tsSC350 positive electrode shows increased frequency at high potentials, as seen in the $900\text{ }\mu\text{F}/\text{cm}^2$ line, due to strong screening effects by positive potentials from neighboring polyatomic anions. Capacitance over 10 Hz , primarily responsible for line filtering, originates from quick ion exchange and electronic polarization. Both 3D-tsBC and 3D-tsSC350 exhibit plateau capacitances ranging from 10 Hz to 10^4 Hz , suggesting stable high-frequency responsiveness resulting from the well-defined electrode macropores and surface functionalities. Beyond 10^4 Hz , electronic polarization and parasitic inductance arise. The

capacitance decreases until completed and overcompensated by inductance. On the other hand, 3D-tsSC220 displays a different capacitance mapping. The capacitance drops dramatically from 10 Hz to 10^4 Hz. As the potential increases, the capacitance declines, for example, from 900 to 750 $\mu\text{F}/\text{cm}^2$ in the low-frequency band. A brief capacitance surge at ~ 0.6 V and a dip at ~ 0.8 V indicate predominant Faradaic reactions, as validated by previous electrochemical characterizations of 3D-tsSC220 (**Figure S5.15**).³⁵ The close patterns in phase angle mappings (**Figure 5.3e and 5.3f**) of 3D-tsBC and 3D-tsSC350 indicate equivalent capacitive to resistive ratios in all potentials, eventually resulting in similar filter power efficiency. As high potentials minimize the ohmic resistance, while low potentials reduce ionic impedance due to weak ion polarization, the phase angle showed a basin-like trendline against frequency, with the phase angle minima located at mid-potential. The 45° lines represent the cutoff frequency, which is consistently located around 5 kHz in 3D-tsBC and 3D-tsSC350. This suggests expansive frequency windows for high-efficiency line filtering in both positive and negative electrodes regardless of SoCs. Globally, smaller phase angles in a pseudocapacitive 3D-tsSC350 indicate a more resistive process and slower kinetics than the other two samples. The constant phase elements from 0.6 to 0.8 V confirmed the Faradaic processes.

Frequency-response discrepancies between 3D-tsSC and 3D-tsBC were quantified by 3D deviation mappings ($\text{Dev}(x,y,z)=3\text{D-tsBG}(x,y,z)-3\text{D-tsSG}(x,y,z)$) (**Figure 5.3d and 5.3h**). The larger Z-magnitudes in $3\text{D-tsBC}||3\text{D-tsSC220}$ than in $3\text{D-tsBC}||3\text{D-tsSC350}$ indicate greater differences between positive and negative electrodes in mismatched ECs at various SoCs. Notably, none of the mappings showed absolute symmetric patterns between low-potential and high-potential regimes, suggesting that charging kinetic differences exist universally between positive and negative electrodes in symmetric ECs at specific SoCs. Such differences were also observed

between the positive and negative electrodes in a standard asymmetric activated carbon supercapacitor (**Figure S5.16**). Thus, quantifying and engineering single-electrode frequency-response is necessary to achieve matched charge-exchange kinetics between positive and negative electrodes, mitigating phase divergence-induced irreversibility in FECs.^{36,37}

To investigate the deterioration process caused by the kinetic differences, the cycling performance and CEs of the matched and mismatched ECs were evaluated during ultrafast charging/discharging (at a current of 8.96 A/g (20 mA/cm²)) (**Figure 5.4a**). The matched capacitor 3D-tsBC||3D-tsSC350 retained 91.4% capacitance after 1.2 M cycles (1647 hours), whereas the mismatched 3D-tsBC||3D-tsSC220 retained 80.9% for 1141 hours. The 3D-tsBC, SC350, and SC220 symmetric capacitors were also characterized (**Figure S5.17**). The cycling was marginally better in all symmetric capacitors than in asymmetric capacitors. After 1.2 M cycles, 3D-tsBC (1.2 V), 3D-tsSC220 (1.0 V), and 3D-tsSC350 (1.0 V) had capacitance retentions of 92.8%, 92.7%, and 93.2%, respectively. Hence, instead of electrode fatigue resulting from lengthy cycling, 3D-tsBC||3D-tsSC220 rapid capacitance degradation was primarily due to the coupling effect of the two electrodes. Phase angle cycling was measured every 100 cycles (**Figure 5.4b**). After 1.2 M cycles, matched 3D-tsBC||3D-tsSC350 showed an 80.02° phase angle (96.0% retention), and mismatched showed a 69.95° phase angle (86.0% retention). After 1.2 M cycles, the mismatched capacitor is no longer eligible for line filtering since typical operations require more than 80°. Bode plots after the first cycle, the 0.5 M-th cycle, and the 1.0 M-th cycle show that the characteristic frequency (f_0) at 45° phase angle decreases significantly in 3D-tsBC||3D-tsSC220, inferring a severe shrinking of the line-filtering frequency range in addition to the phase angle decay. The mismatched 3D-tsBC||3D-tsSC220A shortens to 47.2% of the frequency range (starting from 120 Hz) after 1.0 M cycles, while the matched capacitor only lost 11.5%.

The fast reversibility deterioration in mismatched electrode pairs can be attributed to the instantaneous charge deficiency of the electrode that shows slower charge-exchange kinetics, for example, 3D-tsSC220 in the mismatched ECs. We examined the electrode polarization by monitoring the working potentials of positive sulfur-doped carbon electrodes in matched and mismatched ECs over the first 0.3 M (300 k) cycles, where a major degradation occurred. Initial cycling potentials of 3D-tsSC350 and 3D-tsSC220 electrodes were -0.1 to 0.8 V (vs. Ag/AgCl, equivalent to 0.1–1 V vs. SHE) (**Figure 5.4c**) spanning the half-divided 0.9 V range, suggesting that in the beginning, proportionate capacitance balancing leads to non-polarized electrodes within stable potentials. After 38 k cycles, 3D-tsSC220's potential declined to 0 V, near its stable limit. A range of 0.9 V was retained until 0.2 M cycles.³⁸ The 3D-tsSC220 shows a potential range widening to 1.2 V (-0.2 to 1.0 V) after ~0.22 M cycles, with a sudden rise of the upper boundary, driving 3D-tsSC220 to operate beyond its stable potential. Steady cycling from -0.2 to 1.0 V afterwards suggests an irreversible electrode change, which may explain the significant performance degradation at the same cycling periods. On the other hand, 3D-tsSC350 maintains its steady potential across the 300 k cycles, displaying less reversibility deterioration.

Long cycling beyond the stable potential leads to irreversible electrode structural and compositional transitions (**Figure 5.4d-i**). SEM images of 3D-tsSC220 and 3D-tsSC350 before cycling show intact macroporous structures. The open structures and large pore areas maximize ion accessibility, promoting high capacitance and fast frequency-response (**Figure 5.4d and 5.4g**). After 0.4 M cycles, 3D-tsSC220 showed a crumpled and flaky surface, indicating a significant pore structural collapse (**Figure 5.4e**). Agglomerated and micrometer-sized carbon particles were found after 1.0 M cycles (**Figure 5.4f**). The substantial structural change is confirmed by the statistical SEM image processing captured at ten random regions. 3D-tsSC220 shows a porous

area retention of 11.6% after 1.0 M cycles, whereas 3D-tsSC350 achieved ~60% porous area retention. Additionally, the 3D-tsSC350 electrode only flattens a bit with less visible change after matching EC cycling (**Figure 5.4h and 5.4i**). The irreversible transition of 3D-tsSC220 was also evident in the C 1s XPS spectra as peak intensities of oxygen-containing motifs grow as cycle numbers increase (**Figure 5.4j-l, S5.18**). The electrode experienced electrochemical corrosion, including gas evolution and carbon dissolution, beyond the stable potential range. These irreversible processes reconstruct the carbon surface and add defects to the conductive carbon lattices, thus impeding ionic/electronic transport, causing a reduction in the frequency-response. Furthermore, the peak area of the S2p spectra shrinks, indicating the loss of sulfur-doped electrochemical active sites, which may explain the substantial capacitance decay in 3D-tsSC220 (**Figure S519**). Hence, matching the frequency-response kinetically suppresses the charge imbalance-induced capacitor polarization; and a consistently stable individual-electrode potential inhibits the deteriorative side reactions, leading to high EC reversibility and long cycling.³⁹

4.2.3. OPTIMIZE FILTERING PERFORMANCE OF EC-BASED CAPACITORS VIA MATCHING STRATEGY

AC, the main electricity supply form, is widely employed in power transmission and distribution. However, mobile phones and household electronics operate in DC. AC to DC conversion using the rectifier filter circuit is critical.⁷⁻⁹ Filter capacitor performance affects rectifier filter circuit filter efficiency and output quality. FECs based on aqueous electrolytes have garnered interest as next-generation filter capacitors due to their high capacitance, safety, and recyclability. They hold the potential to replace current AECs filter capacitors, which exhibit bulk occupancy and low

capacitance, enabling miniaturized high-power devices such as integrated processors, wearable gadgets, and electric vehicles.

The matched FEC, 3D-tsCASC-1.8V, exhibits a competitive high-frequency capacitance, phase angle at 120 Hz, and voltage window. It outperforms several organic-electrolyte-based and aqueous ECs (**Figure S5.20**). We constructed and tested single-unit (3D-tsCASC-1.8V), three-unit (3D-tsCASC-5.4V), five-unit (3D-tsCASC-9V), and ten-unit (3D-tsCASC-18V) serial capacitors to demonstrate their compatibility in high-voltage AC line filtering (**Figure S5.21**). 3D-tsCASC-18V shows a total capacitance of $76.8 \mu\text{F}/\text{cm}^2$, accounting for 93.5% of the theoretical ten-unit capacitance, indicating the strong constructive connection between serial ECs with minimum phase divergence (**Figure S5.22**). The frequency-response typically decelerates due to building up a high resistance in serial capacitors.⁴⁰ Both 3D-tsCASC-9V and 3D-tsCASC-18V demonstrate large phase angles at 120 Hz close to that of 3D-tsCASC-1.8V, surpassing the phase angle of a commercial aluminum capacitor (Nichicon, 16 V, 10000 μF , abbreviated as CAEC) due to fast and aligned charge-exchange kinetics (**Figure 5.5a**). The f_0 of 3D-tsCASC-18V is 2840 Hz, higher than that of CAEC (1100 Hz), showing a wide operating frequency window at high voltages. Suppressed serial resistive effects were further supported by a consistent relaxation time constant of 3D-tsCASC-1.8V, 3D-tsCASC-9V, and 3D-tsCASC-18V at 0.35 ms (**Figure S5.23**). Besides, power loss, emerging from asynchronized output of capacitors, was characterized by the dissipation factor (DF).⁴¹ For a standard filter capacitor, the DF should be less than 0.3. 3D-tsCASC-1.8V has a lower DF (0.12) than CAEC (0.17). As the unit number grows, 3D-tsCASC-9V and 18V's DF at 120 Hz rise to 0.20 and 0.27, respectively (**Figure 5.5b**). Low DF is crucial for serial capacitors to mitigate thermal dissipation-induced circuit failure.

The effective charge number, $C_V V$ (where C_V is volumetric capacitance and V is voltage) is a standardized measurement of filter efficiency. The high-voltage 3D-tsCASC-1.8V shows a higher $C_V V$ of 0.60 C/cm³, compared with symmetric ECs with similar overall voltages, for example, a two-unit 3D-tsBC symmetric EC shows 0.28 C/cm³ at 2 V and a two-unit 3D-tsSC symmetric EC shows 0.31 C/cm³ at 2.4 V, displaying high-voltage advantages resulting from matching individual-electrode potentials (**Figure 5.5c**). Additionally, $C_V V$ decays rapidly from a single-unit to a three-unit due to serial capacitance charge loss. However, a five-unit (3D-tsCASC-9V) and a ten-unit (3D-tsCASC-18V) show less decline in $C_V V$ because high voltage overweighs charge loss.⁴² Both high-voltage FECs show higher $C_V V$ than the standard CAEC, indicating the superiority of using FECs compared with conventional electrolytic capacitors, especially for volume-limited microgrids and miniaturized IC components. The superiority is further supported by the high volumetric capacitance of D-tsCASC-18V (43.6 mF/cm³), substantially greater than CAEC (7.3 mF/cm³) or the serial symmetric capacitors at the same operating voltage.⁴³

A rectifier-coupled AC-to-DC conversion circuit was assembled to characterize the filtering performance of 3D-tsCASC-18V and CSEC-16V (**Figure 5.5g**). We applied 16 V AC power at various frequencies of 120 Hz (**Figure S5.24**), 500 Hz (**Figure S5.25**), and 1000 Hz (**Figure S5.26**). In all three frequencies, 3D-tsCASC-18V showed lower voltage variances and filter noise in DC outputs compared with CAEC. This is because of the enhanced capacitance and reduced RC constant of ECs suppress the voltage ripple (V_r is defined by $V_r = V_0 - V(t) = V_0 \left(1 - e^{-\frac{t}{RC}}\right)$).⁴⁴ The improvement was achieved over a wide frequency range because matching positive and negative electrode potentials effectively minimized serial power loss. To evaluate the FECs' lifespans, we recorded output after continuous 120 Hz AC filtering for 100 and 1000 hours (**Figure 5.5d-f**). The output voltage is stable for the 3D-tsCASC-18V with no observable ripples. The

voltage variation was 23 mV and 34 mV after 100 and 1000 hours, less than the CAEC output during the same period. The matched frequency-response of the positive and negative electrodes enables FECs to have a long lifespan that rivals electrolytic capacitors.¹⁰ Therefore, wider voltage and longer reversibility can be rationally engineered by matching positive and negative electrodes of ECs, resulting in more efficient filter capacitors with comparable lifespans to electrolytic capacitors.

4.3 CONCLUSIONS

Here we have demonstrated that matching positive with negative electrodes, thermodynamic electrode potentials, and charge-exchange kinetics can regulate the EC voltage and reversibility. Notably, a wide potential gap between two electrodes increases the full-capacitor voltage without decomposing the electrolyte; pairing electrodes with aligned frequency-response diminished the instantaneous charge imbalance, which induces electrode corrosion from over-polarization, leading to high reversibility. Coupled with cycling evolution studies, it was further revealed that the unstrained potential shift and temporal phase divergence between two electrodes deteriorate EC reversibility. Furthermore, quantitative analysis of stable electrode potential and frequency response time deciphered the strong correlation of individual electrodes on device-level thermodynamic stability and ultra-fast charging kinetics. Applying the analytical results and matching the positive and negative electrodes enabled a practical FEC with comparable voltage and lifespan to conventional electrolytic capacitors, but with significantly enhanced capacitance and filter accuracy. This work elucidates the synergistic impact of individual electrodes on ultrafast charging devices, offering engineering strategies for FECs in miniaturized digital circuits and green power grids.

4.4 EXPERIMENTAL PROCEDURES

Solid-state Synthesis of carbon precursors (CNDs), boron-doped carbon precursors (BCNDs), and sulfur-doped carbon precursors (SCNDs)

All chemicals were used as received without further purification. Carbon nanodots (CND) were synthesized via solid-state pyrolysis of citric acid and urea in flowing argon. The tunable work function was realized by deliberately selecting amino-aromatic capping reagents. Typically, 30 mmol citric acid (Fisher Scientific, ACS grade), 6 mmol urea (Aldrich, 99%) and 1.6 mmol 3-aminophenylboronic acid monohydrate (Aldrich, 99.9%) were dissolved in 360 mL of deionized water for the synthesis of BCNDs. The solution was freeze-dried at $-40\text{ }^{\circ}\text{C}$ to obtain a homogeneous precursor for the solid-state reaction. After an intermediate grinding, the precursor was heated to $220\text{ }^{\circ}\text{C}$ at 10 K min^{-1} and held at that temperature in a 250 mL min^{-1} Ar flow for 2 hours. The obtained brown products were dissolved in 100 mL of water using ultrasonication. The dispersion was centrifuged at 4750 rpm for 30 min first. The supernatant was collected and dialyzed in regenerated cellulose dialysis tubing with a MWCO of 1 kDa for 48 h to remove any unreacted reactants. Then the obtained BCNDs were freeze-dried before further characterizations and applications. SCNDs were prepared under the same reaction conditions. SCNDs was prepared by freeze-drying a solution of 18 mmol citric acid, 3.6 mmol urea, and 1.6 mmol sulfanilic acid (4-aminobenzenesulfonic acid, Fisher Scientific, ACS grade) in 300 mL of deionized water. The pyrolysis and purification processes are similar to the B-CNDs. Pyrolysis was carried out at $350\text{ }^{\circ}\text{C}$ at first. Then a temperature gradient was applied from 220 to $400\text{ }^{\circ}\text{C}$. The SCNDs with different graphitization degrees were obtained in this manner.

Laser activation of boron-doped activated carbon (3D-tsBC) and sulfur-doped activated carbon (3D-tsSC)

A 10 mg/mL coating solution was first prepared by mixing CND dry powders in ethylene glycol for the laser reaction. The solution was drop-cast onto a stainless-steel sheet. Hydrophilic tapes were used to help control and enclose the drop-cast area. A film formed after baking at 70 °C to evaporate the ethylene glycol. The dry film was irradiated with a CO₂ laser (Full Spectrum FSL laser engraver, 10.6 μm). The laser parameters used were 30% of full power (full power = 45 W) and 30% of full speed (equivalent to 27.9 mm/s). The Z height was adjusted to focus on the top surface of the coating film. The film darkened after laser irradiation. An excess amount of DI water was used to collect the lasered product. The dispersion was centrifuged at 4750 rpm. The dark black precipitate was collected and washed with deionized water three more times, then dried under vacuum at 70 °C overnight. The powder samples prepared with BCNDs are labeled 3D-tsBC while the samples prepared with SCNDs are labeled 3D-tsSC.

Fabrication of high-mass loading activated carbon electrodes

A slurry consisting of 3D-tsC samples, carboxymethyl cellulose/styrene-butadiene rubber (MTI Corp) as a binder and carbon black (MTI Corp, TIMICAL SUPER C65) was prepared in deionized water with a weight ratio of 80:10:10, respectively. The slurry was then deposited on gold-coated polyimide sheets (Stanford Advanced Materials, AU3634, 0.015 mm). A height-adjustable doctor blade printing resulted in a mass loading of approximately 5 mg/cm² on the 3D-tsSC electrode and 6 mg cm⁻² on the 3D-tsBC electrode. The film was dried for 12 h under vacuum.

Assembly of symmetric capacitors and asymmetric capacitors (3D-tsCASCs)

The electrode square slide with a side of 1 cm was prepared. 3D-tsSC and 3D-tsBC were sandwiched with a Celgard membrane (2320) as the separator. 3.0 M Na₂SO₄ was used as the electrolyte. Kapton tape was used to seal the asymmetric capacitor. Two identical specific electrodes were used to make symmetric capacitors.

Assembly of Swagelok cell for in-operando potentiometry

The electrode disks with 3 mm diameter were made. The glassy carbon electrodes were used as the current collectors of the working electrode. After pretreatment, the electrodes were loaded on the surface using a 3.0 M Na₂SO₄ electrolyte. A bare glass carbon electrode was used as the counter electrode. A disk of Celgard membrane (2320) with a 5 mm diameter was sandwiched between two glassy carbon electrodes, pressed against each other tightly, and sealed in the two horizontal openings of a T-shaped Swagelok tube. The reference electrode was loaded to the third perpendicular opening after 30 μ L of electrolyte was filled in the tube. The tube was sealed tightly using parafilm to prevent electrolyte leakage or evaporation.

Electrochemical characterizations of electrochemical filter capacitors

The electrochemical characterizations were performed on a Biologic VMP3 electrochemical workstation. The window voltages were set from 0 to 1.8 V for CV and GCD studies of asymmetric capacitors. The cycling stability test was carried out using a CV scan from 0 to 1.8 V at a scan rate of 100 V/s. Bode plots were recorded every 100 cycles. EIS tests were performed at 10 mV amplitude in the frequency range from 10 mHz to 100,000 Hz. Three-electrode EIS was conducted using a Swagelok cell against a Hg/HgSO₄ reference electrode. Step-potential EIS tests were performed by applying a constant target potential for 100 seconds. The EIS was set at a certain offset voltage to assess the impedance spectra at an amplitude of 10 mV. The EIS mapping of commercial electrodes was carried out using a CORNELL DUBILIER EDLSG105H5R5C

Supercapacitor (1 F, 5.5 V, 30 ohm, standard coin-cell). The activated carbon electrodes were taken from a disassembled CORNELL DUBILIER EDLSG105H5R5C Supercapacitor. The electrodes were rinsed with N-methyl-2-pyrrolidone, dried and punched into 3 mm-diameter discs before assembled a Swagelok cell for the three electrode measurements. A 33511B arbitrary function generator (Agilent Technologies Inc., Tektronix, USA) was used to generate AC voltages at different frequencies to test the filtering performance. The signal was first connected to a GBPC3005W ready-made single-phase silicon bridge rectifier to produce a signal in one direction. The filtering results were collected on an RTB2002 mixed-domain oscilloscope (Rohde & Schwarz, Germany). A series of 3D-tsCASC circuits were formed using ten capacitors connecting in head-to-tail fashion. The cell bundle was sealed using Kapton tape.

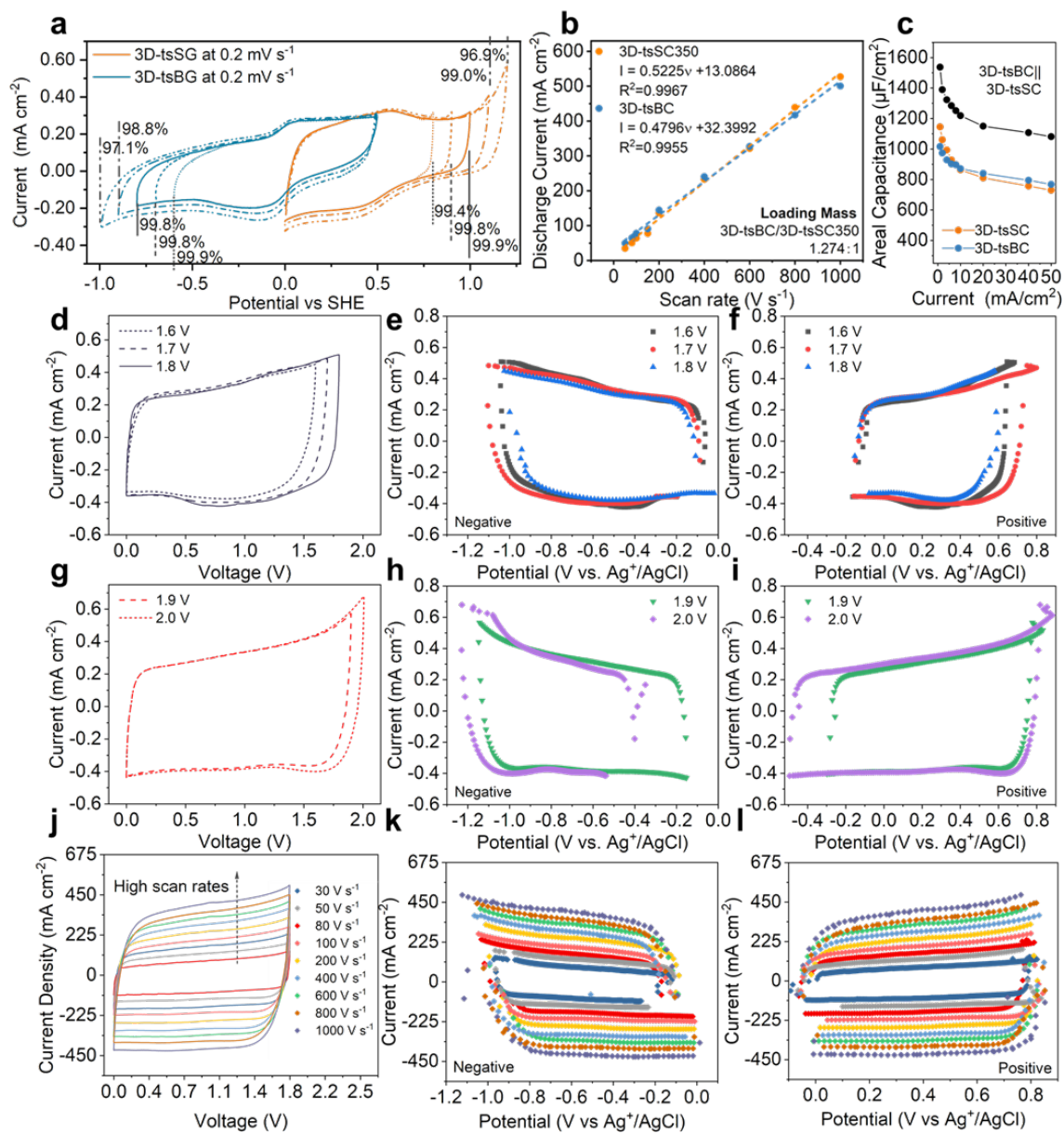


Figure 5.1 a) The slow scan CV curves range of 3D-tsBC and 3D-tsSC shows thermodynamic stability at different voltage ranges. The Coulombic efficiencies of each CV scan are specifically noted. b) With loading mass balance at a ratio of 1.274:1, the discharge current density variation of 3D-tsBC and 3D-tsSC is matched closely at scan rates ranging from 10 to 1000 V/s. Insets are the linear regression equations and coefficients of 3D-tsBC and 3D-tsSC. c) The rate performance curves of 3D-tsBC, a3D-tsSC, and 3D-tsBC||3D-tsSC. Slow CV scans of 3D-tsBC||3D-tsSC d) at 1.6, 1.7, and 1.8 V; g) at 1.9 and 2.0 V. The *in operando* CV profiles of e) 3D-tsBC at 1.6, 1.7, and 1.8 V. f) 3D-tsSC at 1.6, 1.7, and 1.8 V. h) 3D-tsBC at 1.9 and 2.0 V. i) 3D-tsSC at 1.9 and 2.0 V. The CV profiles at different scan rates of j) 3D-tsBC||3D-tsSC. k) 3D-tsBC and l) 3D-tsSC.

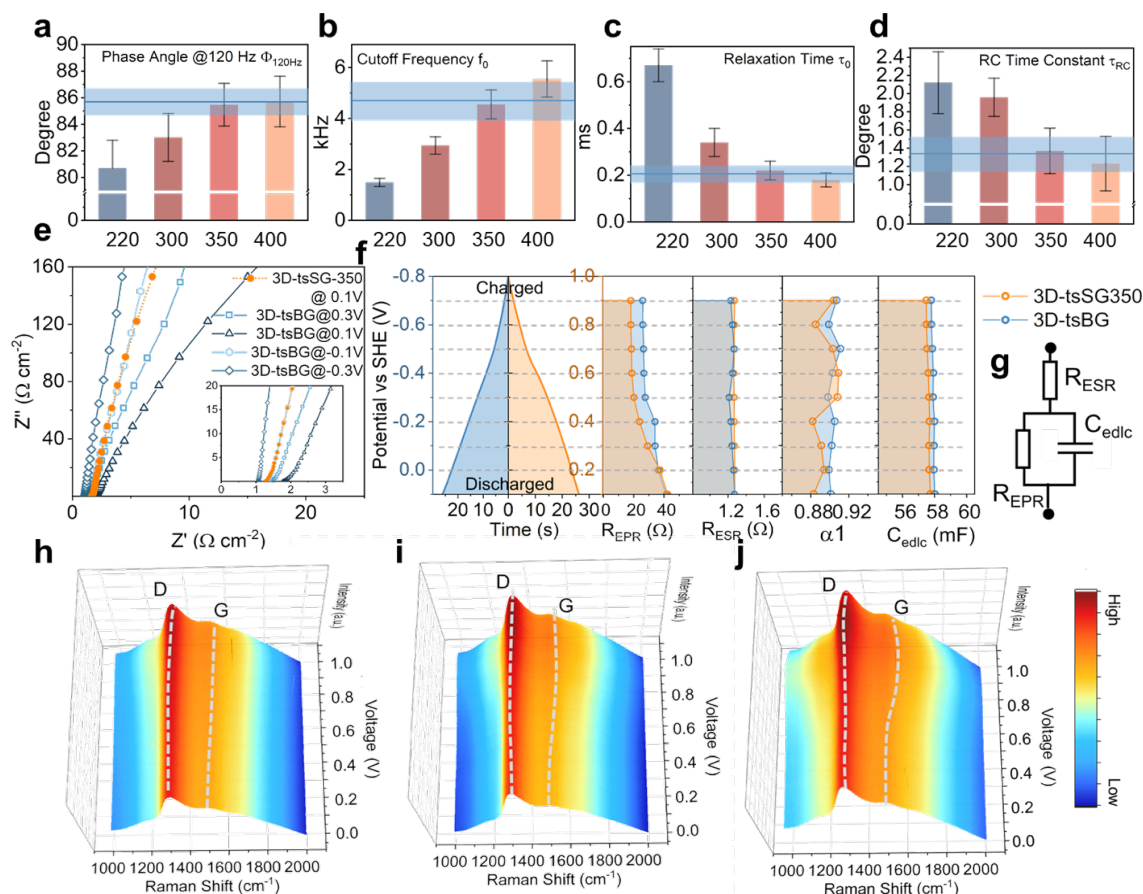


Figure 5.2 Comparison of frequency-response evaluations between 3D-tsSC variants and 3D-tsBC in symmetric capacitors including a) phase angles at 120 Hz in degrees, b) cutoff frequencies in kHz, c) relaxation time in ms and d) RC time constants at 120 Hz in ms. e) Nyquist plots of 3D-tsBG (blue) and 3D-tsSG220, 300, 350, 400. The inset is the high-frequency Nyquist plots. f) GCD curves of 3D-tsBG and 3D-tsSG350. The impedance simulation parameters of three-electrode EIS were compared at each potential step. The simulation was carried out based on three elementary components, i.e., the capacitor representing the supercapacitor capacitance, the equivalent series resistor (ESR) representing the ohmic losses, and the equal parallel resistor (EPR) representing the self-discharge. The roughness of the electrode surfaces was corrected using the α_1 factor. The voltage ranges for 3D-tsBG from 0.1 V (fully discharged) to -0.8 V (fully charged), and for 3D-tsSC350 from 0.1 V (fully discharged) to 1.0 V (fully charged). The circuit is the simulation model. g) The solution equivalent circuit of high-frequency ECs. The *in situ* Raman spectra of h) 3D-tsBC, i) 3D-tsSC220, and j) 3D-ts350.

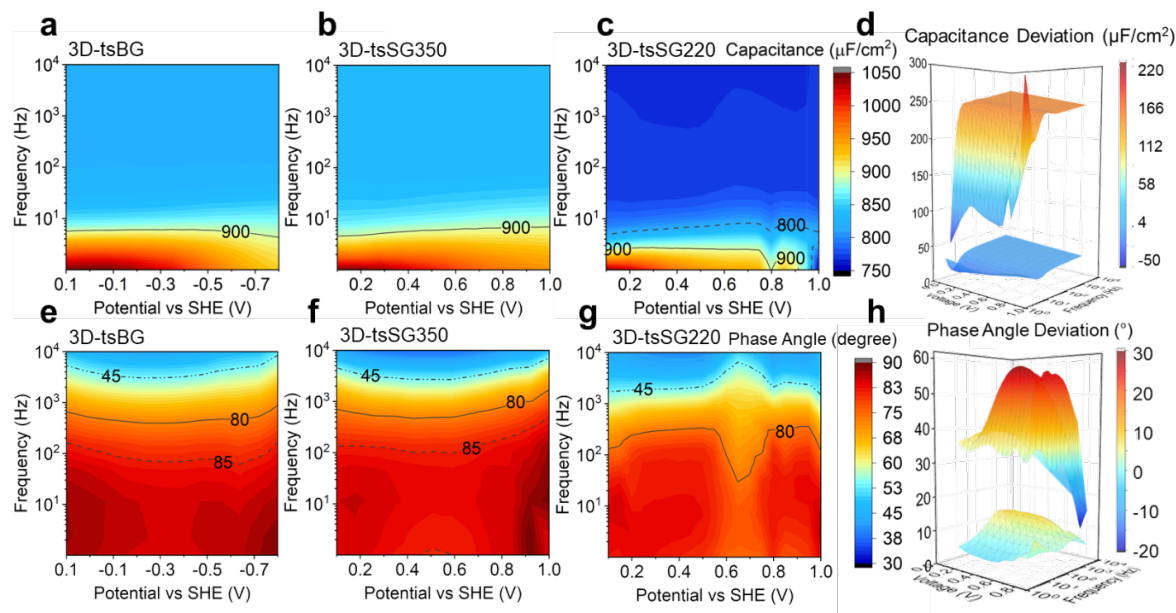


Figure 5.3 a-c) Specific areal capacitance-frequency-potential plots of 3D-BC, 3D-tsSC350 and 3D-tsSC220. e-g) Phase angle-frequency-potential contour plots of 3D-BC, 3D-tsSC350 and 3D-tsSC220. The color scales are on the right. The solid contour lines in (a-c) are 900 $\mu\text{F}/\text{cm}^2$ and dash lines are 800 $\mu\text{F}/\text{cm}^2$. The solid contour line in (e-g) are 80° and dash lines are 85°, dash-dot lines are 45°. d) Phase angle deviation-frequency-potential mapping by subtracting phase angles of 3D-tsSC220 (top) and 3D-tsSC350 (bottom) from 3D-tsBC at each point. h) Capacitance-frequency-potential deviation mapping by subtracting capacitances of 3D-tsSC220 (top) and 3D-tsSC350 (bottom) from 3D-tsBC at each point.

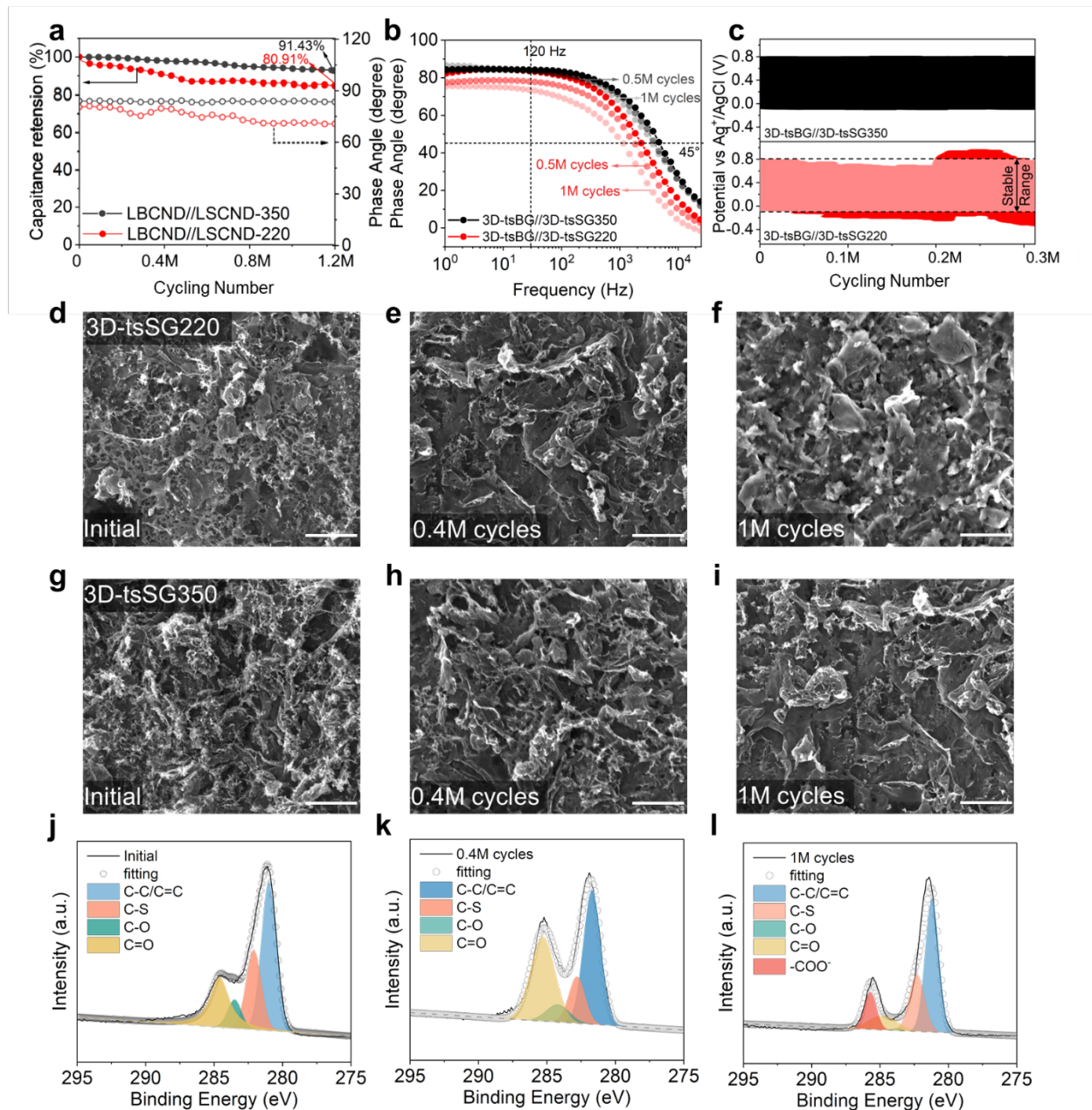


Figure 5.4 a) The capacitance retention and phase angle retention at 120 Hz over 1.2 M cycles. b) The phase angle Bode plots of asymmetric capacitors of matched 3D-tsBC||3D-tsSC350) and mismatched 3D-tsBC||3D-tsSG220. The plots of each asymmetric capacitor after 0.5 M and 1 M cycles. f) The variations of the electric potential of the positive electrode of asymmetric capacitors of matched 3D-tsBC||3D-tsSG350 and mismatched 3D-tsBC||3D-tsSC220 against Ag⁺//AgCl reference electrodes. The top-view SEM images of the positive electrode in (d-f) mismatched 3D-tsBC||3D-tsSC220 and (g-i) matched 3D-tsBC||3D-tsSC350 before cycling, after 0.4 M cycles, and after 1 M cycles. The XPS C 1s core spectra of 3D-tsSC220 in mismatched capacitors j) before cycling, k) after 0.4 M cycles, and l) after 1 M cycles.

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4.5 SUPPORTING INFORMATION AND FIGURES

General characterization:

A Jasco FT/IR-4100 with a single reflection ATR unit was used for FT-IR spectroscopy. A Bruker D8 Discover powder X-ray diffractometer was used to record the CuK α radiation ($\lambda = 1.5406 \text{ \AA}$) XRD patterns. A Renishaw InVia Raman Microscope with a 633 nm laser captured Raman spectra in individual spectral or mapping modes. Single Lorentzian functions with R²-values of 0.99 were used to fit the Raman spectra. Fluorescence baseline subtraction and Lorentz peak centers deconvolved the powder Raman spectra. Peak positions were determined via Raman spectra of several materials. An estimation of the coherence lengths of graphenic domains along lateral ab direction (L_a) was based on Raman spectroscopy using the equation below.

$$L_a (\text{nm}) = (2.4 \times 10^{-10}) \lambda_{\text{nm}}^4 \left(\frac{I_G}{I_D} \right)$$

In situ Raman spectra were acquired one by one, with setting time of 60 s and an exposure time of 10 s at intervals across potential range of 0.0 –1.8 V. Total spectra were obtained during the 11th cycle of measurement. A 3 or 5 kV FEI Nova 230 Nano SEM was used for SEM. Al or Cu foil substrates were used to support samples. A 120 kV FEI T12 TEM performed TEM. 5 μL ethanol-diluted powder dispersions were drop-cast onto Lacey-carbon supported TEM grids to produce TEM samples. A Kratos Axis Ultra DLD spectrometer with a monochromatic Al K α X-ray source ($h\nu = 1486.6 \text{ eV}$) produced XPS spectra. Carbon tape (Ted Pella) was used to calibrate high-resolution spectra. CasaXPS processed raw data (version 2.3.16). C 1s spectra were fit using Gaussian–Lorentzian line shapes for all spectral components except the sp² C component, which was fit with an asymmetric line shape to reflect the metallic nature of the samples. All samples used FWHM and position limitations for consistency. UPS measurements were performed on the same instrument with an unfiltered HeI (21.22 eV) gas discharge lamp and a total instrumental energy resolution of 100 meV.

High-frequency capacitance balance in symmetric capacitors:

The frequency dependency of capacitance was conducted deliberately by tuning the mass loading of 3D-tsBC and 3D-tsSC350 separately. At a mass loading of 1.274: 1, the capacitance is closely aligned with the positive and negative electrodes. At 120 Hz, a high specific areal capacitance of 857.02 $\mu\text{F}/\text{cm}^2$ was measured in 3D-tsBC, whereas a value of 868.07 $\mu\text{F}/\text{cm}^2$ was found in 3D-tsSC350. The balance was maintained in a broad frequency domain ranging from 2 to 2×10^4 Hz. A capacitance balance in asymmetric capacitors is widely adopted. The standard protocol should be extended to a wide frequency range in the filter capacitors. Otherwise, at any time scale, a working potential exceeding the thermodynamically stable potential window would invoke an instant failure of the whole device, largely compromising the cycling life.

The macroporous carbon structure of 3D-tsBC and 3D-tsSC

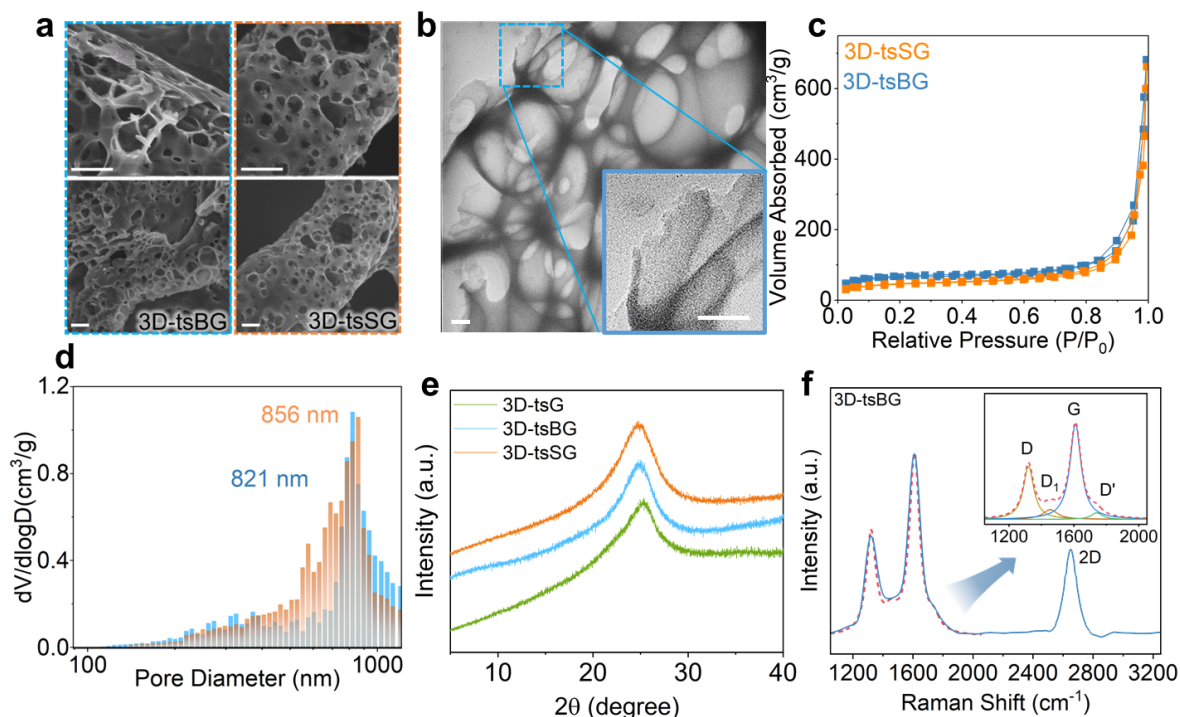


Figure S5.1 a) Typical SEM images of 3D-tsBC (left) and 3D-tsSC (right). The scale bars are 1 μm . b) The magnified TEM and HRTEM of images of 3D-tsBC. c) The nitrogen adsorption-desorption isotherms and d) pore size distribution curves of 3D-tsBC and 3D-tsSC. d) The XRD patterns of 3D-tsC, 3D-tsBC and 3D-tsSC. e) A typical Raman spectrum 3D-tsBC and a peak fitting (inset).

The resulting 3D interconnected macroporous framework promotes fast ion accessibility in high-frequency regimes due to its large specific area. The macroporous structures were confirmed by scanning electron microscopy (SEM), transmission electron spectroscopy (TEM), and nitrogen adsorption/desorption isotherms. The SEM imaging (**Figure S5.1a**) reveal hollow foam structures in both samples with a pore size of $\sim 0.5\text{--}2\ \mu\text{m}$ and a high pore density. The TEM images (**Figure S5.1b**) show that most pores have solid edges and open faces with interconnected channels. The surface areas and pore size distribution of the 3D-tsBC and 3D-tsSC were measured using nitrogen

gas absorption. In **Figure S5.1c**, the nitrogen isotherms show type I isotherm curves with extensively overlapping adsorption and desorption sections, suggesting strong pore structures with mitigated collapse. 3D-tsSC had a surface area of 527 m²/g, while 3D-tsBC had a surface area of 495 m²/g. The presence of macroporosity was verified by a sharp rise along the y-axis in enlarged pictures of the high P/P₀ range (0.8-1) in the isotherm. In 3D-tsBC and 3D-tsSC, respectively, the Barrett-Joyner-Halenda (BJH) plot showed the existence of mesopores and a preponderance of macropores,

with mean pore diameters of 821 and 856 nm and total pore volumes of 2.56 and 2.92 cm³ g⁻¹ (**Figure S5.1d**). The smaller pore volume in a large pore diameter verifies the interconnected porous frameworks. Unlike smaller and deeper pores, shallow and macro-pores have a larger capacitance and lower resistance at high frequencies. In a porous electrode transmission line model, a high C low R transmission engenders a large deviation in phasors, leading to a large bandwidth for high-frequency filtering.

The degree of graphitization and turbostratic graphitic features 3D-tsBC and 3D-tsSC

An ideally near-zero electrical resistance was realized in 3D-tsBC and 3D-tsSC carbon electrodes due to their strong turbostratic graphene features. These graphitic features were scrutinized using electron-diffraction patterns in X-ray diffraction (XRD) and Raman spectroscopy. Turbostratic graphenic features are observed in carbon materials where a few graphitic layers are assembled in an arbitrary orientation without a predetermined order. In XRD patterns, the graphitic (002) peaks emerge at a slightly lower angle for all 3D-tsC (25.18°) samples (**Figure S5.1e**). This signifies

turbostratic graphene because rotation and translation of the graphene layers expand the interlayer distance. Because of the doping effects, the downshift is more pronounced in 3D-tsBC (24.94°) and 3D-tsSC (24.35°). The d-spacing values of 3D-tsC, 3D-tsBC, and 3D-tsSC were 3.54, 3.63, and 3.75 Å, respectively.⁸ The expanded interlayer spacings likely contribute to the high capacitance achieved in milliseconds.⁹ The Raman spectra in **Figure S5.1f** show peaks at Raman shifts of 1331 cm⁻¹ (D), 1450 cm⁻¹ (D₁), 1582 cm⁻¹ (G), 1817 cm⁻¹ (D'), and 2652 cm⁻¹ (2D).^{10,11} The D and G bands correspond to vibration of defective aromatics and graphitic lattices, respectively. The D' band corresponds to the Kekule modes of six or seven-membered ring breathing modes adjacent to heteroatoms. The 2D band corresponds to the double resonance of two close-packed layers. Therefore the I_{2D}/I_G ratio can be used to quantify the turbostratic features.^{12,13} The I_{2D}/I_G ratio is 0.5134 in 3D-tsBC, higher than most values reported previously for boron-doped carbon, indicating electronic decoupling in 3D-tsBC without stacking order.^{14,15} The value is smaller than that in 3D-tsC due to the 2D peak weakening in doped graphene lattices.⁸ The close fitting of the 2D peak by a single Lorentzian peak with a narrow FWHM for the 3D-tsBC also signals turbostratic features since the 2D peak in AB- or ABC-stacked graphenic layers better fits with a doublet.¹⁰ An estimated coherence length of graphenic domains along the lateral ab direction (L_a) based on the I_D/I_G ratio infers a small L_a of 18.3 nm in 3D-tsBC (I_D/I_G = 0.9127 ± 0.0489), suggesting the large interlayer steric effect in turbostratic graphitic layers results in the formation of a curved or a small crystallite.¹⁶

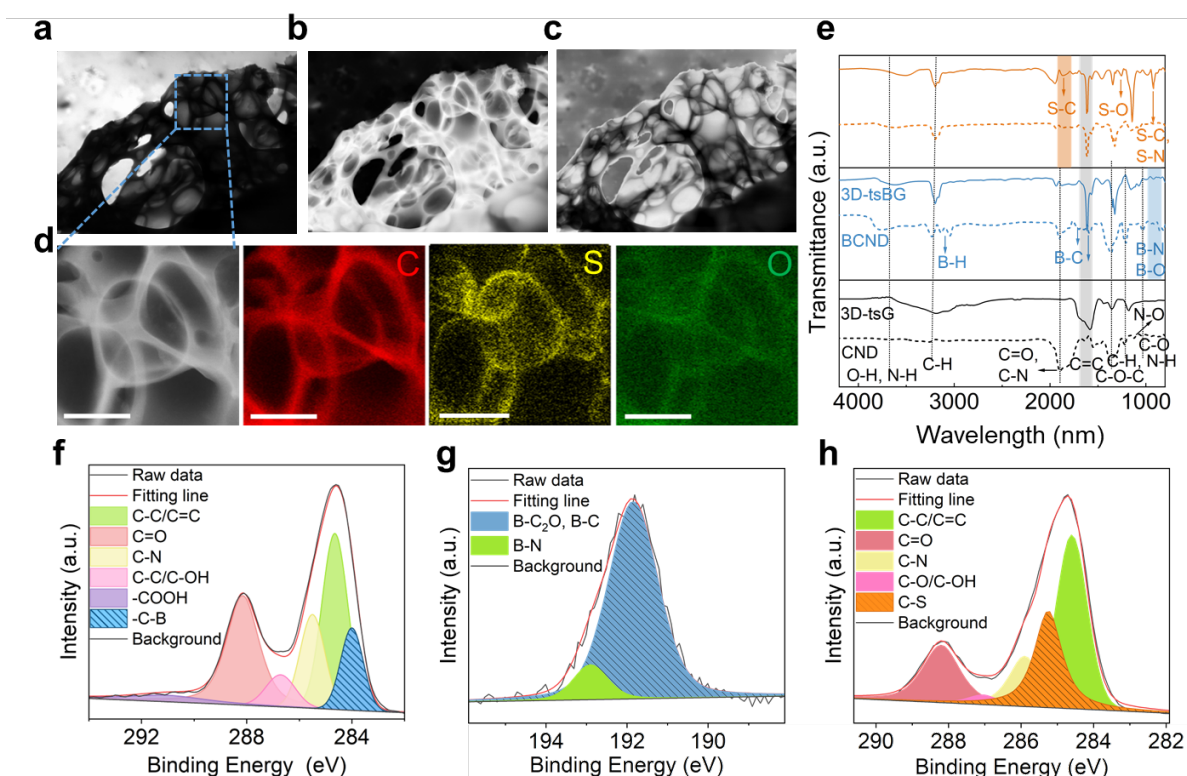


Figure S5.2. STEM images a) in a bright field, b) in a dark field, c) in HAADF, d) The magnified HAADF images and EDS element mapping of C, S, and O specifically. e) The FTIR spectra of before-laser CNDs and BCNDs, SCNDs (dash lines), and after-laser 3D-tsC, 3D-tsBC, and 3D-tsSC (solid lines). Peak fitting of XPS core spectra of f) C1s in 3D-tsBC, g) B1s in 3D-tsBC, and h) C1s in 3D-tsSC.

The doping and chemical functionalization on 3D-tsBC and 3D-tsSC

Clearly, the separation of stable potentials is attributed to the heteroatom types. The difference in heteroatoms were confirmed through various techniques, including Raman spectroscopy, energy

dispersive X-ray spectrometry (EDS), and X-ray photoelectron spectroscopy (XPS). In Raman spectra (**Figure S5.1f**), the stiffening of the G-band confirms chemical doping in 3D-tsBC.¹⁷ The blue shift of the G-band results from the nonadiabatic elimination of the Kohn anomaly at the G-point. A peak broadening stands for non-blocked decay channels of phonons into electron-hole pairs.¹⁸ **Figure S5.2d** shows high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and EDS mapping of the 3D-tsSC materials. The results clearly demonstrate the presence of C, S, and O, confirming the successful doping of the S element into the 3D-tsSC materials. The doping was then deliberately studied using XPS spectra (**Figure S5.3**). The atomic percentages of boron and sulfur dopants are calculated by integrating their peak areas in XPS survey spectra. After considering the atomic sensitivity factors, a formation temperature at 220 °C generates 3D-tsC with doping levels of 5.35% boron (**Figure S5.3a**) and 4.72% sulfur (**Figure S5.3d**). Peak fitting of B 1s and S 2p XPS core spectra (**Figure S5.2g**) illustrated that in addition to the majority of doping forms B-C (191.8 eV) and S-C (166.8 eV), both dopants remain in their oxo-acid states in some portions. For example, 3D-tsBC shows a deconvoluted peak of B-C₂O at 192.9 eV, while 3D-tsSC displays C-SO₃ (sulfite), C-SO₄ (sulfate) peaks at 168.3 eV and 169.2 eV (**Figure S5.3f**).¹⁹ In C 1s core spectrum of 3D-tsBC (**Figure S5.2f**), the peak assigned to C-C/C=C shifts to lower binding energy, while the peak in 3D-tsSC shifts to higher energy (**Figure S5.2h**). The shift resulting from the C-B peak at 284.1 eV and C-S at 285.4 eV implies major substitutional doping.^{19,20} The bonding analysis is consistent with the polar ligand detected in FT-IR spectra of 3D-tsBC and 3D-tsSC compared with that of 3D-tsC in **Figure S5.2c**.

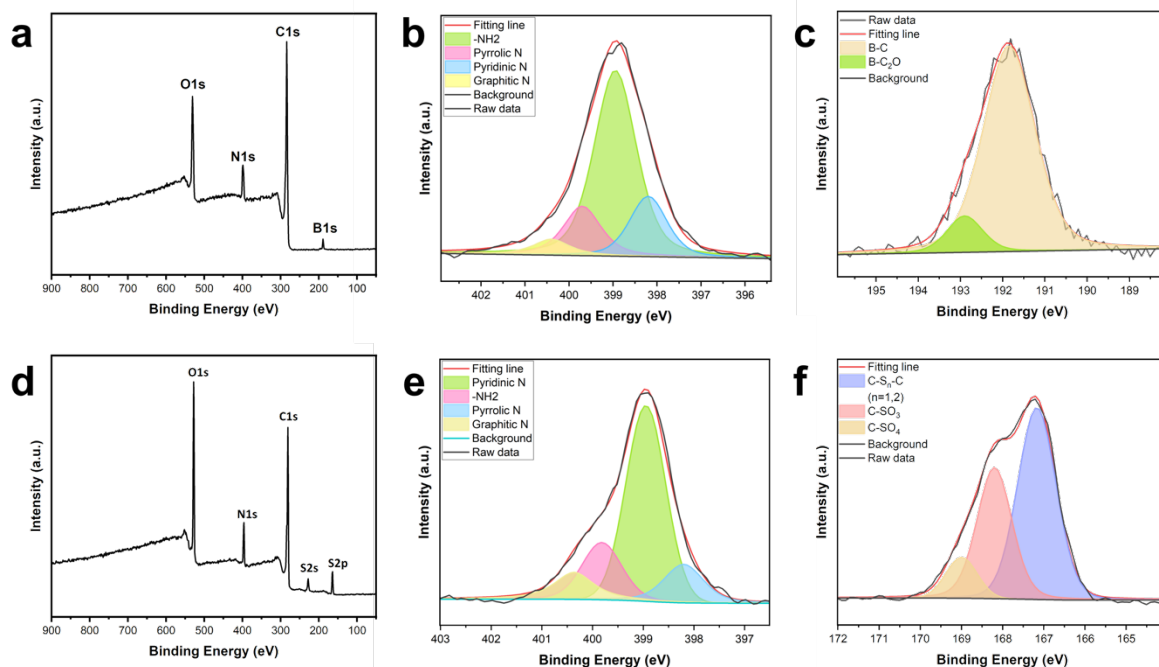


Figure S5.3 a,d) XPS survey spectra of 3D-tsBC and 3D-tsSC. b,d) XPS core analysis of nitrogen in 3D-tsBC and 3D-tsSC. c) XPS spectra of boron in 3D-tsBC f) XPS spectra of sulfur in 3D-tsSC.

The surface terminations and chemical doping in the as-prepared carbon electrodes are anticipated to influence the charge transport processes, such as surface molecular absorption and electron transfer, further leading to changes in CV background current and potential window. The unusually low electrochemical activities of 3D-tsBC and 3D-tsSC can be ascribed to a large amount of surface oxygen binding to sp^2 carbon domains, as indicated by a prominent C=O peak in the deconvoluted C 1s spectra. The gas evolution and other irreversible side reactions involve complex surface-sensitive Faradaic electron transfer rates. A high abundance of oxygen-containing surface

groups give rise to a cathodic blocking current inhibiting Faradaic electron transfer on the electrochemically active sites. In addition, the altered electronic states such as Fermi levels and work functions by chemical doping shift the reduction/oxidation potentials of side redox reactions, leading to varied stable potential ranges of carbon electrodes. Ultraviolet photoelectron spectroscopy (UPS) was used to characterize the electronic energy levels of 3D-tsBC, 3D-tsSC, and undoped 3D-tsC (**Figure S5.4**). The cut-off edge of the secondary electrons (E_{cutoff}) and Fermi level energy (E_{fermi}) was extracted by linearly extrapolating the leading edge of UPS spectra to the baseline. The E_{Fermi} decrease by 0.99 eV indicates the p-doping configuration in 3D-tsBC. A dual doping effect of the oxygen and boron dictates the down-shifted electronic energy states. Since the C–O is a more stable nearest neighbor pair compared with B–O,²¹ The boron dopants, majorly presented as B–C, leads to the broadened band gap at the M point rather than the Dirac point. Thus p-doping induced by boron is predominant in 3D-tsBC. In 3D-tsSC, E_{Fermi} shifts up by 0.90 eV, indicating n-doping due to the high electronegativity of both sulfur and oxygen-containing groups. The work functions difference of 3D-tsSC from 3D-tsBC is calculated to be 2.21 eV corresponding to their distinct electrochemical stability in positive and negative potentials, respectively.

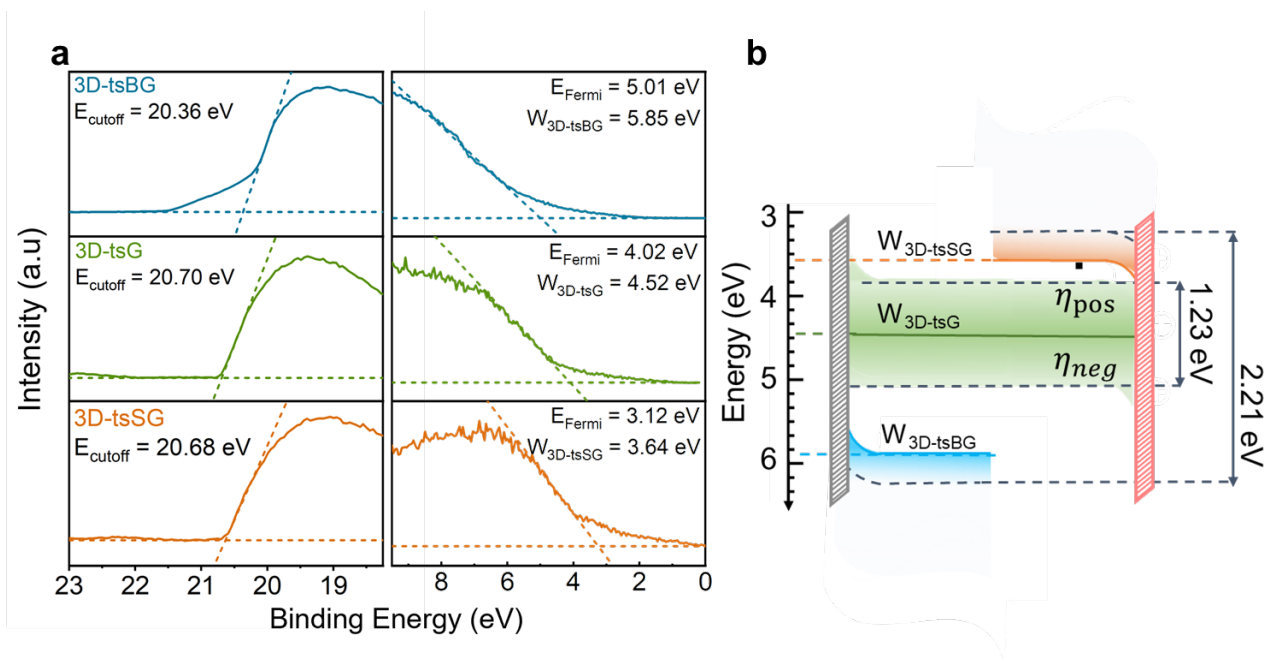


Figure 5.4 a) UPS spectra of 3D-tsC, 3D-tsBC, and 3D-tsSC350. The spectra show a shift of work functions in 3D-tsBC and 3D-tsSC350. Inset are extracted values of E_{cutoff} , E_{Fermi} and work function (W) of each sample. b)) The shift of work function leads to different working potentials of 3D-tsBC and 3D-tsSC.

UPS data and doping effect on work function analysis

The samples were exposed to an argon plasma before the measurements to obtain a clean surface. E_{cutoff} and E_{Fermi} are the cut-off edge of the secondary electrons and the Fermi level energy of the samples. They were extracted by linearly extrapolating the leading edge of UPS spectra to the baseline (**Figure S5.4a**). The W was calculated by subtracting the E_{cutoff} E_{Fermi} difference from the overall incident UV photon energy (21.2 eV).²² It should be noted that 3D-tsBC and 3D-tsSC contain a trivial amount of nitrogen as a minor co-dopant. Thus, the tuned electronic properties should be understood based on the synergistic effects of the dual dopants. In B, N co-doping, the

B–N induces a more stable nearest neighbor pair instead of B–C and N–C.²¹ Thus, the band gap was broadened at the M point rather than at the Dirac point, leading to a smaller gap at the saddle point. In 3D-tsBC, B is higher than N. The downshifting of E_{Fermi} is predominant (p-doping). Thereby, a larger W in 3D-tsBC resulted. However, the shifting is smaller than that in pure boron-doped graphene. In 3D-tsSC, less polarized C–S bonds render a higher pyrrolic and pyridinic nitrogen content.²³ The generating defects compromise the upshifting of the double n-doping effect of sulfur and nitrogen. The overall impact yields an upshifted Fermi level. Therefore, a smaller W is obtained in 3D-tsSC. A slightly less contributor to the W is the electrostatic effect.²⁴ The smaller p orbitals in nitrogen and sulfur tend to retain the negative charge on the graphene plane. In contrast, boron serves the opposite effect and attracts positive charges to the plane. It further expands the separation of W in 3D-tsBC and 3D-tsSC. The expanded gap in W of 3D-tsBC and 3D-tsSC will likely separate the stable potential range when they independently serve as negative and positive electrodes.

The effect of work functions of electrode materials on their stable potential windows

In a stable cell, the cathode E_{Fermi} should be lower than the HOMO level of electrolyte molecules to avoid the irreversible oxidative decomposition. Meanwhile the anode E_{Fermi} should be higher than the LUMO of the electrolyte to avoid the reductive decomposition.²⁵ Therefore a stable voltage window E is determined by the equations below.^{26,27} The expansion of the stable voltage is made possible by a large gap between the positive electrode (W_p) and the negative electrode (W_n), and associated η_p and η_n overpotentials (**Figure S5.4b**).²⁸

$$E = \frac{NA}{F} \Delta W + \eta_p + \eta_n \quad (1)$$

$$\Delta W = W_p - W_n \quad (2)$$

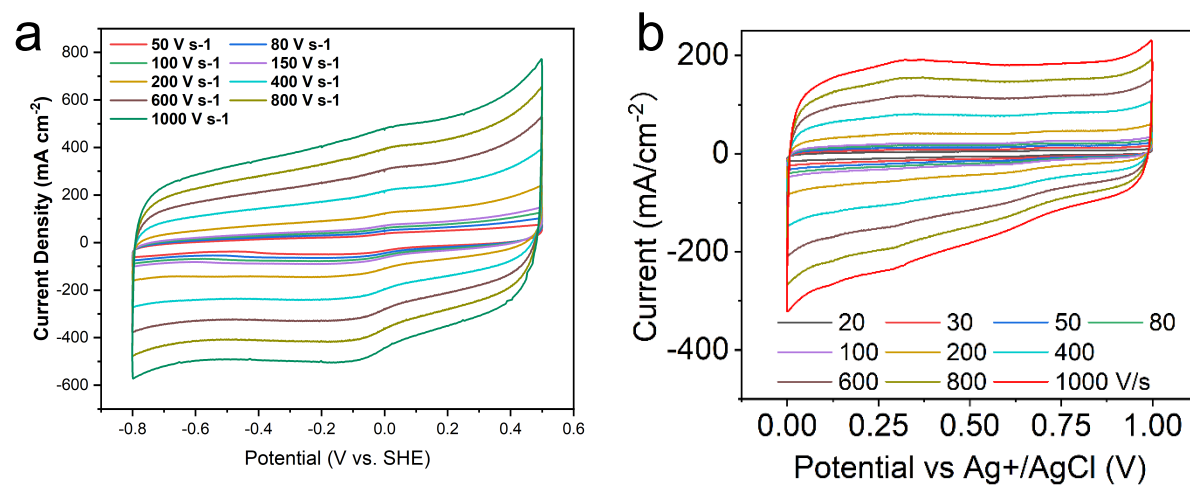
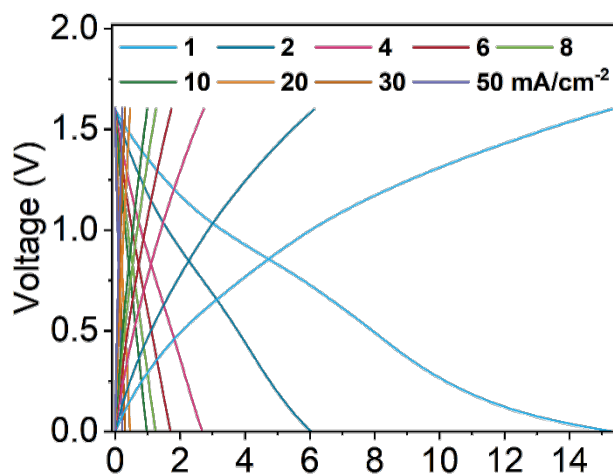


Figure S5.5 CV plots of 3D-tsBC (left) and CV plots of 3D-tsSC (right) at a series of scan rates.



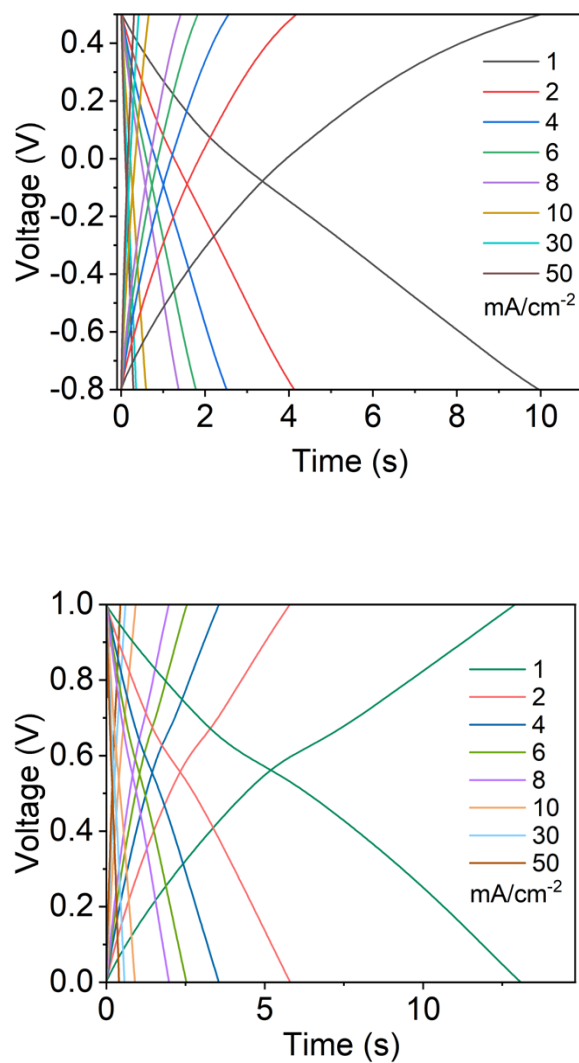


Figure S5.6 GCD profiles of 3D-tsBC||3D-tsSC (top), 3D-tsBC (middle), and 3D-tsSC (bottom) at a series of current densities.

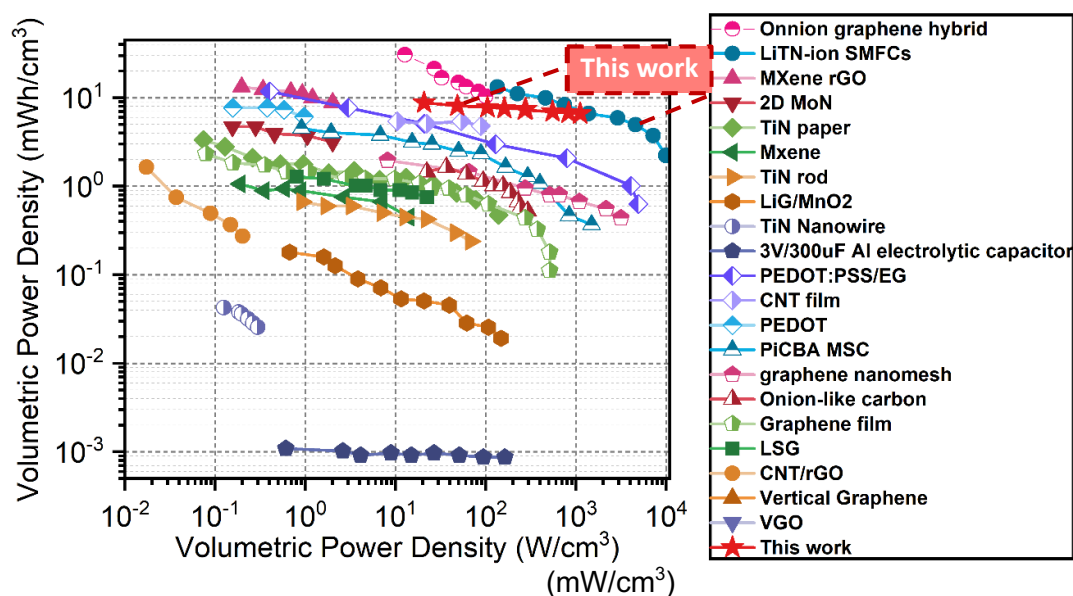


Figure S5.7 Volumetric energy and Power density performance of 3D-tsCASC compared with previously reported work.

It is worth noting that a previous challenge with formerly reported 3D-tsC was its mediocre areal-specific capacitance owing to the small loading mass of laser-scribed CND film.²⁹ To overcome this issue, the converted CND was first purified by washing and centrifuge after laser irradiation. By carefully controlling and increasing the loading mass of the electrode to 5 mg cm⁻², we successfully achieved electrodes with mass loading that closely approaches that of industrial electrodes.³⁰ This improvement resulted in higher capacitance per area without compromising the high-power density of the device. Interestingly, the CV scans retained a quasi-rectangular shape even at high scan rates, a positive indicator of the electrode's high-power capabilities. This observation can be attributed to the presence of vertical and large-volume voids in the 3D microporous structures, offering ultrafast ion diffusion and charge propagations in thick electrodes.

As a result, the specific areal capacitance was increased five times compared with the previous study.²⁹ Another possible capacitance contributor is pseudocapacitance in heteroatom dopants,³¹ especially in 3D-tsSC. The specific capacitance calculated based on GCD curves at a current density of 1 mA cm⁻² is 4.95 mF cm⁻² (areal) and 49.9 F cm⁻³ (Volumetric) in 3D-tsSC, 3.79 mF cm⁻² (areal) and F cm⁻³ (volumetric) in 3D-tsBC, which are both higher than 0.825 mF cm⁻² (areal) and 42.5 F cm⁻³ (volumetric) in 3D-tsC using the same electrode fabrication technique. The assembled 3D-tsCASC shows an enlarged energy density of 19.96 mWh cm⁻³ at a high-power density of 1172.28 mW cm⁻³. The outstanding performance, benefitting from the densified loading mass and expanded voltage, renders the 3D-tsCASC a potent device compared with Li thin film batteries, conventional aluminum electrolytic capacitors, and most aqueous capacitors reported so far (**Figure S5.13**)^{5,6,40–43,32–39} The wide voltage window of 3D-tsCASC makes it comparable with the most current organic ECs.^{44,45} The outstanding volumetric performance showcases its strong competency against conventional electrolytic capacitors.

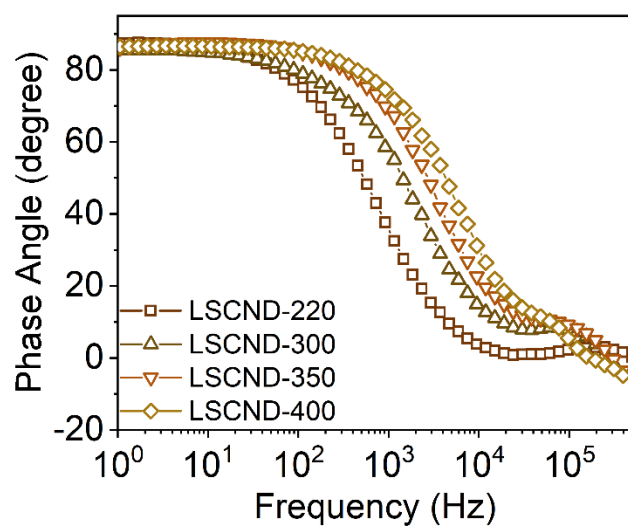


Figure S5.8 Phase angle vs frequency of 3D-tsSC at formation temperatures of 220, 300, 350, 400 °C.

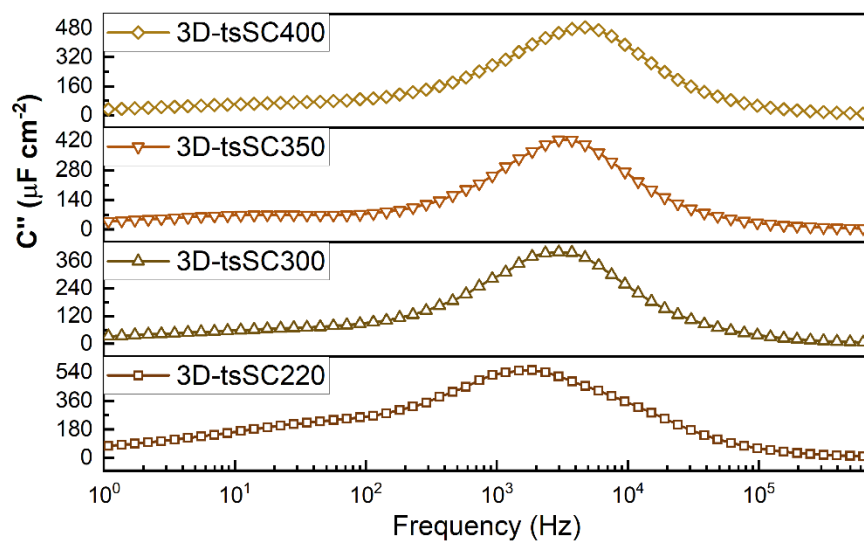


Figure S5.9 Imaginary capacitance (C'') vs. frequency of 3D-tsSC at formation temperatures of 220, 300, 350, 400 °C.

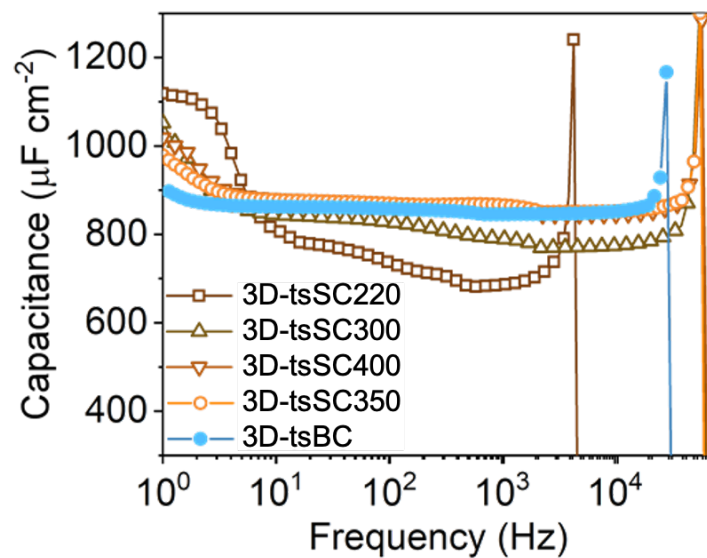


Figure S5.10 Capacitance vs. frequency bode plots of 3D-tsBC and 3D-tsSC220, 3D-tsSC300, 3D-tsSC350 and 3D-tsSC400.

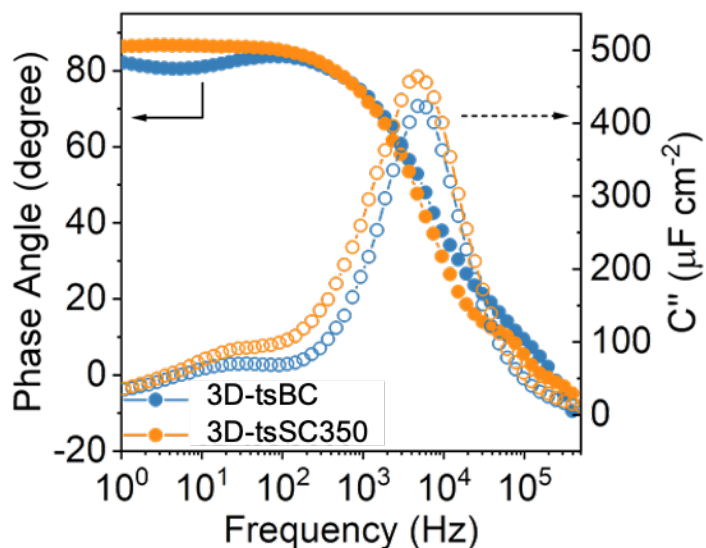


Figure S5.11 The phase angle Bode plots of and imaginary specific areal capacitance of 3D-tsBC and 3D-tsSC350. Both curves show close matches.

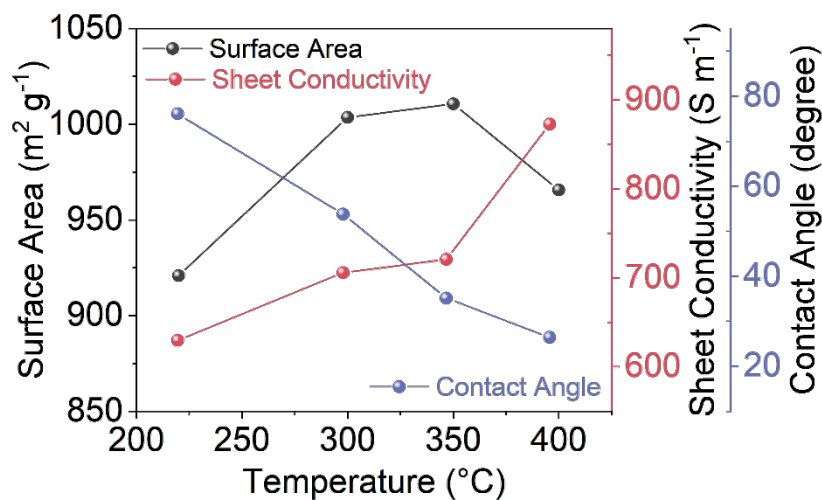


Figure S5.12 The variation of the surface area measured using methylene blue adsorption (black), the sheet electrical conductivity obtained using four-probe measurements (red), and water contact angles (blue) of 3D-tsSC220, 3D-tsSC300, 3D-tsSC350, and 3D-tsSC400.

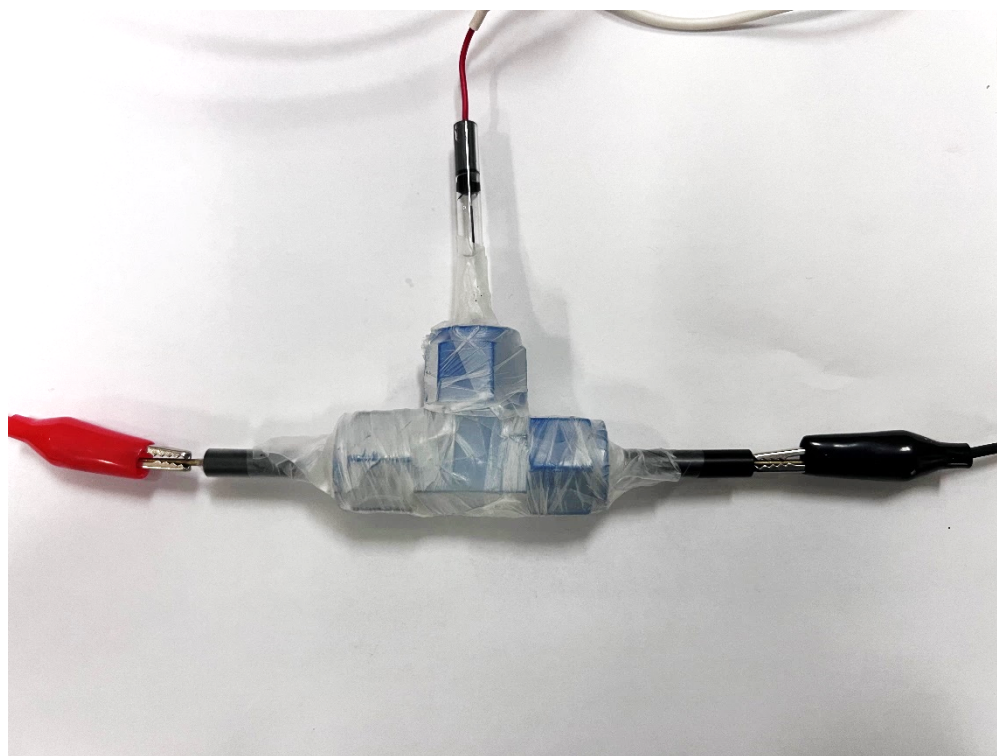


Figure S5.13 Photograph of the Swagelok three electrode cell set-up.

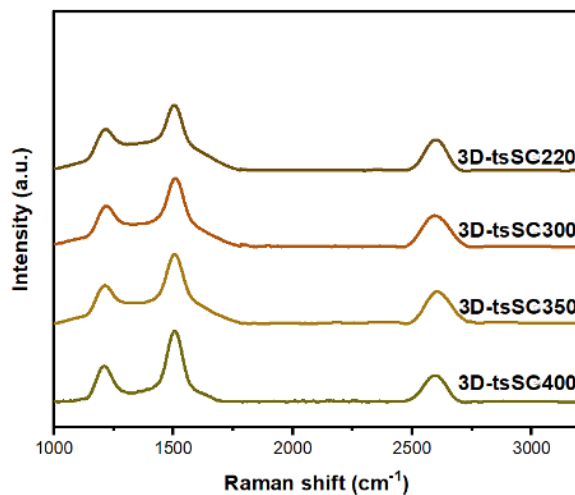


Figure S5.14 Raman spectra of 3D-tsSC at formation temperatures of 220, 300, 350, 400 °C.

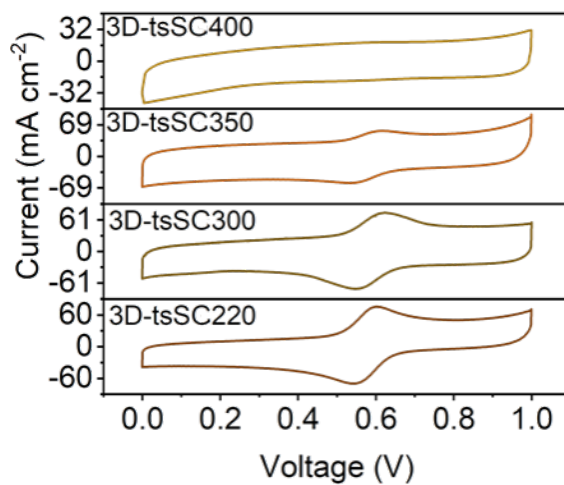


Figure S5.15 CV curves of 3D-tsSC220, 3D-tsSC300, 3D-tsS350 and 3D-tsSC400 at scan rate of 100 mV/s.

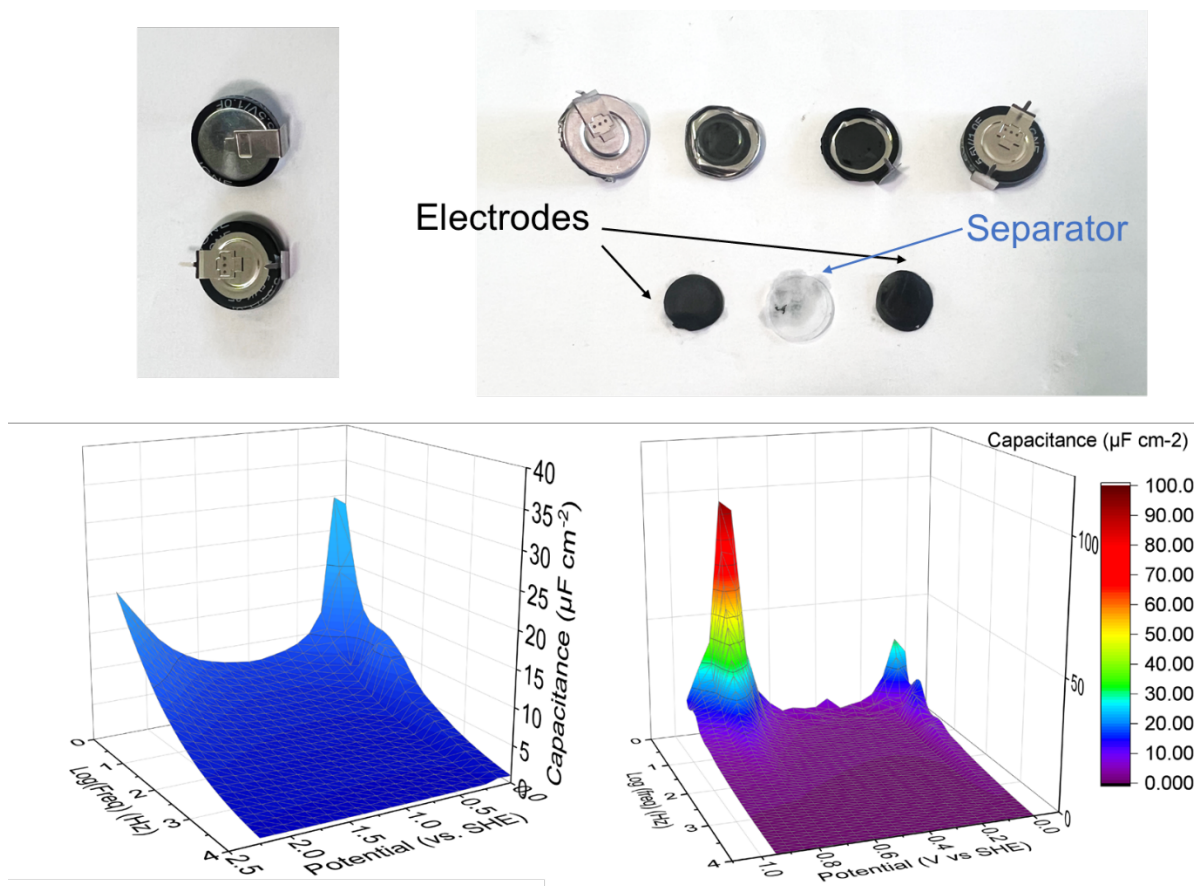


Figure S5.16 Commercial activated carbon supercapacitors and their 3D Bode plots in organic electrolyte (1.0 M TEABF₄ in acetonitrile) and aqueous electrolyte (1.0 M Na₂SO₄).

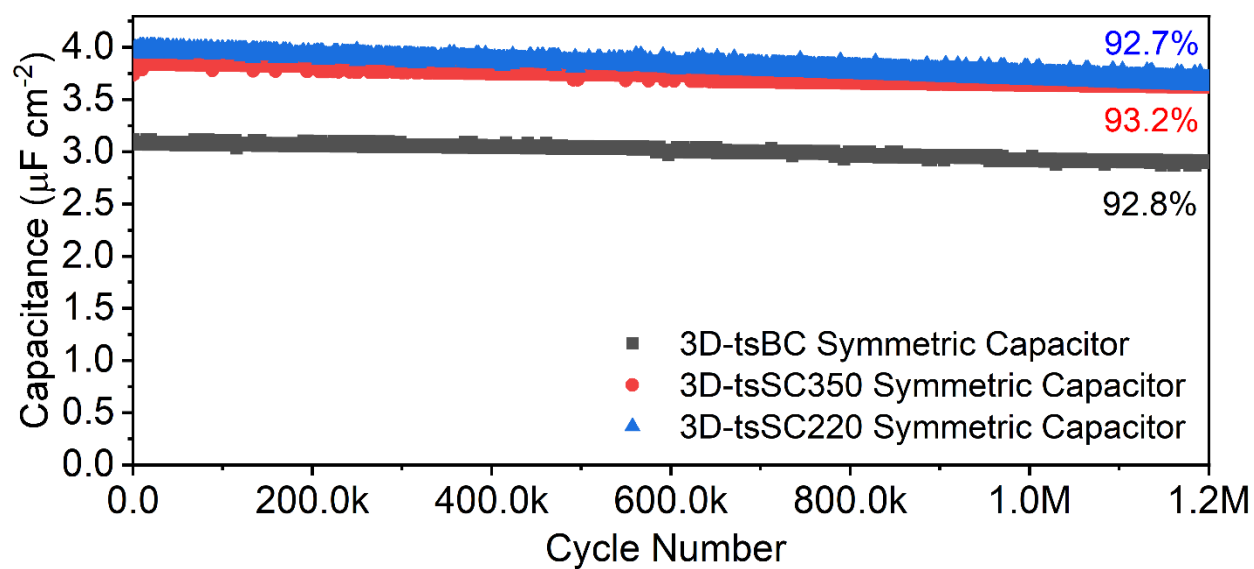


Figure S5.17 Cycling performance of two-electrode symmetric supercapacitors consisting of 3D-tsBC, 3D-tsSC350, and 3D-tsSC220 electrodes.

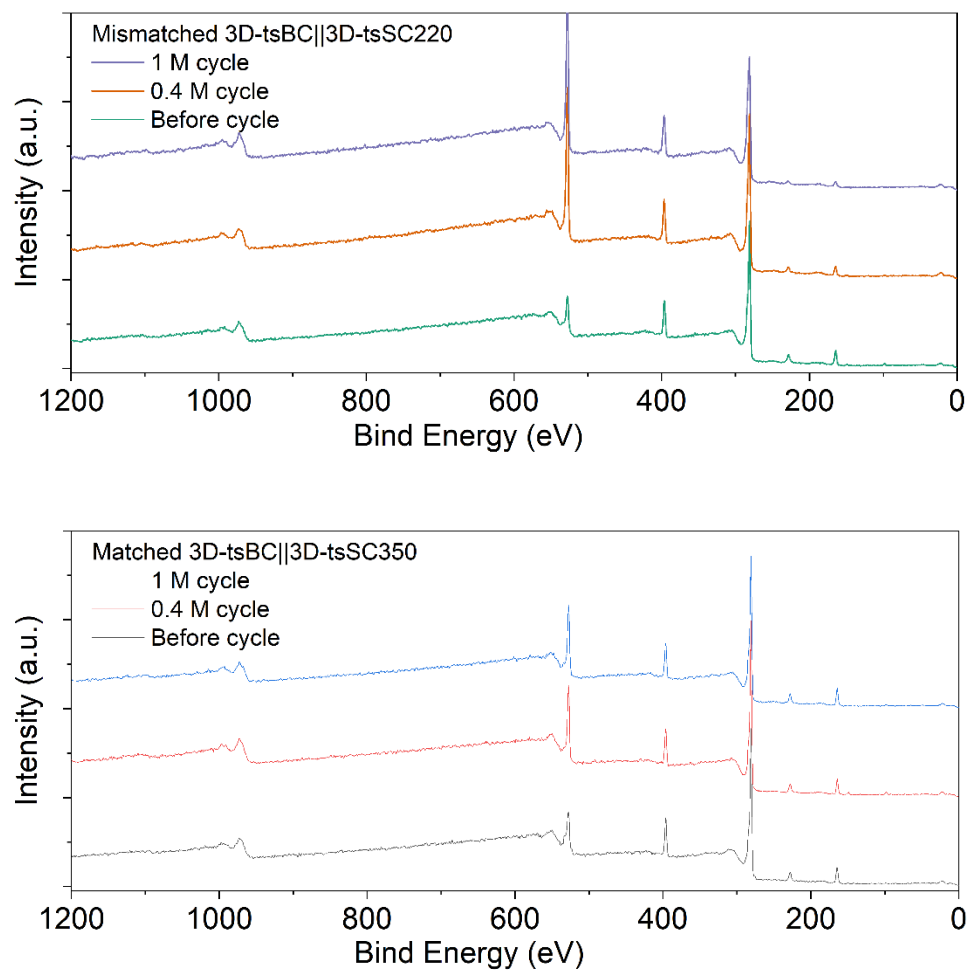


Figure S5.19 The XPS survey spectra of 3D-tsSC220 (top) and 3D-tsSC350 (bottom) after cycling in mismatched and matched capacitors, respectively.

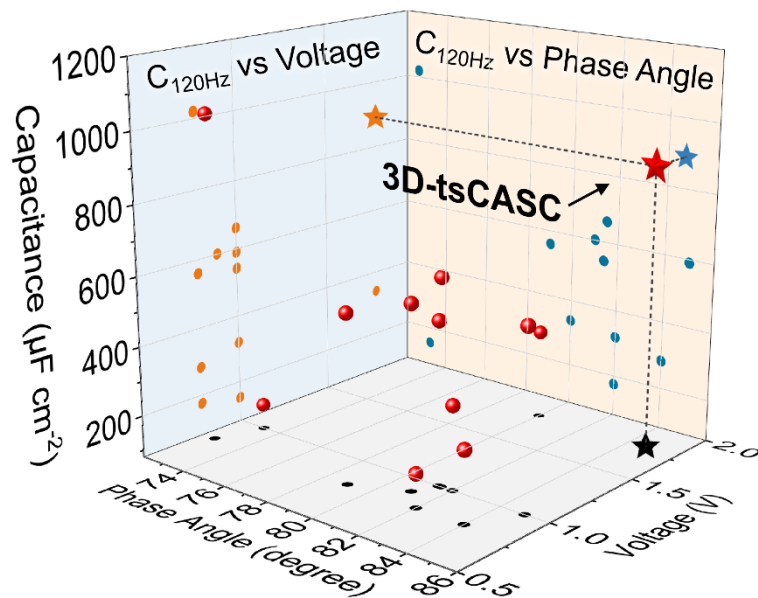


Figure S5.20 The 3D-tsCASC shows best evaluation when compared with existing studies from the perspectives of combined capacitance density at 120 Hz, phase angle at 120 Hz and voltage window for a single capacitor. The explicit data of the compared studies are referenced in **Table S5.3**.

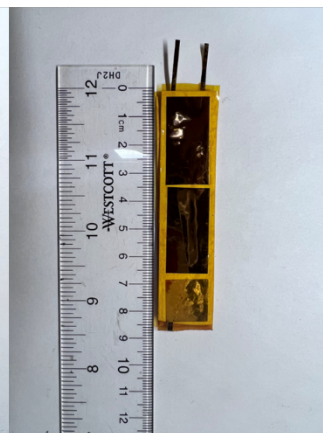
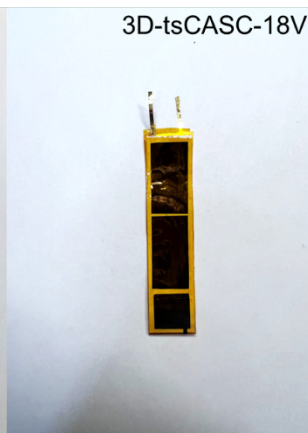
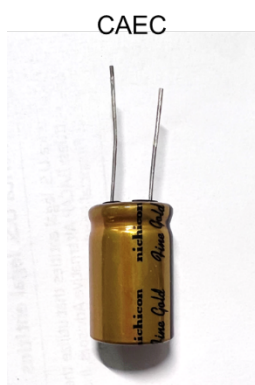


Figure 5.21 Photographs of commercialized aluminum electrolytic capacitor (CAEC) and ten-unit serial asymmetric supercapacitor 3D-tsCASC-18V.

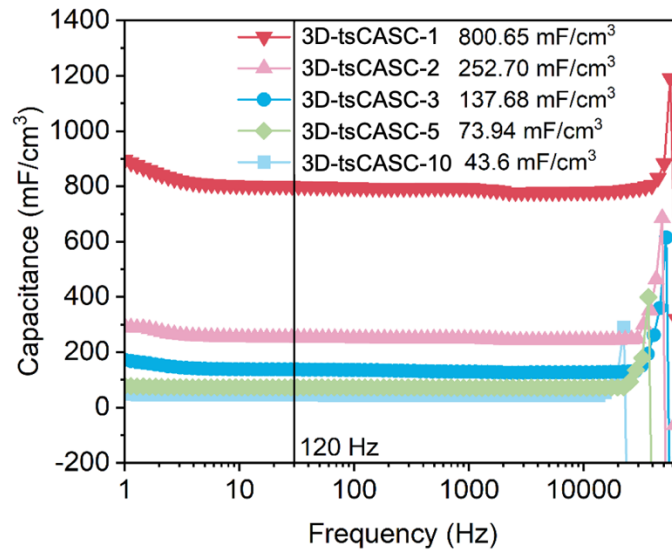


Figure 5.22 The RC capacitance at various frequencies for serial capacitors (3D-tsCASC-1 is 3D-tsCASC-1.8V, 3D-tsCASC-2 is 3D-tsCASC-3.6V, 3D-tsCASC-3 is 3D-tsCASC-5.4V, 3D-tsCASC-5 is 3D-tsCASC-9V, and 3D-tsCASC-10 is 3D-tsCASC-18V).

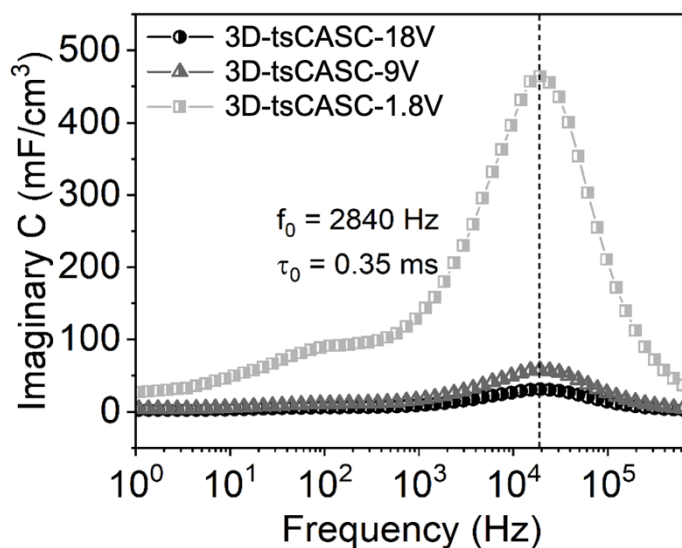


Figure S5.23 The imaginary capacitance at various frequencies for serial capacitors 3D-tsGASC-1.8V, 3D-tsGASC-9V, and 3D-tsGASC-18V.

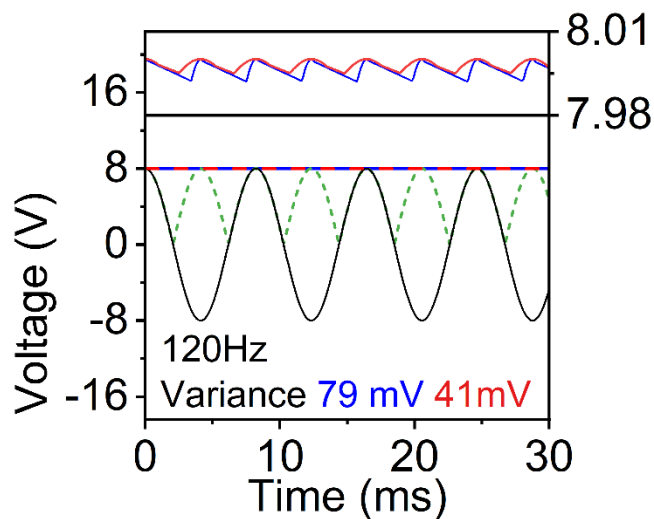


Figure S5.24 The filtering results of 3D-tsCASC-18V and CAEC at input AC frequency of 120 Hz and voltage of 16 V.

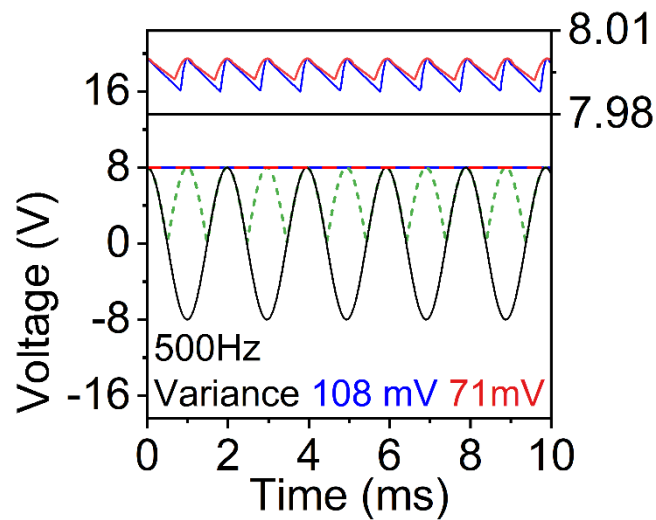


Figure S5.25 The filtering results of 3D-tsCASC-18V and CAEC at input AC frequency of 500 Hz and voltage of 16 V.

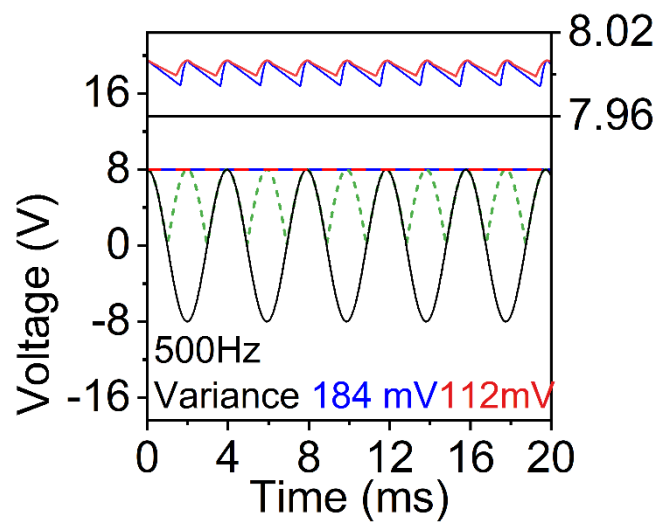


Figure S5.26 The filtering results of 3D-tsCASC-18V and CAEC at input AC frequency of 1000 Hz and voltage of 16 V.

Table S5.1 Major Line Filtering Performance Metrics of Symmetric Capacitors Based on 3D-tsBC and 3D-tsSC.

Sample	Areal Capacitance $C_A @ 120$ Hz ($\mu\text{F}/\text{cm}^{-2}$)	Phase Angle $\Phi @ 120$ Hz (degree)	Relaxation time t_0 (ms)	RC time constant t_{RC} (ms)	Equivalent series resistance ESR (Ω)	Cutoff frequency (kHz)
3D- tsSC220	726.10	80.7	0.67	2.12	2.34	1.49
3D- tsSC300	824.71	83.01	0.34	1.96	1.76	2.94
3D- tsSC350	868.07	85.47	0.22	1.37	1.26	4.55
3D- tsSC400	796.65	85.71	0.18	1.23	1.05	5.55
3D- tsBC	857.02	85.59	0.21	1.33	1.24	4.76

Table S5.2 Impedance Simulation Parameters of 3D-tsBC and 3S tsSG350 in All Voltage

3D- tsSC3									0.9 V
50	0.1 V	0.2 V	0.3 V	0.4 V	0.5 V	0.6 V	0.7 V	0.8 V	
<i>RESR</i>									1.269
(Ω)	1.271	1.27	1.268	1.267	1.265	1.261	1.268	1.267	
<i>REPR</i>									18.14
(Ω)	42.4	37.39	29.24	23.85	20.14	18.82	18.56	18.17	
<i>C_{sc}</i>	57.736	57.674	57.658	57.688	57.658	57.611	57.543	57.499	57.48
α_1	0.901	0.899	0.902	0.905	0.898	0.903	0.911	0.899	7
3D- tsBC	0.1 V	0 V	-0.1 V	-0.2 V	-0.3 V	-0.4 V	-0.5 V	-0.6 V	-0.7 V
<i>RESR</i>									1.23
(Ω)	1.27	1.26	1.243	1.231	1.211	1.248	1.265	1.248	
<i>REPR</i>									25.98
(Ω)	41.52	36.31	34.11	34.01	27.66	26.81	26.51	26.06	
<i>C_{sc}</i>	58.012	57.954	57.962	57.992	57.906	57.928	57.860	57.800	57.78
α_1	0.883	0.894	0.891	0.882	0.908	0.909	0.903	0.885	9
									0.904

<i>Std</i>	7.87E-	7.91E-	1.99E+	2.88E+	4.36E+	1.04E+	2.37E-	1.51E+	3.12E
<i>Dev</i>	02	01	00	00	00	00	01	00	+00
<i>RESR</i>									
<i>(%)</i>									
<i>AVG=</i>									
1.78E									
+00 %									
<i>Std</i>	2.10E+	2.93E+	1.54E+	3.51E+	3.15E+	3.50E+	3.53E+	3.57E+	3.55E
<i>Dev</i>	00	00	01	01	01	01	01	01	+01
<i>REPR</i>									
<i>(%)</i>									
<i>AVG=</i>									
2.54E									
+01									
%									
<i>Std</i>	4.77E-	4.84E-	5.26E-	5.26E-	4.29E-	5.49E-	5.49E-	5.22E-	5.24E
<i>Dev</i>	01	01	01	01	01	01	01	01	-01
<i>Csc</i>									
<i>(%)</i>									
<i>AVG=</i>									
5.10E-									
01									
%									

<i>Std</i>	2.02E+	5.58E-	1.23E+	2.57E+	1.11E+	6.62E-	8.82E-	1.57E+	3.31E
<i>Dev</i>	00	01	00	00	00	01	01	00	-01
<i>αI (%)</i>									
<i>AVG=</i>									
1.21E									
+00									
%`									

Table 5.3 Data Comparison of Areal Specific Capacitance at 120 Hz, Phase Angle at 120 Hz and Voltage of a Single Cell in this Work Compared to Previously Reported Line Filtering Capacitors

Active Materials	Phase angle at	Voltage (V)	C _A at 120 Hz	Reference

	120Hz (degree)		($\mu\text{F}/\text{cm}^{-2}$)	
Vertically aligned graphene	82	0.8	175	Science, 329 (2010). 1637-1639
Single-walled CNT	81	0.9	601	ACS nano 9.7 (2015): 7248-7255
rGO/PEDOT:PSS	81.4	1	543	Ener. Env. Sci., 2018, 11, 559
Tetrathiafulvalene-tetracyanoquinodimethane	73.2	1	151	Small 15.48 (2019): 1901494.
Graphene/CNT	81.5	1	662	<i>Nano Lett.</i> 13 , 72–78 (2013)
Electrochemical rGO	84	0.8	283	<i>Scientific reports</i> 2.1 (2012): 1-5
Perpendicularly oriented graphene	82	1	320	<i>Carbon</i> 71, 94–101 (2014).
Ti3C2/PEDOT:PSS	79	0.8	560	<i>Joule</i> 3, 164–176 (2019).
Vertically oriented graphene nanosheets	85	1	590	<i>J. Electrochem. Soc.</i> 165, A924–A931 (2018)
Edge-oriented graphene	72.6	0.8	1020	<i>Ener. St. Mater.</i> 32, 30– 36 (2020)

ErGO//PEDOT	80	1.8	338	Nature communications 10.1 (2019): 1-9.
3D-tsBC//3D-tsSC350	84.69	1.6	820.6	This work

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CHAPTER 6. LABILE COORDINATION INTERPHASE FOR REGULATING LEAN ION DYNAMICS IN REVERSIBLE ZN BATTERIES

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6.1 INTRODUCTION

The demand for abundant, reliable, and high-density grid-level energy storage solutions continues to grow as we strive to reduce the costs of carbon-neutral power systems.^[1] Large-scale battery packs are increasingly being utilized in global power grids, delivering a substantial capacity of 200 megawatts per year. These battery packs are vital in facilitating our shift from fossil fuels to renewable energy systems.^[2] As the adoption of renewable energy technologies continues to grow, the demand for battery packs is expected to rise further. However, the manufacturing of lithium battery packs is limited by the depletion of lithium supplies and the utilization of hazardous electrolytes. This necessitates exploring alternative solutions for large-scale battery packs, and zinc batteries emerge as a promising cost-effective option. With its intrinsic inertness and superior processibility, the global reserves of zinc are around 1.9 billion tons, 36 times that of lithium (as of 2017).^[3] Furthermore, zinc batteries employ water-based electrolytes, which contribute to their safety and affordability and address concerns of thermal runaway in large-area battery packs and demonstrate improved recyclability.^[4] A zinc battery pack with reduced cost, better thermal management, and relative abundance will enable practical

applications toward smaller and dispersed electrical grids, providing enhanced transmission stability and retention, a critical issue in today's power systems.

Zn metal anodes offer a reliable solution with superior volumetric specific capacity (theoretical capacity 5854 mAh cm^{-3}), which is the key to low-cost and safe Zn battery packs.^[5] Despite their advantages, Zn anodes suffer from poor cycling stability, primarily due to irreversible dendrite formation and hydrolytic processes during the interphase charge transition. Compared to main group cations such as Li, Na, and Mg, the d-block Zn^{2+} hydration shell (mainly $\text{Zn}(\text{H}_2\text{O})_6^{2+}$) exhibits higher covalency. The resultant coordination geometry, complexed by multi-layer H_2O ligands, forms a substantial ion diffusion barrier at the zinc anode. Consequently, this leads to the formation of selectively dendritic electrodepositions that protrude into the high-concentration bulk electrolyte.^[6] Furthermore, the low surface charge density of Zn^{2+} causes a slow dissociative process during the water exchange reaction. This preference for deprotonation over de-solvation leads to substantial hydrogen evolution and corrosion, ultimately resulting in electrochemically inert ZnO or $\text{Zn}_4(\text{OH})_6\text{SO}_4$ (ZHS).^[7] Consequently, these factors contribute to the poor Coulombic efficiency observed during recharging. The compositional and structural inhomogeneity of the Zn anode leads to irreversible loss of zinc and the electrolyte and therefore shortens the battery's lifetime.^[8] As a result, high maintenance costs are expected, limiting the widespread deployment of Zn battery packs.

Regulating dynamics of the de-solvation step during zinc ion electrodeposition is crucial for mitigating the irreversible loss of Zn and electrolyte in Zn metal batteries, particularly under

lean-electrolyte conditions where the high pack-level energy density becomes practical.^[9] In this regard, significant efforts have been directed towards diminishing hydration by employing large-anionic zinc salts and organic solvent additives in electrolytes and constructing host structures with high zinc affinity.^[10] However, both approaches contradict the goal of low-cost design, and their performance is compromised, especially in batteries using a lean electrolyte. An alternative approach involves forming passivation layers on the Zn anode, which can be achieved through inorganic materials such as Zn alloys,^[11] ZnF_2 ,^[7] MOFs,^[12] and organic materials such as polyimides,^[13] and silanes,^[14] among others. However, care should be taken not to create unpredictable kinetic barriers between Zn and adhesive materials, which may arise from lattice defects and phase segregation during cycling. In lean-electrolyte cells, a concentration gradient within heterostructures induces hydrodynamic electroconvection of ion flux when an electrical bias is applied. This phenomenon can potentially promote dendritic deposition, which is undesirable for the stability and longevity of the battery.^[15] Additionally, even a seemingly insignificant hydrogen evolution reaction (HER) can profoundly impact the pH level, especially in lean electrolyte conditions where there is a shortage of solvent and slow mass transfer. These kinetic concerns can be effectively addressed by designing a labile coordination environment for Zn^{2+} at the Zn/electrolyte interphase. Extensive research has been conducted on the lability of ligand substitution and water exchange of Zn^{2+} due to its essential roles in metalloenzymes.^[16] Engineering donor atoms and chelating geometries enable intermediates with different residence times. Facilitating rapid dissociation of water molecules and exchange with labile ligands within a nanosecond timescale at the zinc/electrolyte interphase is particularly advantageous for achieving homogeneity in the de-solvated Zn ion during plating/stripping.^[17] This approach

results in a high degree of reversibility, even under lean electrolyte conditions, as it helps to avoid irreversible consumption of Zn and electrolyte.

The rapid exchange of Zn^{2+} has been observed in zinc metalloenzymes such as farnesyltransferase, indicating the inherent lability of Zn^{2+} coordination^[18,19] This lability was attributed to the carboxylate-shift mechanism, where the carboxylate ligands coordinated to Zn^{2+} rearrange to maintain a constant or nearly constant coordination number throughout the entire catalytic pathway. A coordination sphere containing histidine and carboxylate ligands exhibits the fastest Zn^{2+} exchange kinetics due to its low activation barriers for carboxylate ligand exit or entrance processes. Taking inspiration from natural metalloenzymes, we have created a labile and stable Zn^{2+} coordination ligand environment to improve anode electrolyte interphases at the zinc anode. This was achieved using a scalable conversion reaction from zinc citrates into a carboxylate-rich zinc-coordinated carbon nanodot (ZnCND). The ligands exchange using zinc-histidine complex generates histidine-rich zinc-coordinated carbon nanodot (H-ZnCND). It was discovered that, because of its high Zn^{2+} affinity and superior anticorrosion properties, the H-ZnCND@Zn anode can effectively suppress hydrogen evolution, chemical corrosion, and passivation during cycling. In this study, the synthesized 50%H-ZnCND@Zn anode demonstrates excellent wettability and fast Zn^{2+} mitigation ability, so it quickly homogenizes the distribution of the Zn^{2+} flux. This leads to instantaneous Zn crystal nucleation instead of dendritic growth. The chemically grafted interphase of 50%H-ZnCND@Zn provides an ultralong cycling lifespan, maintaining a low overpotential of 62.5 mV for more than 200 hours, even at a high current density of 20 mA cm^{-2} . Furthermore, it effectively suppresses side reactions and pH increase that consume electrolyte, enabling extended cycling of $\text{Zn}||\text{LiMn}_2\text{O}_4$ under practical

conditions using a lean electrolyte ($10 \mu\text{L mAh}^{-1}$).^[20] The lean-electrolyte cell retained a high capacity of 230.7 mAh g^{-1} with excellent Coulombic efficiency of 99.3%. These remarkable results are attributed to the high thermodynamic stability and kinetical lability of the interphase based on 50%*H*-ZnCND. These findings open up new possibilities for developing durable metallic anodes for grid-scale and high-density energy storage applications. Furthermore, the selection approach based on the coordination stability and lability holds promise for other interfacial studies in the field of aqueous batteries.

6.2 SYNTHESIS, CHARACTERIZATIONS, AND ION-EXCHANGE LABILITY OF *H*-ZnCND INTERPHASES

A tunable zinc coordination environment was realized by forming coordination of Zn^{2+} with nanosized carboxylate-rich carbon nanodots (CNDs). The CNDs were produced by a facile single-step thermal condensation of citric acid without using solvents, followed by washing and purification. This scalable synthesis resulted in an acceptable reaction yield of 43.5%. The imidazole motifs were introduced into the CNDs by incorporating histidine during the thermal condensation step. This led to histidine-rich (*H*-ZnCNDs) formation through a simple esterification reaction between carboxylic groups in citric acid and primary amines in amino acids.^[21] Characterization studies using atomic force (AFM) and size distribution analysis revealed that most ZnCND and *H*-ZnCND had a diameter of approximately 4 nm (**Figure 6.1a** and **S6.1**). Moreover, the X-ray diffraction (XRD) patterns confirmed the presence of a graphitic lattice at the core of each CNDs (Figure S6.2). The size distributions were supported by transmission electron microscopy (TEM) images (Figure S6.3). Comparison of the Fourier-transform infrared (FT-IR) spectra of ZnCND and *H*-ZnCND with those of citric acid and

histidine confirmed the successful incorporation of carboxylate and imidazole motifs into the ZnCND and H-ZnCND (**Figure S6.1b**).^[22] Further investigation of molecular bonding was carried out by deconvoluting C1s in ZnCND and C1s and N1s peaks in H-ZnCND X-ray photoelectron spectra (**Figure 6.1c**).^[23] Incorporating Zn leads to a broadband absorption from 300 to 500 nm much more potent than that observed with carboxylate CNDs, indicating the presence of metal-to-graphite charge-transfer absorption (**Figure 6.1d**).^[24] The Zn^{2+} coordination was further studied in electron paramagnetic resonance (EPR) spectra. Both ZnCND and H-ZnCND symmetric signals with close intensity and shape centering at ~ 285 mT (**Figure 6.1e**).^[25] The calculated g tensor values 1.978 and 1.983 are attributed to unpaired electrons in unsaturated Zn cations. These values indicate electron transfer from the electron donor ligands to the coordination environment of the zinc ions within the system.^[26] The Zn^{2+} coordination was also validated by observing Zn 2p_{1/2} and Zn 2p_{3/2} peaks in the survey XPS

The as-prepared ZnCND and H-ZnCND were grafted onto Zn anodes by a solution-phase reaction using tannic acid as a crosslinker. The foil turned a dark color after 2 hours, indicating that the Zn anodes were successfully functionalized (**Figure 6.2a** and **6.2b**, inset). The scalability of this functionalization process is feasible for scalable production, as it can be adapted to different foil sizes. Surface morphology analysis using AFM, and scanning electron microscope (SEM) revealed that the H-ZnCND was evenly coated on Zn foils, as shown in **Figures 6.2b** and **6.2c**. The AFM images further demonstrated a smooth surface. The homogenous H-ZnCND coating was due to the close binding of Zn metal with zinc-coordinated H-ZnCND. With no zinc ions the pristine carbon nanodot (CND) coating is prone to agglomeration (**Figure S6.4**), leading to unideal inhomogeneity and roughness. The film thickness and surface roughness of the

coating can be regulated by precisely adjusting the reaction time (Figure S6.5). According to energy-dispersive X-ray spectroscopy (EDX) mapping of the cross-sectional area, a homogeneous distribution of elemental Zn, C, N, and O in the functionalization layer was obtained, which is consistent with the composition of H-ZnCND (**Figure 6.2d**). The XRD pattern of functionalized Zn foils shows predominant peaks of pure Zn (**Figure 6.2e**). The faint peaks at 12.3° and 25.4° corresponding to the (100) and (002) graphitic planes suggest the successful functionalization of H-ZnCNDs.^[28]

X-ray photoelectron spectroscopy (XPS) analysis was conducted on the functionalized Zn electrode to investigate the chemical environment and composition of the H-ZnCND layer. Strong signals corresponding to C-C (284.8 eV), C-N (286.7 eV), C-O (289.4 eV), and N-H (399.5 eV) bonds are visible in the high-resolution XPS C1s, N1s and O1s (**Figure 6.2g**) spectra, confirming the presence of these chemical groups in the H-ZnCND layer. This further supports the effectiveness of the solution-phase crosslinking method employed in this work.^[29] XPS depth profiles were also obtained to examine the elemental composition at various depths of the H-ZnCND layer (**Figure 6.2f**). By progressively removing material from the surface using Ar⁺ ion beam etching and analyzing the resulting spectra at different depths, valuable information about the elemental composition and chemical environment at various layers of the H-ZnCND coating can be obtained. The homogeneity of the H-ZnCND layer on the Zn electrode was demonstrated by the steady increase in the intensity of the Zn⁰ signals with increasing etching time and the absence of noticeable shifts. The thickness of the H-ZnCND layer was estimated to be between 90 and 100 nm based on the loss of C and N signals after 120 s of sputtering. This estimation is consistent with the cross-sectional SEM data. It is worth noting that the H-ZnCND layer is much

thinner than artificial SEI layers commonly reported for Zn anodes, which often fall in the micrometer range. The thinner H-ZnCND layer is a result of the highly efficient crosslinking reaction, and it has the potential to minimize the loss of the volumetric energy density of Zn metal.

The deconvolution of core spectra of C1s, N1s, and O1s as etching reveals an evolution of more hydrophilic imidazole and C=O, C-O compositions near the top surface of the H-ZnCND layers. This gradient distribution of bonding configuration across the film thickness effectively inhibits the formation of a distinct interphase between Zn and the surface passivation layer. This ensures good wettability near the electrolyte and facilitates a homogeneous electrical field distribution around the Zn metal. As a result, the coating remains stable during electrochemical plating/stripping processes. By modifying the H-ZnCND with varying degrees of histidine functionalization, we achieved a controlled modulation of the histidine and carboxylate motifs within the coating layers. The nitrogen-to-oxygen ratios (N/O) observed in the XPS survey spectra (**Figure 6.1e, S6.6 and S6.7, Table S6.1**) reflect the different compositions of histidine to carboxylate, noting that the oxygen may come from oxygen-containing motifs other than carboxylates. The N/O ratios are 0, 0.412, and 0.774 in the ZnCND, 50%H-ZnCND, and 100%H-ZnCND coatings, respectively, indicating an increasing amount of histidine.

In **Figure 6.2h**, The Raman spectrum of ZnCND@Zn indicates the surface is grafted with a high concentration of carboxylate (CO_2^-) ligands. The characteristic peaks includes rocking of CO_2^-

($\nu(\text{CO}_2^-)$) at $\sim 568\text{ cm}^{-1}$, bending of CO_2^- ($\delta(\text{CO}_2^-)$) at $\sim 777\text{ cm}^{-1}$, out-of-plane vibration of CO_2^- ($\gamma(\text{CO}_2^-)$) at $\sim 838\text{ cm}^{-1}$, symmetric stretching of CO_2^- at 1681 cm^{-1} and antisymmetric stretching of CO_2^- at 1692 cm^{-1} . In contrast, the 100%H-ZnCND@Zn shows predominant peaks of the imidazole side chain, such as the antisymmetric bending of C=NH-C at 1343 and 1383 cm^{-1} ; the antisymmetric rocking of C-NH₂ at 1215 and 1250 cm^{-1} , antisymmetric bending of C-NH₂ at 1416 cm^{-1} . The Raman spectrum of 50%H-ZnCND shows a combined feature of carboxylate and imidazole peak pattern, indicating the coexistence of both ligands.

Thermogravimetry (TG) and differential thermal analysis (DTA) revealed a distinct mass loss at $\sim 200\text{ }^\circ\text{C}$ in the ZnCND-coated Zn foils. This mass loss can be attributed to the conversion of carboxylate into CO_2 and CO (**Figure 6.2i**).^[30] In H-ZnCND, another significant mass loss was observed at $\sim 290\text{ }^\circ\text{C}$, ascribed to the decomposition of imidazoles into NO_x , NH_3 , and HCN. The positive correlation of the peak DTA at $\sim 290\text{ }^\circ\text{C}$ with the percentage of histidine indicates a higher histidine content in the 100%H-ZnCND coated Zn foils than in the 50%H-ZnCND coated Zn foils.

6.3 THE EFFECT OF LABILE INTERPHASE-COORDINATED MODULATION ON DEPOSITION KINETICS AND SIDE REACTIONS

The electrochemical stabilities, and kinetics of the H-ZnCND electrode at various functionalization percentages were studied during the Zn electrodeposition process to understand the impact of labile interphase modulation. The H-ZnCND greatly enhances the kinetical lability of the coordination between Zn^{2+} and the interphase during the deposition process. The apparent energy barrier (E_a) determined from the electrochemical impedance spectra (EIS) at various

temperatures supports the faster ion diffusion mechanism in the H-ZnCND anodes (**Figure 6.3a**).^[31] Notably, the E_a value for 50%H-ZnCND at 16.8 kJ mol^{-1} is significantly lower than that of the bare Zn (21.7 kJ mol^{-1}), indicating that the presence of histidine in the H-ZnCND electrode enhances Zn^{2+} transfer kinetics and accelerates the de-solvation step. This is supported by the observation of a decreasing E_a as the percentage of histidine increases. Accelerated mass transfer is also responsible for this result.^[11] The wettability of the H-ZnCND anodes also shows improved mass transfer, as evidenced by a smaller contact angle compared to bare Zn. Faster reaction kinetics are made possible by the electrolyte's substantially smaller contact angle (30.3°) on H-ZnCND compared to bare Zn (89.6°) (**Figure 6.3b**). These findings are further backed by enhanced Zn^{2+} transference numbers in H-ZnCNDs.

The thermodynamic stability of the Zn^{2+} coordination layer at various ratios of carboxylates to histidine was investigated by assessing the likelihood of HER reactions. In **Figure 6.3c**, the linear sweep voltammetry (LSV) shows that the 50%H-ZnCND exhibits a more negative on-set potential for HER ($-1.602 \text{ V vs. Ag/AgCl at } 10 \text{ mA cm}^{-2}$) compared with bare Zn (-1.575 V). However, with a higher histidine content, 100%H-ZnCND shows an enhanced on-set potential of HER ($-1.547 \text{ V vs. Ag/AgCl at } 10 \text{ mA cm}^{-2}$), thus a higher HER activity. The on-set potential in LSV curve indicates the beginning of HER. More negative on-set potential represents a lower HER activity, as clearer border between HER and Zn deposition potential may be drawn if the hydrogen on-set reduction potential is delayed, which will favor Zn reduction and inhibit HER. These results agree with the low thermodynamic stability of histidine-metal complexes at applied potentials, as widely studied in imidazole-based HER electrocatalysts.^[33–37] Tafel plots in **Figure 6.3d** also confirm the role of carboxylates in stabilizing the Zn^{2+} coordination and preventing

HER, while introducing a large amount of histidine destabilizes the Zn^{2+} coordination. The Tafel curves showed that ZnCND and 50%H-ZnCND-anchored anode had much lower current density over a wider voltage range from -1.5 V to -1.9 V (vs. Ag/AgCl) than that of pure Zn, suggesting slower HER kinetics with the labile interphase.^[32] The ZnCND showed the most suppressed HER kinetics, indicating that the carboxylate ligands are mainly responsible for Zn^{2+} affinity since their coordination with Zn^{2+} is more thermodynamically stable than that in $\text{Zn}(\text{H}_2\text{O})_6^{2+}$.^[18] Additionally, **Figure 6.3d** demonstrates how the corrosion potential rises from bare Zn at 1.091 V (vs. Ag/AgCl) to ZnCND at 1.027 V , 50%H-ZnCND at 1.034 V . The 100%H-ZnCND reduces the corrosion voltage to 1.143 V (vs. Ag/AgCl), indicating the strong tendency for HER compared with bare Zn. The high histidine content in 100%H-ZnCND could lead to excessive electrolyte consumption. When Zn is combined with 50%H-ZnCND, the corrosion current drops from 2.65 mA cm^{-2} for bare Zn to 0.73 mA cm^{-2} . The 50%H-ZnCND layer can obstruct Zn corrosion, as seen by the reduced corrosion current and higher corrosion potential. The results demonstrate that carboxylate 50%H-ZnCND significantly inhibits the electrochemical reduction of H_2O , or HER, compared to bare Zn. Combining these facts with a lower E_a and higher transference number found at the 50%H-ZnCND interphase compared to the unfunctionalized Zn surface, it was determined that 50%H-ZnCND provides the optimal ratio for the coordination interphase, striking a balance between thermodynamic stability and kinetical lability in Zn^{2+} coordination. These results are consistent with previous computational and experimental studies on Zn^{2+} in metalloenzymes.^[18,19,38–41]

The regulated Zn^{2+} diffusion in the presence of the stable and labile 50%H-ZnCND interphase leads to a 2D deposition that spreads homogeneously over the electrode, in contrast to the 3D

local deposition observed with bare Zn.^[42] The chronoamperometry (CA) curve in **Figure 6.3e** confirmed this nucleation behavior. Within 300 s, the bare zinc current increased steadily at a 150 mV overpotential, displaying a typical 3D diffusion and unordered nucleation of zinc ions. The 50%H-ZnCND current, in contrast, showed a steady density that came from 2D diffusion. Since the bare foil and Zn crystalline nuclei in **Figure 6.3e** are equivalent to Zn^{2+} , the subsequent deposition will occur in a 3D diffusion mode and ensue in all directions. The strong affinity led by the thermodynamically stable coordination between Zn^{2+} and the 50%H-ZnCND interphase, facilitated by the fast exchange resulting from labile Zn^{2+} exchange between carboxylates and histidine, promotes swift 2D diffusion and predominantly 2D homogeneous deposition.

The homogeneous Zn^{2+} deposition on 50%H-ZnCND was further investigated using *in situ* optical microscopy and time-lapse imaging during the deposition of Zn (**Figures 5.3f** and **6.3g**). Top-view imaging under a microscope allowed the observation of the nucleation process. In the case of the 50%H-ZnCND example, bright nucleation sites were observed, indicating a homogeneous dissolution and consistent growth during both the plating and stripping processes. In contrast, bare zinc showed a distinct increase in aggregation and irreversible plating/stripping processes. The lack of a controlled and homogeneous deposition process on bare zinc further highlights the advantages of the 50%H-ZnCND interphase in promoting stable and uniform Zn^{2+} deposition. In Figure S6.8, The SEM images the cross sections of 50%H-ZnCND@Zn anode shows that the protection layer remains intact while the volume changes significantly after undergoing stripping/plating for 50 cycles. After deposition, the surface of bare Zn anode is more like to fracture and form dendrites.

To investigate the species and molecular specificity at the electrical double layer (EDL) interphase, we employed *in situ* Raman spectroscopy during the electrodeposition of Zn^{2+} onto bare Zn and 50%H-ZnCND anode surface (**Figure 6.3h** and **6.3i**). *In situ* Raman spectra of the ZnSO_4 electrolytes system at the interphase were measured when the symmetric cell was discharged at 5 mA cm^{-2} . On a bare Zn anode surface, the electrostatic shielding of the Zn^{2+} inner Helmholtz layer leads to the accumulation of SO_4^{2-} ions. This is evidenced by a Raman peak at 980 cm^{-1} , corresponding to the vibrational mode of SO_4^{2-} .^[45] As the deposition time increases, there is a gradual decrease in the concentration of the Raman peak at the bare Zn anode surface, indicating the locally reduced SO_4^{2-} concentration. Due to the need for charge balance in EDL, the result is linked to an inhomogeneous Zn^{2+} distribution.^[45] That is because, during the electrodeposition on the bare Zn anode, the electric field promotes the migration and deposition of Zn^{2+} ions only onto the top of protrusions of the electrode due to the tipping effect, leading to an uneven concentration of Zn^{2+} species at the bare Zn anode surface. However, the distribution was effectively homogenized in the presence of labile 50%H-ZnCND. As the deposition duration increased on the electrochemical interphase of the 50%H-ZnCND anode, SO_4^{2-} Raman peak persisted continuously in the EDL. The homogenous Zn^{2+} concentration results from additional adsorption sites and fast exchange of Zn^{2+} ions facilitated by the 50%H-ZnCND layer.

The effectiveness of the H-ZnCND interphase in protecting Zn anodes against side reactions is supported by XRD patterns (**Figure 6.4a**) and Nyquist Plots (**Figure 6.4a**). The presence of the 50%H-ZnCND significantly reduces the intensity and distribution depth of ZnSO_4OH , a characteristic secondary ion from $\text{Zn}_4(\text{OH})_6\text{SO}_4$ (ZHS), indicating suppressed side reactions.^[43]

In striking contrast to the situation of bare Zn, the Zn deposition on the 50%H-ZnCND preferentially occurs on the (200) plane rather than on the (001) plane even after 100 cycles.

Figure 6.4a shows that the JCPDS (card no. 87-0713) data mainly were used to assign the Zn diffraction peaks, specifically the (002), (100), and (101) lattice planes. The following formula was used to determine the relative texture coefficients (RTCs) for each Zn lattice plane (Equation 1).^[44]

$$RTC_{(hkl)} = \frac{I_{(hkl)}/I_{0(hkl)}}{\sum(I_{(hkl)}/I_{0(hkl)})} \times 100 \quad (1)$$

$I_{0(hkl)}$ is the intensity of the JCPDS (card no. 87-0713) data, and $I_{(hkl)}$ is the intensity acquired from the sample. Zn deposition on 50%H-ZnCND shows higher RTCs ratios between (002) and (100) lattice planes increased from 3.82 before cycling to 7.23 after 100 cycles. This indicates that the (002) planes, parallel to the sheet surface, were more exposed to Zn deposition than the (100) planes, which tend to protrude from the Zn surface. In contrast, on bare Zn electrodes, the RTCs ratios of (002) to (100) lattice planes decreased from 3.59 to 2.63 after 20 cycles, suggesting a higher propensity for dendrite formation. The findings support the reduced dendrite formation in the 50%H-ZnCND electrode. The Nyquist plots of cycled anodes revealed a significantly smaller resistance for the cycled 50%H-ZnCND@Zn compared to that of bare Zn anodes (**Figure 6.4b**). This suggests that the 50%H-ZnCND layer provides adequate protection, resulting in a minimal phase transformation.

We conducted a comprehensive investigation into the nucleation and growth behavior of zinc on both bare Zn and 50%H-ZnCND anode surfaces. Our study focused on measuring the nucleation overpotential, a widely recognized parameter commonly used to assess the energy needed for Zn nuclei formation during plating. This was achieved by acquiring the voltage profiles of Zn plating on a Cu substrate in various interphases at 1 mA cm^{-2} , as shown in **Figure 6.4c**. The 50%H-ZnCND interphase exhibits a significantly lower nucleation overpotential at approximately 43.4 mV compared to the pure Zn surface at 64.3 mV. This difference can be attributed to a lower energy barrier for Zn deposition at the 50%H-ZnCND anode interphase, facilitated by the presence of the adsorbed H-ZnCND. The decrease in overpotential correlates with the histidine content, further supporting the role of H-ZnCND in reducing nucleation overpotential.

Furthermore, the 50%H-ZnCND layer effectively promotes nucleation, producing more uniform, compact, and dense Zn nuclei. **Figure 6.4d** displays the SEM images of Zn foils at fixed current densities of 5 mA cm^{-2} . The top images represent varying Zn deposition amounts ranging from 0.1 to 5.0 mA h cm^{-2} . The Zn deposits formed on the bare Zn anode exhibit loose, distinct, and obliquely dispersed flake structures. Furthermore, the size of these flakes gradually increases with higher levels of Zn deposition. Notably, the newly deposited Zn preferentially accumulates on the partially formed flakes rather than the bare substrate, as shown in **Figure 6.4d**. This behavior can be attributed to the concentration of electrons in regions where Zn deposition is more favorable, leading to the partial accumulation of Zn and the formation of Zn dendrites.

However, in the presence of 50%H-ZnCND, the shape of the deposited Zn is remarkably distinct from that of the bare Zn electrode (**Figure 6.4d** bottom). With an increasing amount of Zn deposition, the size of the flakes exhibits global growth instead of localized growth observed on the bare Zn anode. This observation provides evidence that 50%H-ZnCND effectively regulates the uniform distribution of the Zn^{2+} , leading to a notable increase in preferential sites for Zn deposition on the electrode surface. Consequently, the Zn deposits exhibit dense and compact morphologies without significant flake separation.^[46] The dendrite-free deposition is likely facilitated by the rapid exchange of Zn^{2+} between the carboxylates and imidazole motifs in 50%H-ZnCND.

The controlled concentration gradient and dispersion of the electric field at the anode/electrolyte interphase are critical factors in achieving uniform nucleation and deposition of Zn^{2+} . These factors are often facilitated by a protective layer, such as that found in 50%H-ZnCND. This protective layer helps maintain a stable concentration gradient and enhances the diffusion coefficient of Zn^{2+} , promoting uniform deposition of Zn.^[47]

To further understand the influence of the 50%H-ZnCND layer on the prevention of dendrite formation, finite element analysis (FEA) was employed to simulate the dynamic fluctuation of the electric field and concentration gradient throughout the Zn^{2+} deposition process after 0 hour, 1 hour, 2 hours and 5 hours, as shown in **Figure 6.4e-h**. The results demonstrate that the 50%H-ZnCND anode displays a remarkably confined electric field around the Zn dendrites due to the presence of carbon nanodots even after 5 hours, which effectively minimizes the adverse tip

effects of Zn dendrites. It should be noted that the current intensification present in the gap between carbon nanodots is not practical in the 50%H-ZnCND anode the gaps are negligible in real situation due to strong π - π stacking and hydrogen bonding between 50%H-ZnCND. In addition, the ion diffusion behavior was studied by analyzing the fluctuation of the concentration field as the 50%H-ZnCND layer develops. In the neighboring bare Zn anode, the concentration of Zn^{2+} remains relatively low (below 1.0 M) in the buried regions. In contrast, a higher Zn^{2+} concentration was obtained at the top of the deposition as dendrites form, as indicated by the curved direction of the concentration flux. These top-to-bottom concentration gradients accumulate a large amount of Zn^{2+} at the dendrite tips, leading to a significant driving force for dendritic development. However, on the 50%H-ZnCND anode, a notable concentration of Zn^{2+} is observed near the flat surface instead of at the points. The remarkable differences observed can be attributed to the 50%H-ZnCND layer, which facilitates uniform Zn^{2+} flow and rapid 3D diffusion. This layer comprises H-ZnCND clusters with various 3D diffusion channels, and a high concentration of carboxylate and imidazole is enriched near the tips, forming a dynamic coordination layer. Consequently, Zn^{2+} ions are forced to deviate from the electric field and distribute homogeneously along the flat Zn surface, promoting uniform Zn deposition.

6.4 HIGHLY REVERSIBLE ZN PLATING/STRIPPING PERFORMANCE OF H-ZnCND IN A LEAN ELECTROLYTE

To evaluate the electrochemical performance of the 50%H-ZnCND, we conducted the Zn stripping/plating experiments in symmetric coin-type cells. In contrast to Zn foil, the symmetrical cell based on the 50%H-ZnCND exhibited a low polarization of 108 mV at a high

current density of 20 mA cm^{-2} , with a cycling capacity of 5 mAh cm^{-2} , which is equivalent to a degree of discharge (DOD) of 14.6 %. This result confirms the Zn^{2+} conductivity of 50%H-ZnCND and indicates a lower energy barrier for Zn nucleation, promoting uniform Zn plating at fast rates compared to bare Zn (**Figure 6.5a**). In contrast, the Zn foil-based cell experienced a sudden and irreversible short circuit after 8.5 hours of cycling, likely due to the continuous growth of dendrites. Comparatively, the 50%H-ZnCND-based cell exhibited an exceptionally extended cycling life of over 200 hours with minimal voltage hysteresis. The superiority of the 50%H-ZnCND cells was particularly evident even at a high Zn utilization rate (**Figure 6.5b**). For instance, by increasing the applied current density to 10 mA cm^{-2} and cycling capacity to 10 mAh cm^{-2} (DOD = 23.95%), the cycle life of the 50%H-ZnCND-based cell (198.8 hours) was almost 23 times longer than that of the Zn foil (8.7 h). A similar trend was observed at a low current density of 1 mA cm^{-2} and a capacity of 1 mAh cm^{-2} , where the 50%H-ZnCND symmetric cell showed a nearly 300-fold improvement in lifespan compared to bare Zn symmetric cells. (Figure S6.9). The extended lifespan is superior to most existing Zn anodes. Whereas the 100%H-ZnCND@Zn cells underwent a short circuit after 350 cycles (Figure S6.10). The cell failed after 1260 cycles confirming the high HER activity in 100%H-ZnCND is detrimental to reversible zinc battery cycling. Furthermore, the 50%H-ZnCND interphase layer was engineered with different layer thicknesses by repeating thermal cross-linking reactions (Figure S6.11). The symmetric cells using thicker 50%H-ZnCND interphase layer showed a stable cycling at 1 mA cm^{-2} and 1 mAh cm^{-2} (Figure S6.12a and S6.12b). The higher thickness, however, induced early short circuit in symmetric cell (Figure S6.12c and Figure S6.12d). Thus, the layer thickness in 50%H-ZnCND@Zn anode is optimal.

Figure 6.5c shows the rate performance of symmetric cells based on bare Zn, ZnCND without histidine, and 50%H-ZnCND. At all current densities, the 50%H-ZnCND cells exhibited lower voltage hysteresis, indicating the enhanced kinetics of 50%H-ZnCND. **Figure 6.5d** summarizes the voltage hysteresis on bare Zn, ZnCND without histidine, and 50%H-ZnCND at various current densities, highlighting its effectiveness in enhancing Zn affinity and facilitating accelerated ionic mitigation.

To further investigate the effects of the H-ZnCND layer on Zn electrodeposition characteristics, Zn was electrodeposited onto Cu electrodes with and without the 50%H-ZnCND layer in coin cells. We measured the reversibility of high-current Zn plating/stripping on Cu and 50%H-ZnCND@Cu electrodes with an areal capacity of 1 mAh cm^{-2} at a current density of 10 mA cm^{-2} . As shown in **Figure 5.5e**, the Zn||50%H-ZnCND@Cu cell demonstrates an initial Coulombic efficiency (CE) of 98.9% (vs. 96.8% for the control

cell) with a low plating/stripping overpotential. Furthermore, it maintains a high average CE of 99.7% throughout 300 cycles (vs. the fluctuating CE and early failure of the control cell). As shown by the voltage–capacity curves in the inset of **Figure 6.5e**, the Zn nucleation overpotential of 50%H-ZnCND (64.5 mV) at a high current density of 10 mA cm^{-2} is lower than that of an exposed Cu electrode (107.8 mV). This observation indicates that 50%H-ZnCND exhibits a reduced energy barrier for Zn nucleation, enhancing the efficiency of the nucleation process. Furthermore, with an areal Zn deposition capacity of 1 mAh cm^{-2} , the deposited layer on the 50%H-ZnCND coated Cu (50%H-ZnCND@Cu) electrode exhibits a flatter reversibility and enhanced reaction kinetics of the Zn plating/stripping process following the introduction of

50%H-ZnCND onto the Cu electrodes. Similar conclusions can be drawn from the cyclic voltammetry (CV) profiles (**Figure 6.5f**), in which the overpotential of Zn electroplating on the 50%H-ZnCND@Cu electrode is more significant than that on bare Cu electrode ($|BB| = 19.7$ mV). In addition, a higher response current density at the 50%H-ZnCND@Cu electrode can alleviate Zn^{2+} diffusion behavior and facilitate a homogeneous Zn nucleation deposition. The cycling performance surpasses the previously reported results for an artificial interphase on a Zn anode and outperform the majority of advanced Zn-based anodes (**Figure S6.13**), demonstrating the efficacy of 50%H-ZnCND in mitigating irreversible electrodeposition of Zn.

The 50%H-ZnCND effectively alleviates electrolyte consumption during the Zn plating/stripping process, preventing battery failure due to electrolyte depletion, especially in a lean electrolyte. To confirm this theory, Zn plating/stripping tests were performed in a $Zn||50\%H-ZnCND@Cu$ cell, investigating the impact of electrolyte loading on cyclic stability. The asymmetric cells were cycled at 2 mA cm^{-2} with 1 mAh cm^{-2} areal capacity. As shown in **Figure 6.5g**, the Coulombic efficiency (CE%) remains stable during the initial cycles, but sharply declines after several cycles with limited electrolyte levels ($10\text{ }\mu\text{L mAh}^{-1}$). For example, at the 10th cycle, satisfactory Zn plating/stripping behavior is observed, but by the 30th cycle, it degrades. However, normal Zn plating/stripping recovers, and CE returns to 93% after injecting an additional $10\text{ }\mu\text{L}$ of electrolyte (Note that dot scatters in **Figure 6.5g** are before adding additional electrolyte. Circle scatters are after adding additional electrolyte.) The cycling life was also extended using electrolyte at $20\text{ }\mu\text{L mAh}^{-1}$ under the same charge/discharge setting (**Figure S6.14**). In contrast, the 50%H-ZnCND electrode exhibits sustained cycling in a flooded cell for 60 cycles. These results demonstrate the importance of electrolyte loading on cycling stability, confirming that

electrolyte consumption is a primary factor of Zn anode failure. Furthermore, the 50%H-ZnCND interphase effectively preserves the electrolyte from side reactions, ensuring enhanced stability.

6.5 VALIDATION OF H-ZNCND ELECTRODE FOR PROTOTYPE ZN BATTERY APPLICATIONS

In the investigation of the applicability of H-ZnCND, a zinc-metal full battery ($\text{Zn}||\text{LiMn}_2\text{O}_4$) was constructed and tested. **Figure S6.15-6.17** depicts the XRD, SEM, and EDS characterization of commercially available LiMn_2O_4 powder. The inclusion of the 50%H-ZnCND layer demonstrates notable benefits. The results indicate that the 50%H-ZnCND $||\text{LiMn}_2\text{O}_4$ exhibits lower polarization voltage and enhanced diffusion kinetics compared to the bare $\text{Zn}||\text{LiMn}_2\text{O}_4$ configuration, as evidenced by CV profiles in **Figure 6.6a**. Furthermore, the 50%H-ZnCND $||\text{LiMn}_2\text{O}_4$ configuration demonstrates superior rate performance at various current densities up to 5 C, as shown in the galvanostatic charge/discharge (GCD) profiles in **Figures 6.6b** and **6.6c**. In addition, electrochemical impedance spectroscopy (EIS) experiments also confirm lower initial and cycled resistances for the 50%H-ZnCND@Zn $||\text{LiMn}_2\text{O}_4$ configuration (**Figure S6.18**). After five cycles, the resistance of uncoated $\text{Zn}||\text{LiMn}_2\text{O}_4$ increases significantly, which can be attributed to the passivation layer formed on the zinc electrode due to dendritic formation or irreversible side reactions.

In addition, the 50%H-ZnCND $||\text{LiMn}_2\text{O}_4$ system exhibited a superior reversible capacity of 109 mAh g⁻¹ with nearly 100% CE and ultrahigh capacity retention of 94.7% over 500 cycles at 1 C (**Figure 6.6d**). In contrast, the capacity of the bare $\text{Zn}||\text{LiMn}_2\text{O}_4$ system underwent rapid

degradation eventually leading to a cell short circuit. Surface morphology analysis of the cycled Zn anodes revealed important information about the capacity degradation mechanism. Morphological analysis of the cycled Zn anode is covered with disordered dendrites and "dead Zn," whereas the 50%H-ZnCND anode retained its initial morphology, enabling seamless transport of Zn^{2+} .^[48]

The potentiostatic intermittent titration technique (PITT) analysis provides insights into the H^+ and Zn^{2+} diffusion kinetics and interfacial mass transfer resistance (**Figure 6.6e**).^[45,49] After stabilizing the three electrodes at plateau potentials of 0.40 V vs. Zn^{2+}/Zn , a 10 mV-adjusted increasing potential step was applied. The results show that the 50%H-ZnCND system exhibited faster Zn^{2+} transfer kinetics, and lower interfacial impedance (**Figure 6.6e**). The kinetic lability of 50%H-ZnCND, even under the lean electrolyte condition, results in more rapid Zn^{2+} transfer kinetics and superior interfacial compatibility, as evidenced by the higher current peak with continuous discharge and noticeably lower interfacial impedance (**Figure 6.6f**) in both flooded and lean electrolyte. These findings indicate that the 50%H-ZnCND layer effectively tunes the Zn^{2+} deposition dynamics, homogenizes the Zn^{2+} distribution, enhances the structural stability of the cycled Zn anode, thus preventing adverse side reactions by limiting water molecules interactions near the electrode surface. These findings are consistent with the EIS results, further supporting the beneficial role of the labile 50%H-ZnCND layer in enhancing the reversibility of Zn^{2+} deposition.

A lean electrolyte addition ($10\ \mu\text{L}\ \text{mAh}^{-1}$) was used to assemble the $\text{Zn}||\text{LiMn}_2\text{O}_4$ cells with bare Zn or 50%H-ZnCND@Zn anodes (**Figure 6.6f**). The lean electrolyte cell with 50%H-ZnCND@Zn exhibits cycle stability as determined at a high current density of 1 C. This lean-electrolyte cell exhibits a high degree of reversibility (100% CE). The capacity remains at 95.5% after 100 cycles, which is higher than that of a bare Zn anode. A serial connected four-unit cell pack illuminated six 3 V red light emitting diodes in parallel for more than two days using their high capacity of $106.7\ \text{mAh}\ \text{g}^{-1}$ (Figure S6.19). The lean-electrolyte cell using a bare Zn anode rapidly decayed and died within 31 cycles from the formation of Zn dendrites. This result demonstrates the scalability of labile 50%H-ZnCND in large Zn battery packs using a minimal amount of electrolyte. SEM images were used to compare the surface morphologies evolution of bare Zn and 50%H-ZnCND@Zn anodes after the first and fiftieth cycles using a lean electrolyte. During cycling, it is clear that the bare Zn electrode's surface becomes rougher, exhibiting dendrite-like flakes (**Figure 6.6g**), and after 50 cycles, the surface roughness increases. The 50%H-ZnCND@Zn electrode, in contrast, kept its surface relatively smooth and free of dendrites. The 50%H-ZnCND protective layer effectively stabilizes the Zn/electrolyte interphase and prevents Zn dendritic growth, as demonstrated by the distinct surface morphologies in lean-electrolyte cells.^[50] Additionally, the versatility of 50%H-ZnCND was demonstrated in flooded $\text{Zn}||\text{LiMn}_2\text{O}_4$ cells (**Figure 6.6h**). Coupling with other cathodes, for example, in a 50%H-ZnCND@Zn||VOPO₄ full cell, the 50%H-ZnCND@Zn anode exhibited a high reversible capacity of $91\ \text{mAh}\ \text{g}^{-1}$ at $1\ \text{A}\ \text{g}^{-1}$ after 2000 cycles. In contrast, the bare $\text{Zn}||\text{V}_2\text{O}_5$ full cell has a shorter life span of 570 cycles (Figure S6.20 and S6.21). Overall, the superior cycling stability and rapid kinetics of the 50%H-ZnCND@Zn have been demonstrated. In general, the suppressed hydrogen evolution and homogeneous Zn deposition in the 50%H-ZnCND@Zn leads to

improved cycle stability and faster kinetics of the 50%H-ZnCND@Zn symmetric battery, the 50%H-ZnCND@Zn||VOPO₄ battery and the H-ZnCND||LiMn₂O₄ battery.

6.6 CONCLUSIONS

This study demonstrates the potential of the bio-inspired carbon nanodot coordination substrate, 50%H-ZnCND, for optimizing zinc electrolyte interphases in high-performance Zn batteries. Theoretical calculations and experimental findings show that the 50%H-ZnCND interphase demonstrates thermodynamic Zn²⁺ affinity and kinetic ligand exchange lability. This interphase effectively suppresses the irreversible metal and electrolyte consumption by favorably binding Zn²⁺ ions. During electrochemical cycling, the labile 50%H-ZnCND interphase improves the Zn deposition kinetics by spatially regulating the uniform growth of Zn. Remarkably, even at a high current density of 20 mA cm⁻², the labile coordination interphase of 50%H-ZnCND@Zn demonstrates exceptional cycling stability of more than 200 hours with an ultralow overpotential of 62.5 mV. The use of this artificial interphase not only results in the realization of high Zn reversibility at high current density, but also significantly improves the cyclability of Zn||LiMn₂O₄ full cells under realistic conditions with a lean electrolyte (10 μ L mAh⁻¹).^[51] This work highlights the promising potential of a novel labile coordination interfacial in enabling high-performance large-scale zinc batteries.^[52] Furthermore, the insights gained from this study could provide valuable guidance for the rational selection and design of anode electrolyte interphases in various aqueous battery technologies. By leveraging the success and lessons learned from existing metal-based batteries, the developed artificial interphase offers a promising approach to enhance the performance and stability of aqueous battery systems.

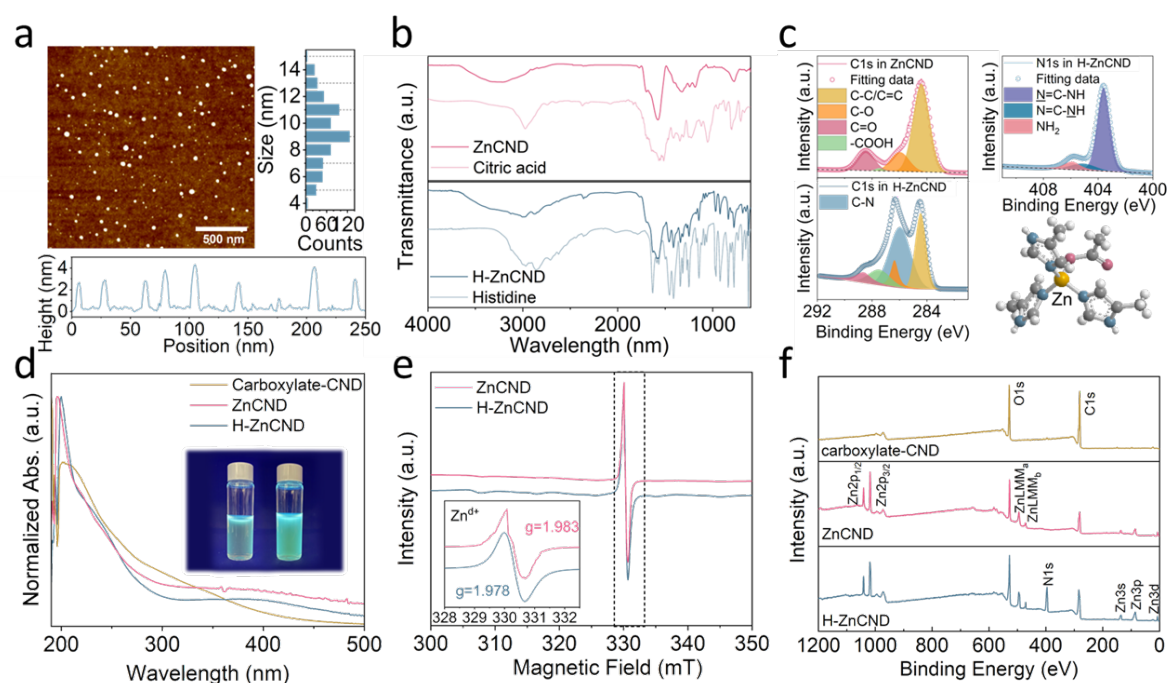


Figure 6.1 a) Typical AFM images of his-ZnCNDs, their particle size distribution and height profile. b) FT-IR spectra of ZnCND and citric acid on the top, H-ZnCND and histidine at the bottom. c) XPS spectra deconvolution of C1s in ZnCND (top left), N1s in H-ZnCND (top right), and C1s in H-ZnCND (bottom left) and molecular representation of Zn²⁺ coordination sphere in the H-ZnCNDs. d) UV-vis spectra of carboxylate-CND, ZnCND, and H-ZnCND. e) EPR spectra of ZnCND and H-ZnCND and zoom-in detail spectra. f) Survey XPS spectra of carboxylate-CND, ZnCND, and H-ZnCND.

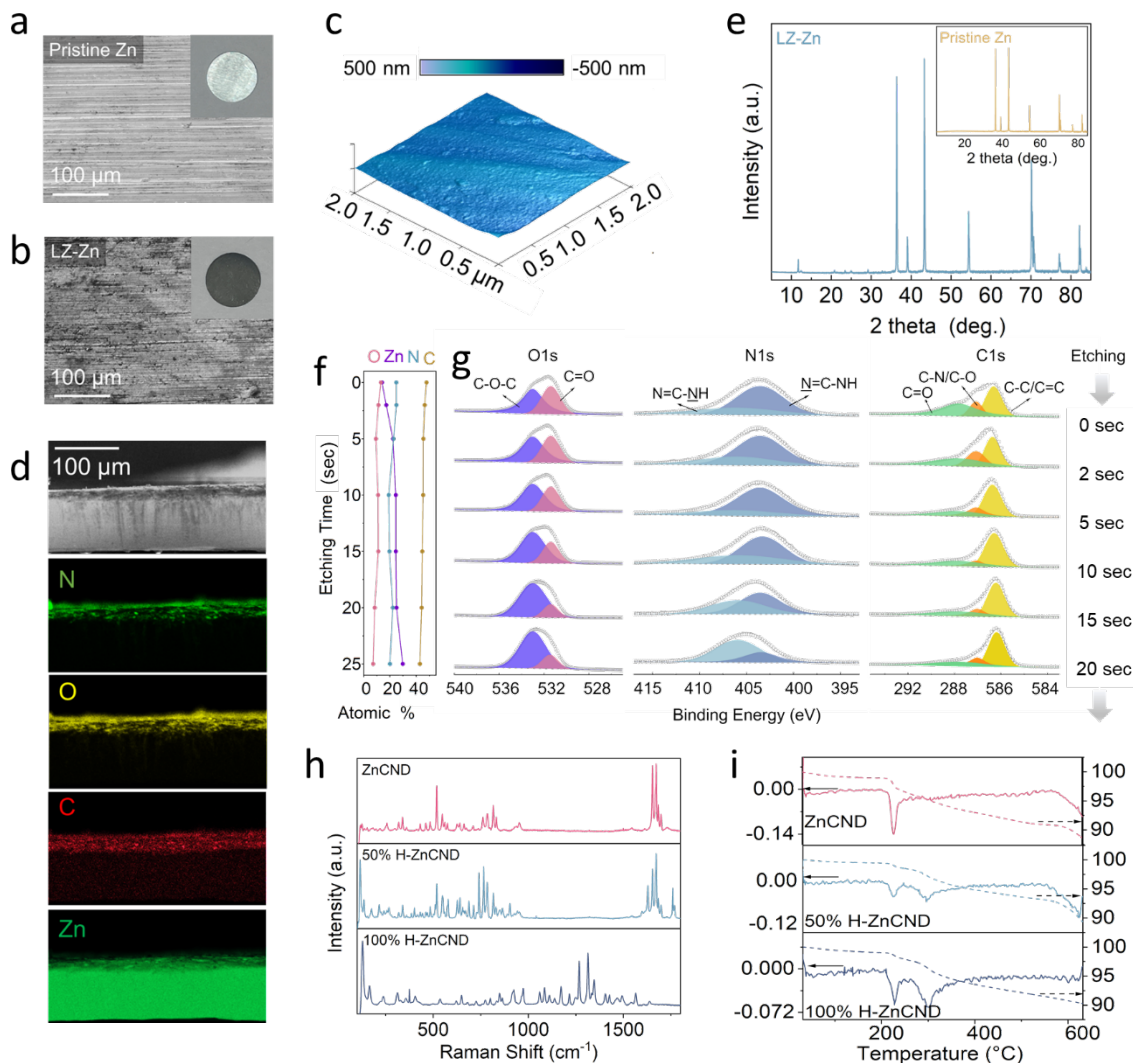


Figure 6.2 a, b) The top-view SEM images of bare Zn and 50%H-ZnCND@Zn, insets are photographs of the electrode surfaces. c) Typical AFM image of 50%H-ZnCND@Zn. d) Cross-sectional SEM images of 50%H-ZnCND@Zn, and the corresponding EDX mapping images. e) The XRD patterns of 50%H-ZnCND@Zn. f) Compositional evolution of 50%H-ZnCND@Zn from 0 sec to 20 sec using Ar⁺ etching XPS spectra. g) The depth profile XPS spectra of O1s, N1s and C1s from 0 sec to 20 sec using Ar⁺ etching. h) Raman spectra of ZnCND@Zn, 50%H-

ZnCND@Zn, and 100%H-ZnCND@Zn. i) TGA curves and differential thermal analysis of ZnCND@Zn, 50%H-ZnCND@Zn, and 100%H-ZnCND@Zn.

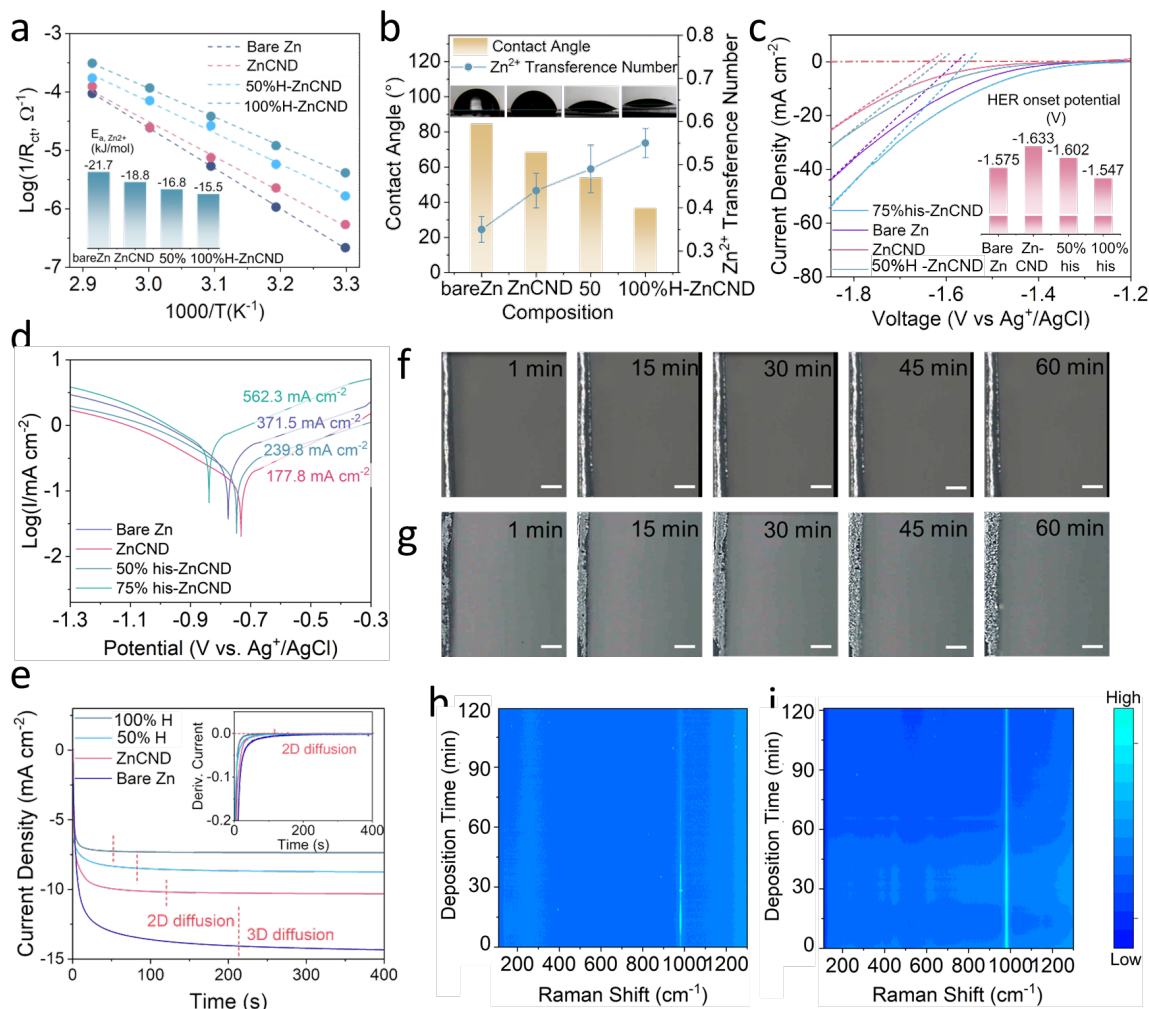


Figure 6.3 a) Corresponding Arrhenius curves and comparison of activation energies, b) The electrolyte contact angles and Zn^{2+} transference number variation, c) LSV curves in 2.0 M ZnSO_4 , d) Tafel plots in 1.0 M H_2SO_4 of bare Zn, ZnCND, 50%H-ZnCND and 100%H-ZnCND. e) Chronoamperograms at -150 mV of bare Zn, ZnCND, 50%H-ZnCND, and 100%H-ZnCND. In situ optical microscopy photos of Zn^{2+} plating processes of f) 50%H-ZnCND@Zn anode and

g) pure Zn anode. In situ Raman spectra evolution over electrodeposition time of h) bare Zn, i) 50% H-ZnCND.

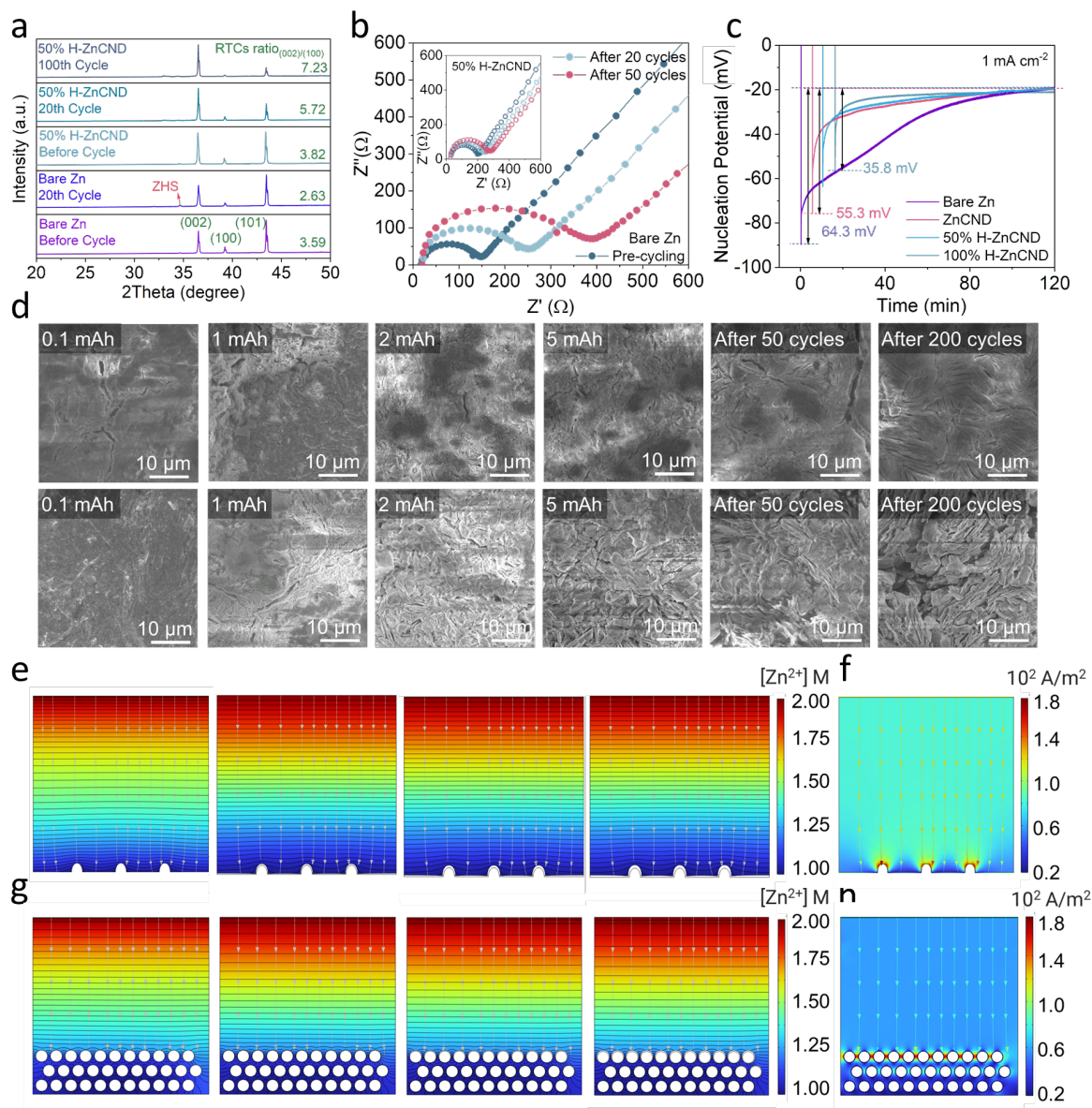


Figure 6.4 a) The XRD patterns of cycled 50% H-ZnCND and bare Zn electrodes. b) Nyquist plots of bare Zn electrode before cycling, after 5 cycles, and 20 cycles in symmetric cells and of 50% H-ZnCND@Zn electrode (inset). c) Nucleation overpotential of bare Zn, ZnCND, 50% H-

ZnCND, and 100%H-ZnCND in asymmetric cell (vs. Cu electrode). d) Ex situ SEM images of plated 50%H-ZnCND@Zn(top) and Zn(bottom) in 2.0 M ZnSO₄ at different cumulative capacities and cycles. FEA dual-field simulations reveal that during the electrodeposition a redistribution of Zn²⁺ concentration occurs in e) the bare Zn anode, g) and in the 50%H-ZnCND@Zn anode; current density field distribution of f) a bare Zn anode and j) the 50%H-ZnCND@Zn anode.

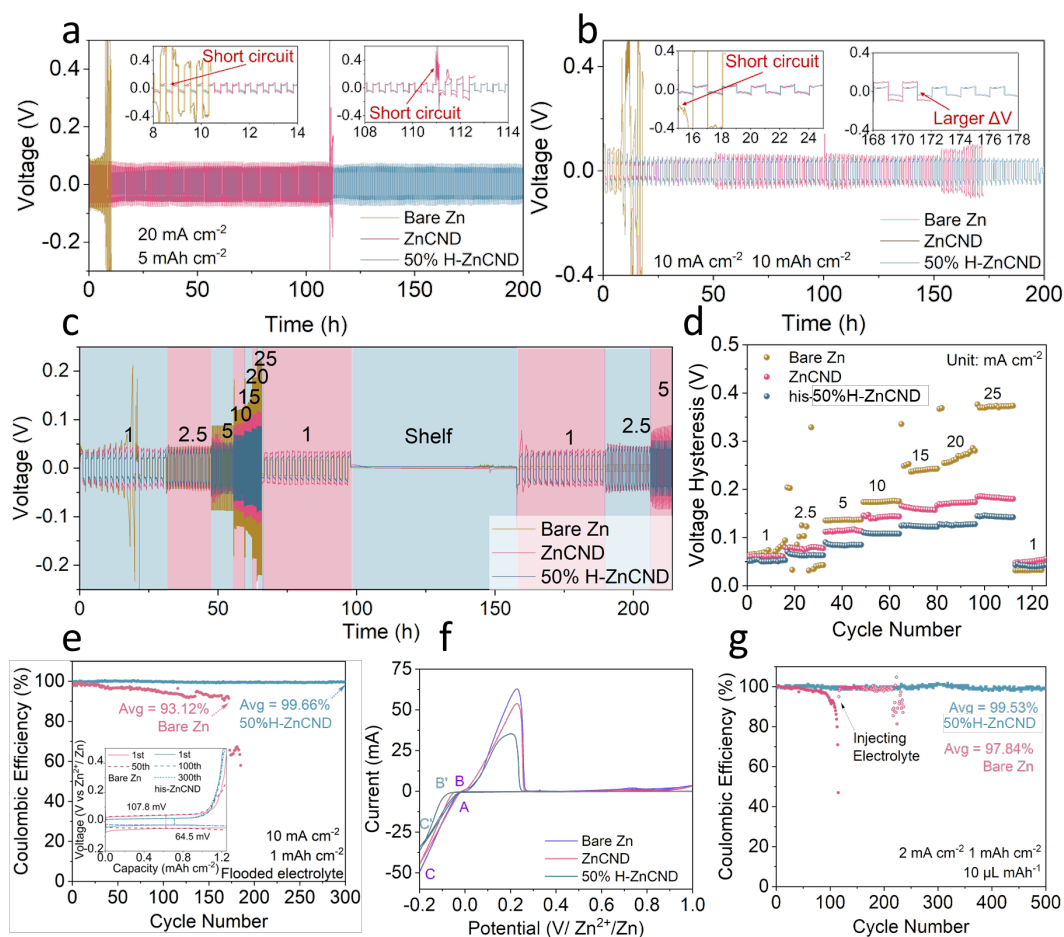


Figure 6.5 Symmetric cell cycle performance of pure Zn, ZnCND@Zn, and 50%H-ZnCND@Zn electrodes under the conditions of a) 20 mA cm⁻², 5 mAh cm⁻²; b) 10 mA cm⁻², 10 mAh cm⁻². d) Rate performance of the symmetric cells at current densities of 1, 2.5, 5, 10, 15, 20, and 25 mA cm⁻² and areal capacities of 1 mA h cm⁻² and a shelf-life test, as well as e) corresponding voltage

hysteresis. e) Coulombic efficiency of Cu//Zn asymmetric cells using pure Zn and 50%H-ZnCND@Zn electrodes under the conditions of 10 mA cm^{-2} , 1 mAh cm^{-2} (inset is the GCD profile). g) The CV profile of Cu//Zn asymmetric cells using pure Zn, ZnCND@Zn and 50%H-ZnCND@Zn anodes. f) Coulombic efficiency of Cu//Zn asymmetric cells using pure Zn and 50%H-ZnCND@Zn electrodes under the conditions of 2 mA cm^{-2} , 1 mAh cm^{-2} using $10 \mu\text{L}$ mAh^{-1} electrolyte.

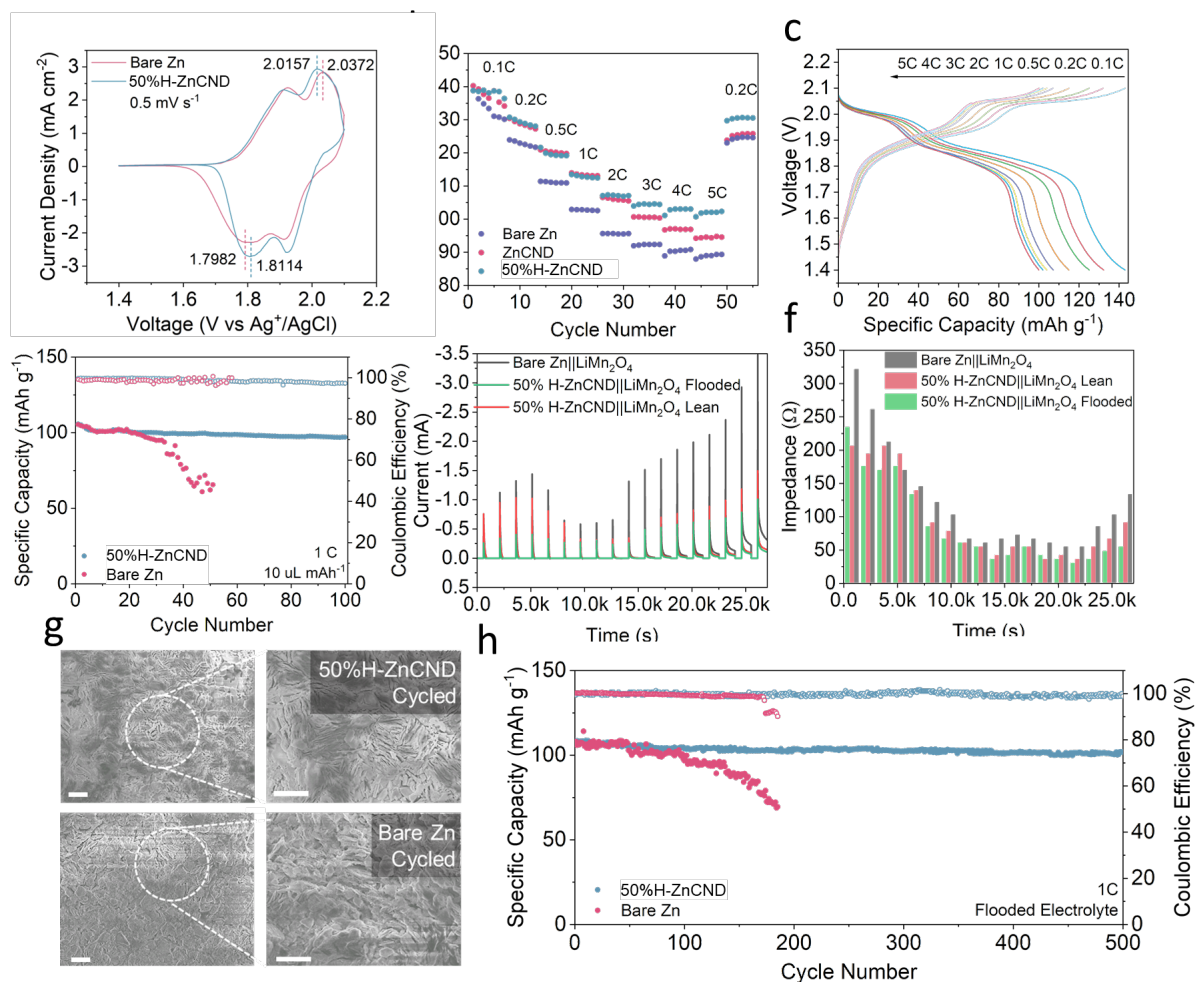


Figure 6.6 The electrochemical performance of Zn||LiMn₂O₄ full cells using bare Zn and 50%H-ZnCND@Zn anode. a) CV profiles, b) rate performance, c) GCD profiles at different current

densities, d) cycling performance and CEs at 1 C using lean electrolyte condition ($1 \mu\text{L mAh}^{-1}$). PITT in situ e) current and f) EIS profiles of the $\text{Zn}||\text{LiMn}_2\text{O}_4$ cell using bare Zn and the 50%H-ZnCND@Zn anode at lean electrolyte condition ($1 \mu\text{L mAh}^{-1}$). g) The top-view SEM images of cycled 50%H-ZnCND and bare Zn anode at lean electrolyte condition and their zoom-in images. h) Cycling performance and Coulombic efficiency of $\text{Zn}||\text{LiMn}_2\text{O}_4$ cell using bare Zn and the 50%H-ZnCND@Zn anode at 1 C using the flooded electrolyte.

6.7 EXPERIMENTAL METHOD

Preparation of Zn-histidine and Zn-citrate complex precursor solutions:

All chemicals were used as received without further purification. A 0.25 M solution of the amino acid L-histidine (ThermoFisher, reagent grade) was prepared in degassed/Nitrogen saturated diluted Tris-HCl buffer solution with a pH 10 (Sigma Aldrich). To this solution, 1.0 M ZnCl_2 was added to reach a concentration of 0.125 M with a molar ratio of 2:1 amino acid to Zn^{2+} . The resulting solution was incubated at room temperature overnight before further use. Depending on the specific amino acid used, the solution was denoted as Zn-his. For the synthesis of ZnCND, a solution of 0.125M zinc citrate dihydrate (Sigma Aldrich, 97%) was prepared in DI water. This solution was denoted as Zn-CA.

Scalable Synthesis of Zn^{2+} coordinated ZnCND and H-ZnCND reagents:

The synthesis was performed based on a modified literature procedure. Initially, 0.48 g of citric acid (2.5 mmol, Sigma Aldrich, > 99.5%) was dissolved in every 10 mL of the precursor solutions. The precursor was prepared by mixing Zn-his and Zn-CA in different volume ratio to obtain a variety of samples, including 50%H-ZnCND (5 mL Zn-his and 5 mL Zn-CA), 100%H-ZnCND (10 mL Zn-his and 5 mL Zn-CA). The mixed solutions were then heated at 180 °C for 40 h under a nitrogen atmosphere. The resulting light brown products were dispersed in 500 mL deionized (DI) water with the assistance of ultrasonication. Subsequently, the mixed solution was centrifuged at 4750 rpm for 30 min first. The supernatant was collected and dialyzed in regenerated cellulose dialysis tubing with a molecular weight cut-off (MWCO) of 1k Da for 48 h to remove any unreacted reactants. Finally, the solution is freeze-dried for further characterizations.

Preparation of pristine CNDs:

For comparison, the pristine carbon nanodots were prepared by a modified approach. Citric acid (20 g) was heated in a muffle furnace at 180 °C for 40 h under air. After this thermal treatment, the obtained solid was dispersed in 100 mL water under the help of ultrasonic. The dispersion was centrifuged at 4750 rpm for 30 min first. The supernatant was collected and dialyzed in regenerated cellulose dialysis tubing with MWCO 1k Da for 48 h to remove unreacted reactants. Then the obtained CNDs were freeze-dried before further characterizations and applications.

Formation of labile Zn^{2+} coordination interphase on zinc anodes (H-ZnCND@Zn):

The polished zinc foil, with a thickness of 0.1 μm , was thoroughly rinsed in ethanol and acetone to before the treatment. A total of 0.0625 g of the corresponding his-ZnCND was dispersed in 50 mL methanol with the assistance of ultrasonication. To activate the Zn foil surface, 0.005g of tannic acid (Sigma Aldrich, ACS grade) was added to solution. The solution was stirred until it reached a homogenous state. A clean Zn foil measuring 4cm x 4cm was immersed in the aforementioned solution and heated under reflux conditions at 60 $^{\circ}\text{C}$ for 30 minutes, resulting in uniform coatings on the surface of the Zn foil. After washing with methanol and ethanol, the obtained Zn foil was dried under vacuum at room temperature. The H-ZnCND-modified Cu foils were obtained through the same procedure, where only the metallic Zn foil was replaced with a Cu foil. Both the modified Zn foils and the bare Zn foils were punched into discs with a diameter of $\Phi 10$ mm, which were subsequently used as Zn anodes without any further treatment.

Synthesis of LMO Cathodes:

The LMO cathode material was prepared by mixing 70 wt% LiMn_2O_4 (Lib-LMO, MTI Corporation), 20 wt% conductive carbon (KS-6, MTI Corporation), and 10 wt% PVDF in N-Methyl-2-pyrrolidone (Sigma-Aldrich), and the slurry mixture was then coated on a graphite paper and dried in a vacuum oven at 60 $^{\circ}\text{C}$ for 24 hours. The specific capacity of the LMO cathode was calculated based on the weight of the active materials. The mass loading of LMO under unconstrained testing conditions was $\approx 16.7 \text{ mg cm}^{-2}$.

Synthesis of VOPO_4 cathodes: Powdered VOPO_4 was produced in accordance with earlier literature.^[1,2] It was specifically refluxed at 110 $^{\circ}\text{C}$ for 20 hours using 24 g of V_2O_5 powder, 140 ml of 85% H_3PO_4 , and 400 ml of DI water. The yellow-green VOPO_4 powder was centrifuged,

cleaned with acetone, and stored at room temperature. The VOPO₄ was produced by calcining the VOPO₄ powder created during the synthesis at 500 °C for 6 hours in air. The powdered VOPO₄ that was produced had a yellow color.

Electrochemical Measurements:

To assemble the symmetric cells, 2032-type coin cells were used, with two identical Zn or H-ZnCND@Zn electrodes having a thickness of 100 µm. The electrolyte consisted of a specific volume of ZnSO₄ (2 mol L⁻¹, Alfa Aesar) aqueous solution. The Zn||Cu was assembled in the same manner replacing the one side of electrode with Cu disc (Φ10 mm). Chronoamperometry (CA) curves of symmetrical Zn||Zn cells using bare Zn or H-ZnCND@Zn were tested at a constant potential of -150 mV. Linear polarization measurements were conducted in a three-electrode configuration, employing bare Zn and H-ZnCND@Zn foils used as working electrode, Zn foil as the counter electrode and a leakless Ag/AgCl electrode (sat. KCl, 0.197 V vs. SHE) as the reference electrode. The corrosion potentials were calculated from the Tafel fit software (Biologic EC-Lab software package). The CV plots of H-ZnCND@Zn||Cu and Zn||Cu two-electrode cells were recorded using a scan rate of 0.5 mV/s over a potential window from -0.2 V to 1 V. For the measurements of full coin cells under flooded electrolyte condition, LMO cathodes with a diameter of 1 cm were paired with H-ZnCND@Zn and bare Zn anodes (thickness: 100 µm) employing 150 µL ZnSO₄ (1 mol L⁻¹) and Li₂SO₄ (2 mol L⁻¹, Alfa Aesar) flooded aqueous solution (pH 4) as the electrolyte. To assemble Zn||LiMn₂O₄ or H-ZnCND@Zn||LiMn₂O₄ pouch cells in a lean-Zn state, the assembly procedure was the same, with the only difference being the amount of electrolyte added according to the designed

specification ($10\ \mu\text{L mAh}^{-1}$, $20\ \mu\text{L mAh}^{-1}$). Galvanostatic cycling tests were carried out at room temperature using a 6-3000 mA, up to 5V potentiostat (MTI, BST 8-3). Moreover, EIS tests were performed using a BioLogic, VMP-3 electrochemical workstation within a frequency range of 0.01 Hz and 100 kHz at a voltage amplitude of 10 mV. Cyclic voltammetry curves at different scan rates over a voltage window of 1.4–2.05 V were also recorded with the VMP-3 electrochemical workstation. In situ Raman spectra of full cells were acquired using a Renishaw InVia Raman microscope with an excitation length of 633 nm. Spectra were acquired one by one, with setting time of 60 s and an exposure time of 10 s at intervals across potential range of 1.4–2.05 V. Total spectra were obtained during the first cycle of measurement.

General characterization:

FT-IR spectroscopy was conducted using a Jasco FT/IR-4100 equipped with a single reflection ATR unit. XRD patterns, on the other hand, were recorded using Bruker's D8 Discover Powder X-ray diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.5406\ \text{\AA}$). Raman spectra were captured using a Renishaw InVia Raman Microscope with a 633 nm laser, either in individual spectral or mapping mode. The Raman peak fitting was performed using single Lorentzian functions, with R^2 -values of 0.99. Fluorescence baseline subtraction and Lorentz peak centers deconvolved the powder Raman spectra. Peak positions were determined based on Raman spectra of several materials.

SEM analysis was conducted using a FEI Nova NanoSEM 230 operated at an accelerating voltage of 3 to 5 kV. Al or Cu foil substrates were used to support the samples. TEM was performed using a FEI T12 TEM operated at 120 kV. The samples were prepared by drop casting $5\ \mu\text{L}$ ethanol-diluted powder dispersions onto Lacey-carbon supported TEM grids.

XPS spectra were acquired using a Kratos Axis Ultra DLD spectrometer with a monochromatic Al K α X-ray source ($h\nu = 1486.6$ eV). XPS depth profiling was conducted using the instrument's Ar⁺ ion source operated at 4kV, 50uA, rastered over a 3x3 mm area for 4 minutes. The atomic composition was determined based on photoelectron peak areas and the relative sensitivity factors provided in CasaXPS Carbon tape (Ted Pella) was used to calibrate high-resolution spectra. CasaXPS software (version 2.3.16) was used for data processing.

For C 1s spectra, Gaussian–Lorentzian line-shapes were fitted to for all spectral components, except the sp² C component, which was fitted with an asymmetric line shape to account for the metallic nature of the samples. All samples used FWHM and position limitations for consistency. The electron paramagnetic resonance measurements were recorded using a Bruker EMXplus operating at a frequency of 9.8 GHz.

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6.8 SUPPORTING INFORMATION AND FIGURES

Parametric calculations and measurement

Zinc cation transference number ($TN_{Zn^{2+}}$)

Zn^{2+} transference number of the and bare Zn electrode were evaluated in symmetrical cells by recording the EIS before and after chronoamperometry measurements with applied voltage polarization as 5 mV for 1000 seconds. The transference number is calculated by the following equation:

$$T = \frac{I_s(\Delta V - I_0 R_0)}{I_0(\Delta V - I_s R_s)} \quad (1)$$

where ΔV is the voltage polarization applied, I_0 and R_0 are the initial current and resistance, I_s and R_s are the steady state current and resistance, respectively.

Coulombic efficiency in Cu//Zn cells (CE)

In specific, asymmetric cells as Cu//Zn cells based on different Zn samples, i.e., bare Zn, pure- and H-ZnCND@Zn, were first conditioned by plating (1 mA cm^{-2} , 1 mAh cm^{-2}) and stripping Zn by charging to 0.5 V during the first cycle. Then, a Zn reservoir was built on the Cu electrode with a capacity of 21 mAh cm^{-2} (Q_t) used for the following cycling. During the following 9 cycles, the current density at 1 mA cm^{-2} was applied for stripping and plating Zn with the capacity of 1 mAh cm^{-2} (Q_c) was plated or stripped in each cycle. In the last step, the final

capacity (Q_s) was observed when plated Zn was stripped by charging to 0.5 V. The Zn plating/stripping CE were calculated in the equation as:

$$CE = \frac{(9Q_c + Q_s)}{(9Q_c + Q_t)} \quad (2)$$

Corrosion voltage and current

Tafel plots were obtained for the symmetric bare Zn and H-ZnCND@Zn electrodes using a ramp rate of 5 mV/s within the potential range of -0.2 V to $+0.2$ V versus open circuit voltage (OCV). The coordinate points marking the intersect of extraction line at the maximum and minimum voltage were identified to determine the corrosion potential and corrosion current, respectively. It was observed that the bare Zn exhibited larger corrosion current densities, indicating its higher susceptibility to corrosion compared to the H-ZnCND@Zn.

HER overpotential

HER overpotential was calculated according to the following equation: overpotential (mV) = (measurement potential (vs Ag^+/AgCl) + 0.197 + $0.059 \times \text{pH} - 0$ (vs REH)) $\times 1000$. The polarization curve (LSV) was measured between -1.0 and -2.0 (vs Ag^+/AgCl) at a scanning rate of 1 mV/s in 2.0 M Na_2SO_4 aqueous solution. The overpotential was calculated at a current density of 10 mA cm^{-2} .

The galvanostatic intermittent titration technique

The galvanostatic intermittent titration technique (GITT) was applied at 0.033 A g⁻¹ for 30 min with 1 h of relaxation. The diffusion coefficient (D) was calculated as

$$D = \frac{4l^2}{\pi\tau} \left(\frac{\Delta E_s}{\Delta E_t} \right)^2 \quad (3)$$

Where l, τ , ΔE_s and ΔE_t represent electrode thickness, relaxing time, potential change by current pulse and potential change during the constant current, respectively.

Areal capacity

In a symmetric cell, the total areal capacity was calculated as following:

$$C_{T,areal} = \frac{2m_{Zn}}{A} \times 820 \text{ mAh/g} \quad (4)$$

Where m_{Zn} is the mass of Zn foil, or the Zn mass in Zn anode, and A is the area of Zn foil.

Finite element analysis

All the model was created utilizing the "Tertiary Current Distribution" and "Phase Field" modules of the COMSOL Multiphysics 5.6 program to simulate the dynamic Zn deposition on electrodes in mild alkaline electrolytes. The complete two-dimensional model's size was set to 2.0 x 2.0 μm for the investigation of the dispersion of the electric field. In a space filled with electrolyte, the process was transiently simulated. The plating/stripping process was simulated using the phase field approach with a current density of 1 mA cm⁻².

The Zn^{2+} transfers by the concentration diffusion in the model follow Fick's law, as shown in equations:

$$N_i = J_i = -D_i \nabla c_i$$

$$\frac{\partial c_i}{\partial t} + \nabla \cdot J_i = R_{i,tot}$$

Where J_i is the ion flux, D_i is the diffusion coefficient of electrolytes ($D_{\text{Zn}} = 1.0 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$

For $\text{ZnSO}_4\text{-H}_2\text{O}$ electrolytes), c_i is the ion concentration of electrolytes ($c_i = 2000 \text{ mol m}^{-3}$), ∇c_i is the concentration gradient.

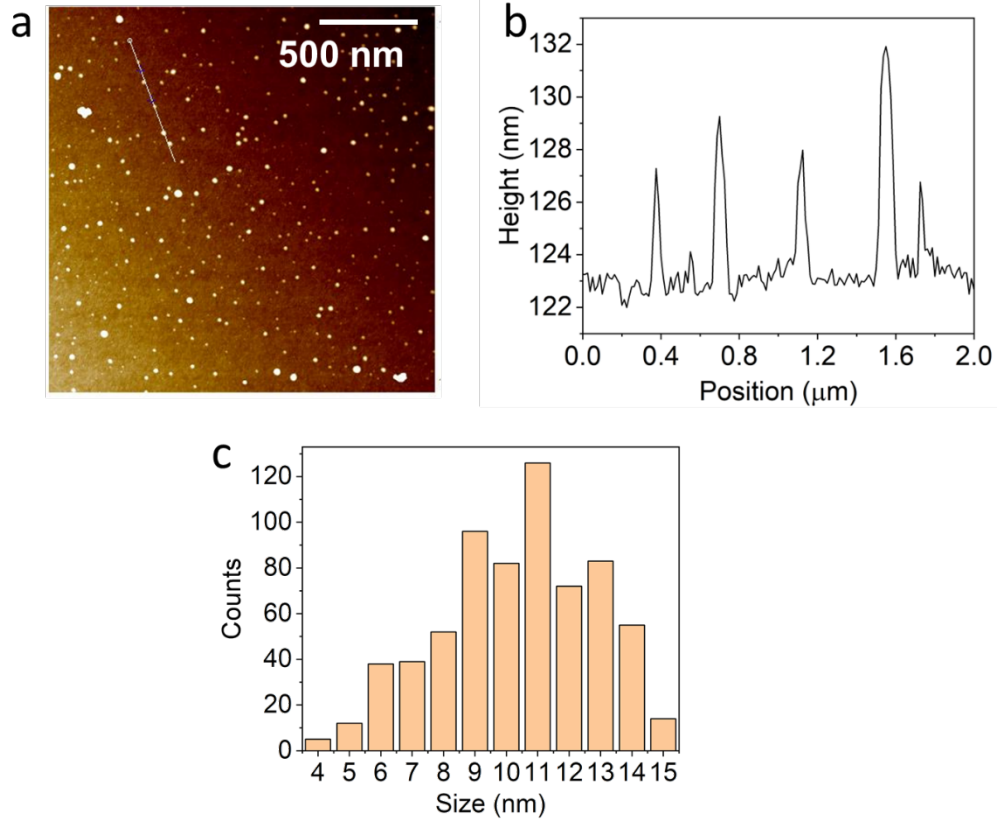


Figure S6.1 a) A typical AFM image of ZnCND, b) the height profiles at the line indicated in Figure S6.1(a), c) the size distribution analysis in the AFM image.

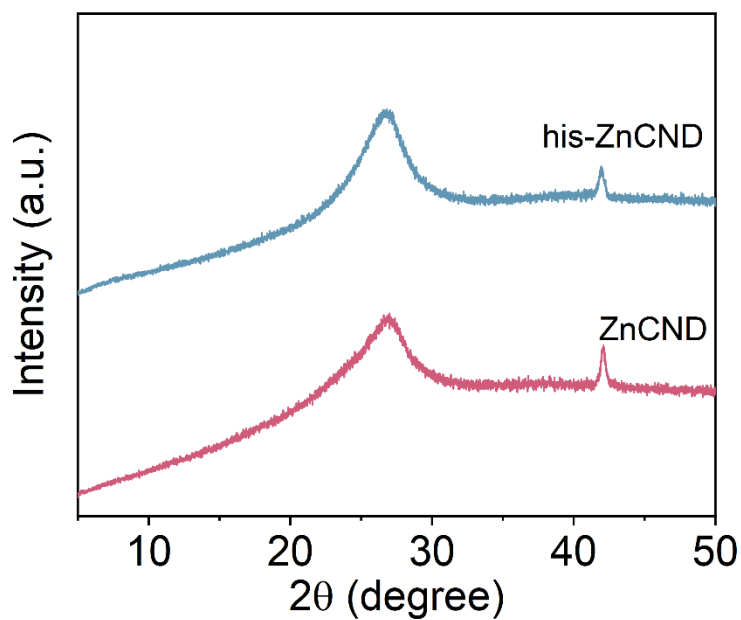


Figure S6.2 XRD pattern of ZnCND and his-ZnCND.

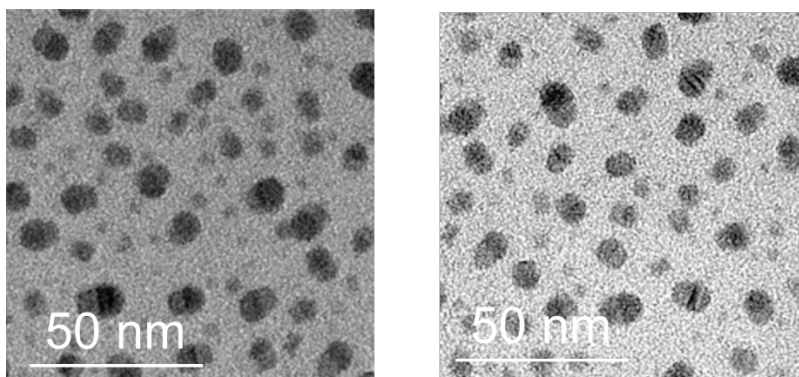


Figure S6.3 TEM images of his-ZnCND (left) and ZnCND (right).

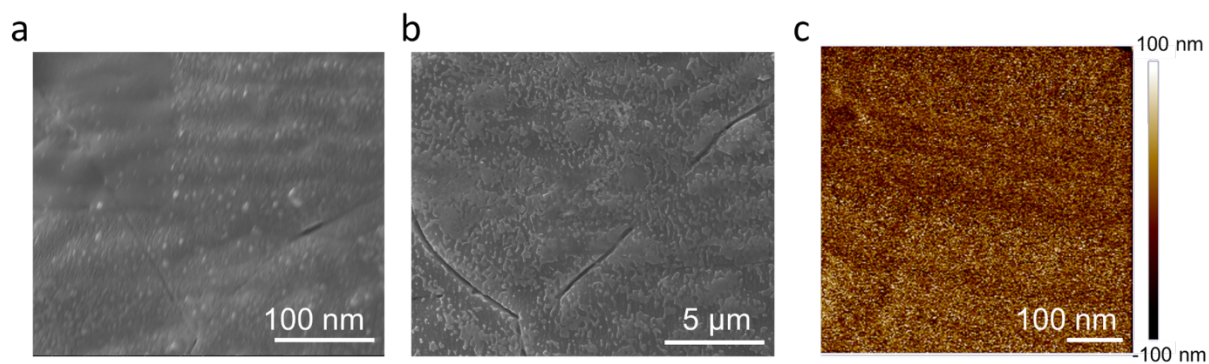


Figure S6.4 Typical top-down SEM images of CND-coated zinc anode a) at high magnitude, b) at low magnitude. A Typical AFM image of CND-coated zinc anode.

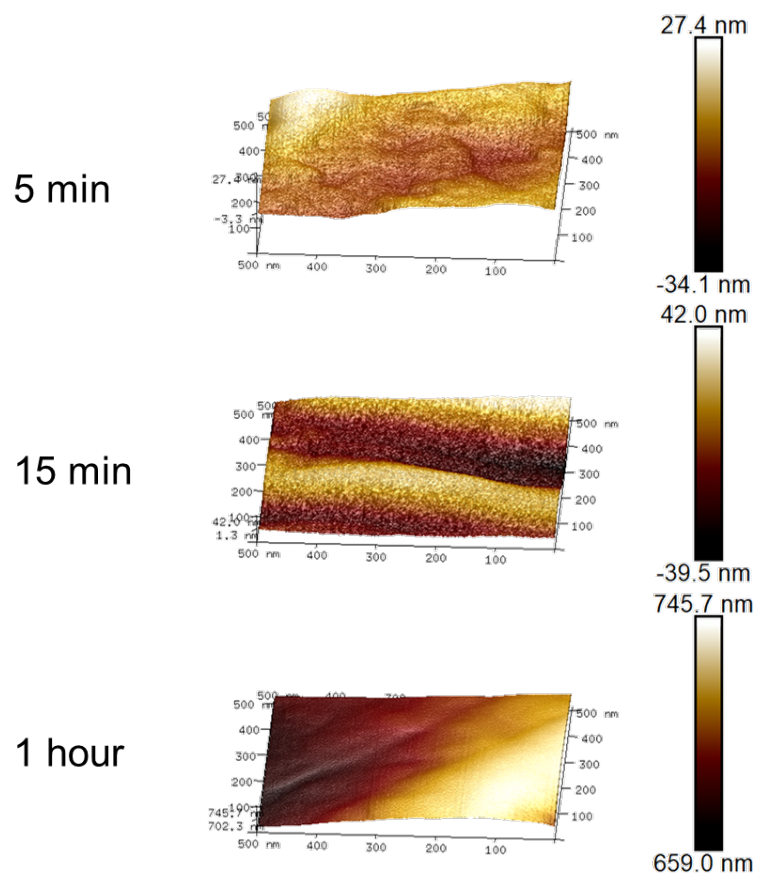


Figure S6.5 AFM images of his-ZnCND taken after reaction times of 5 min, 15 min, and 1 hour.

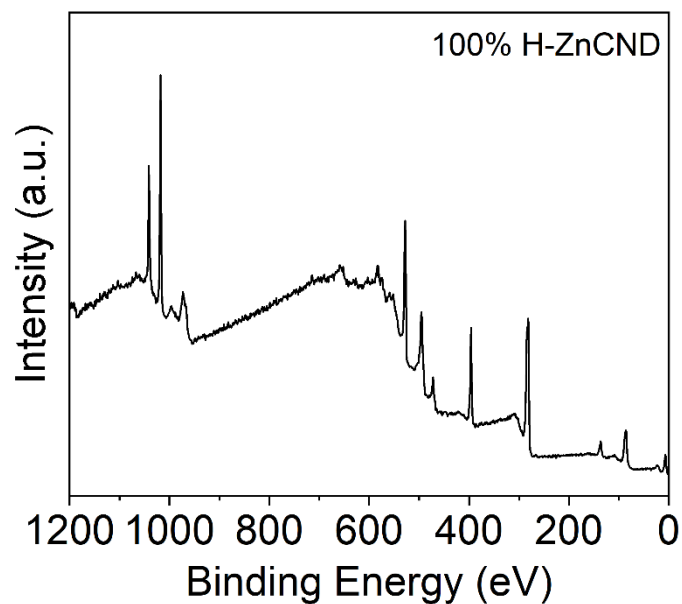


Figure S6.6 XPS survey spectrum of 100%H-ZnCND.

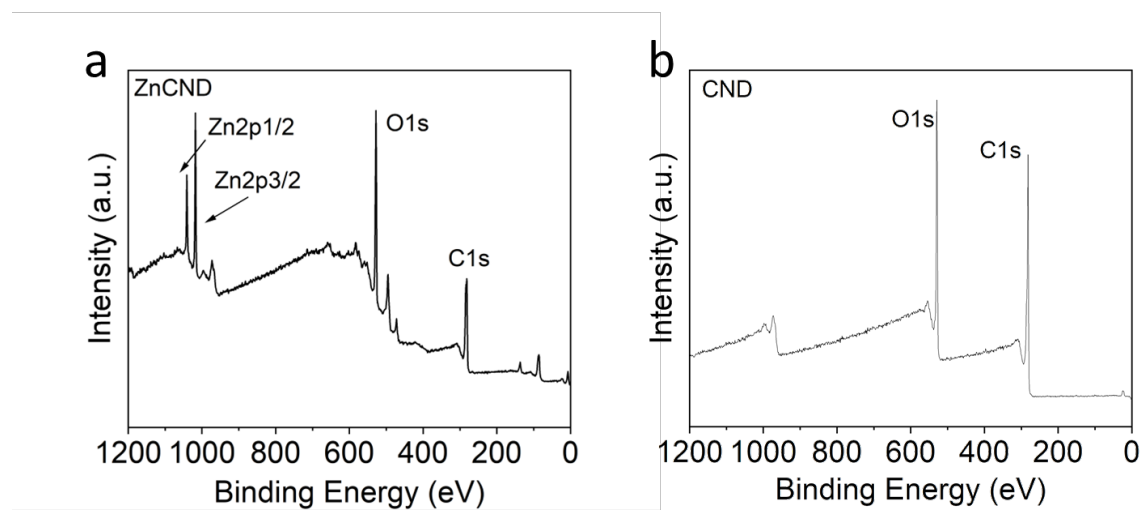


Figure S6.7 XPS survey spectra of a) ZnCND and b) pristine CND.

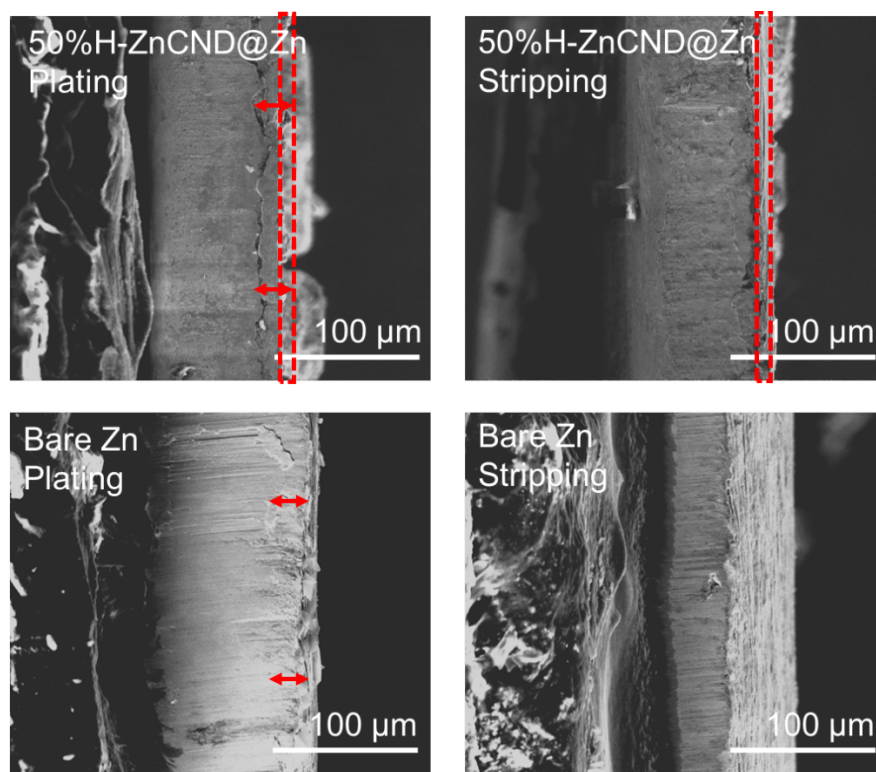


Figure S6.8 Cross-sectional SEM images of 50%H-ZnCND@Zn and pure Zn anode after plating and stripping at a capacity of 10 mAh cm^{-2} .

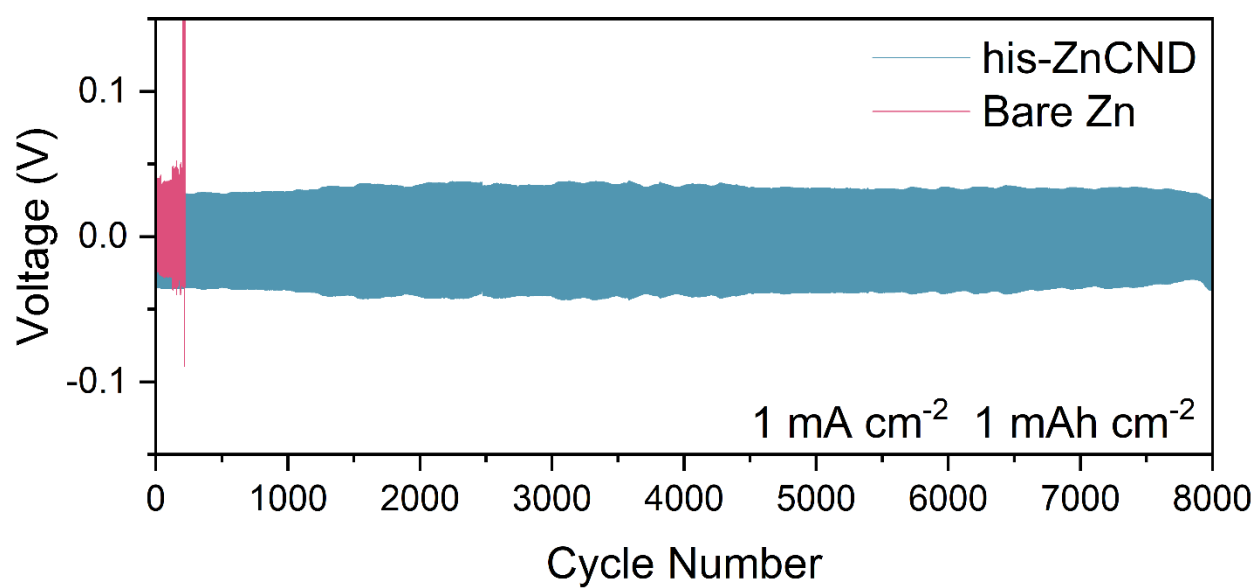


Figure S6.9 Symmetric cell cycle performance of pure Zn and 50%H-ZnCND@Zn electrodes at the conditions of 1 mA cm^{-2} , 1 mAh cm^{-2} .

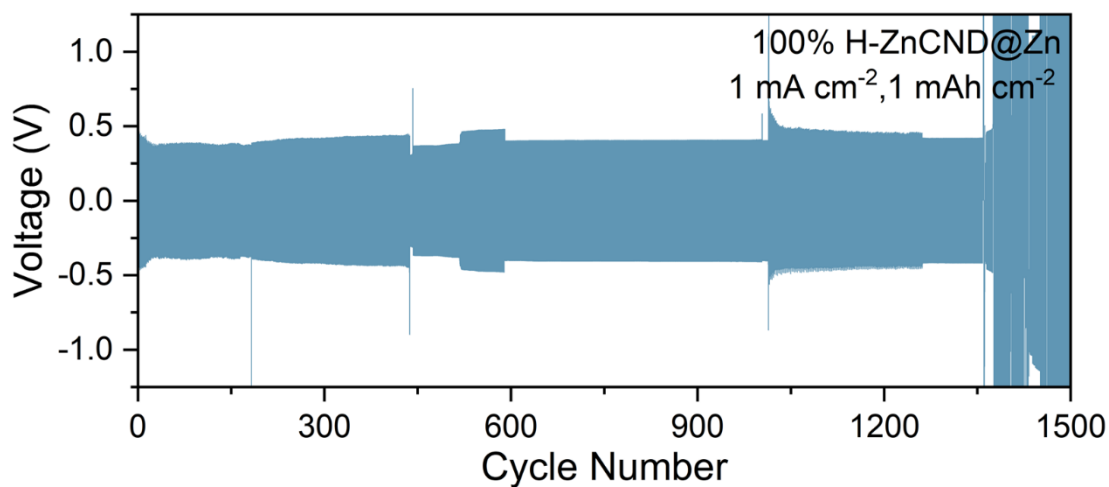


Figure S6.10 Symmetric cell cycle performance of pure Zn and 100%H-ZnCND@Zn electrodes at the conditions of 1 mA cm^{-2} , 1 mAh cm^{-2} .

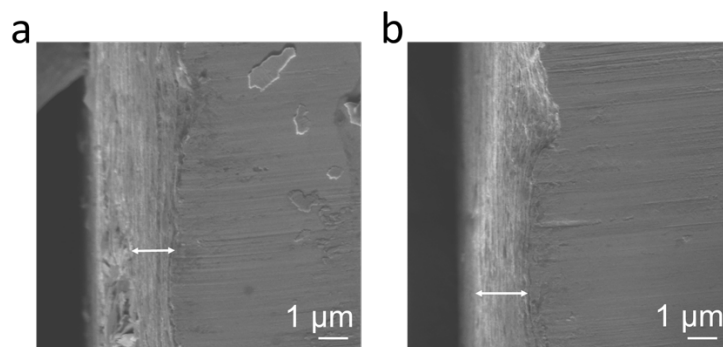


Figure S6.11 The typical cross-sectional SEM image of 50%H-ZnCND-1220@Zn and 50%H-ZnCND-1750@Zn.

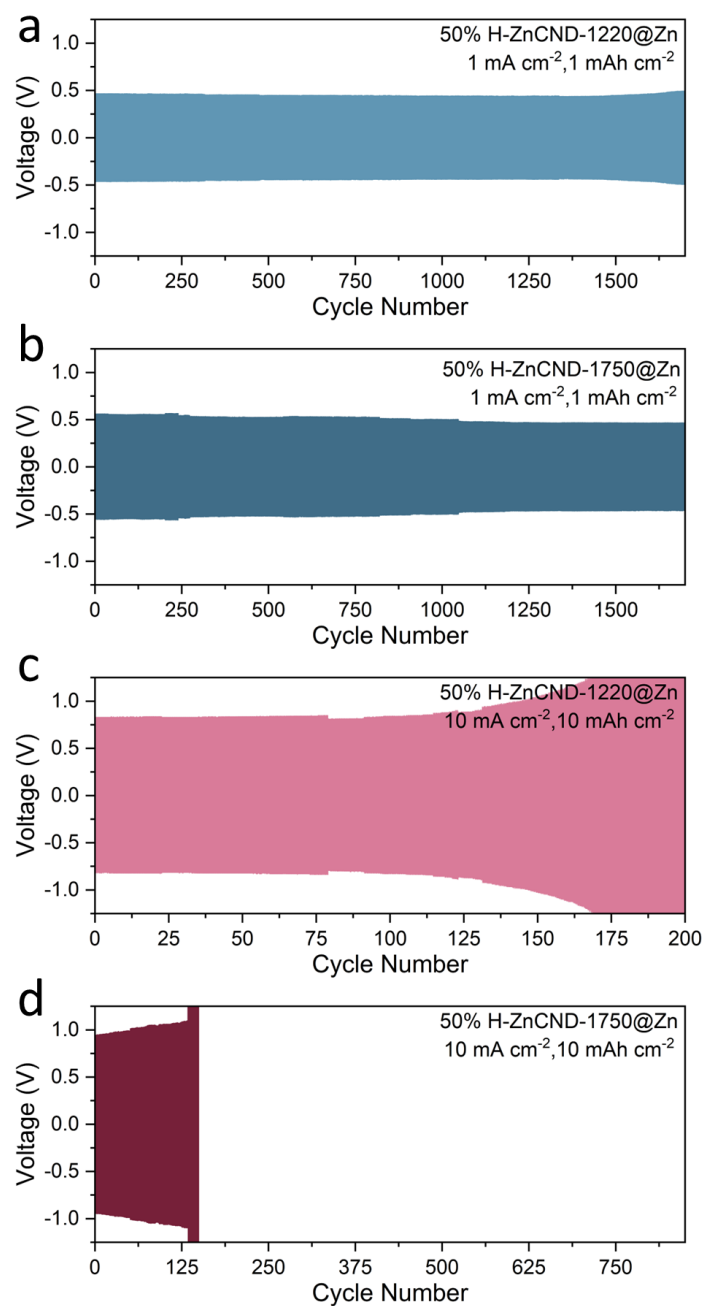


Figure S6.12 Symmetric cell cycle performance of a) 50%H-ZnCND-1220@Zn at 1 mA cm^{-2} , 1 mAh cm^{-2} , b) 50%H-ZnCND-1750@Zn at 1 mA cm^{-2} , 1 mAh cm^{-2} , c) 50%H-ZnCND-1220@Zn at 10 mA cm^{-2} , 10 mAh cm^{-2} , and d) 50%H-ZnCND-1750@Zn at 10 mA cm^{-2} , 10 mAh cm^{-2} .

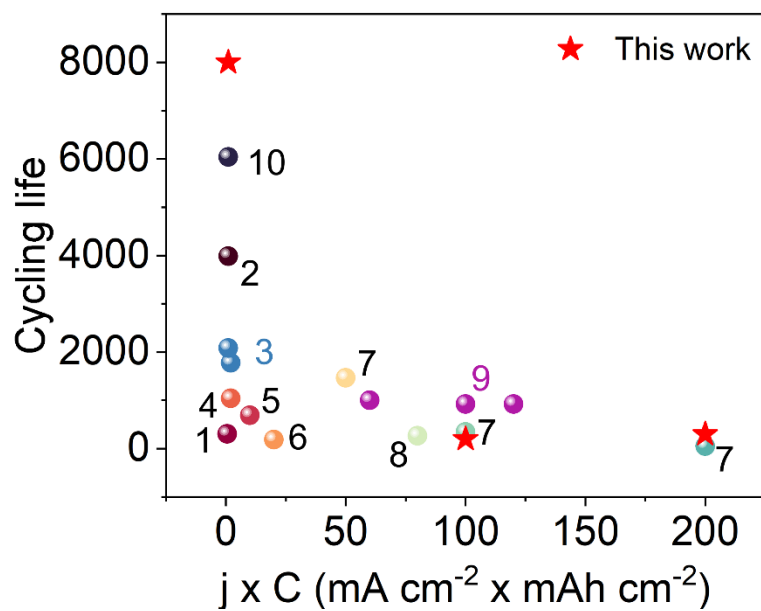


Figure S6.13 The plot compares the cycle life and the product of current density and areal capacity ($j \times c$) applied to Zn in recent reports, alongside the cycling performance of symmetric cells using 50% H-ZnCND@Zn anode. The numbers displayed on the plot correspond to the reference numbers.¹⁻¹⁰

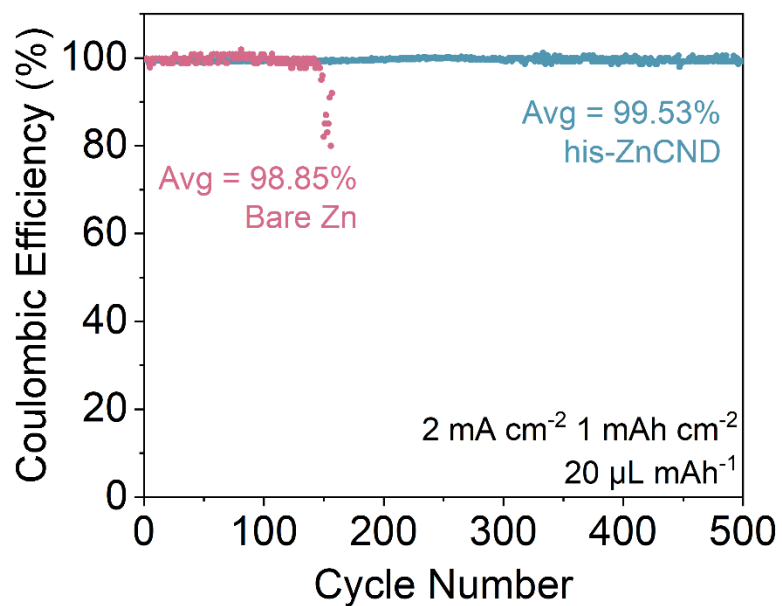


Figure S6.14 Coulombic efficiency of Cu//Zn asymmetric cells using pure Zn and 50%H-ZnCND@Zn electrodes at the conditions of 2 mA cm⁻², 1 mAh cm⁻² using 10 μ L mAh⁻¹ electrolyte.

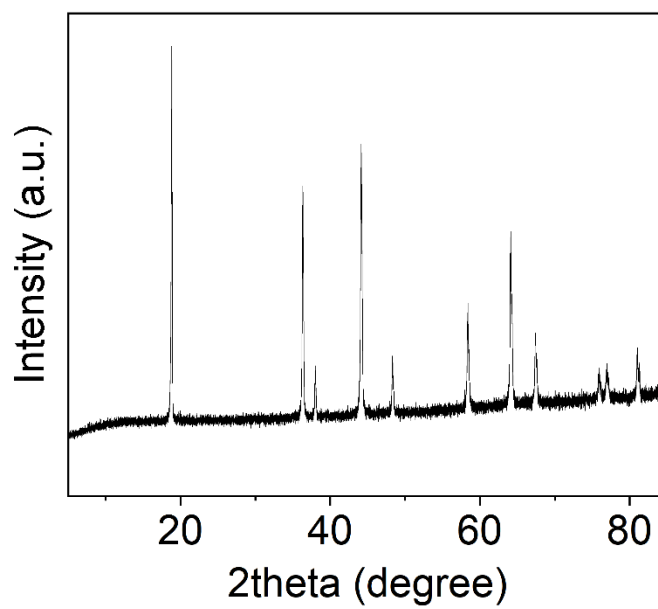


Figure S6.15 XRD pattern of LiMn_2O_4 electrode materials.

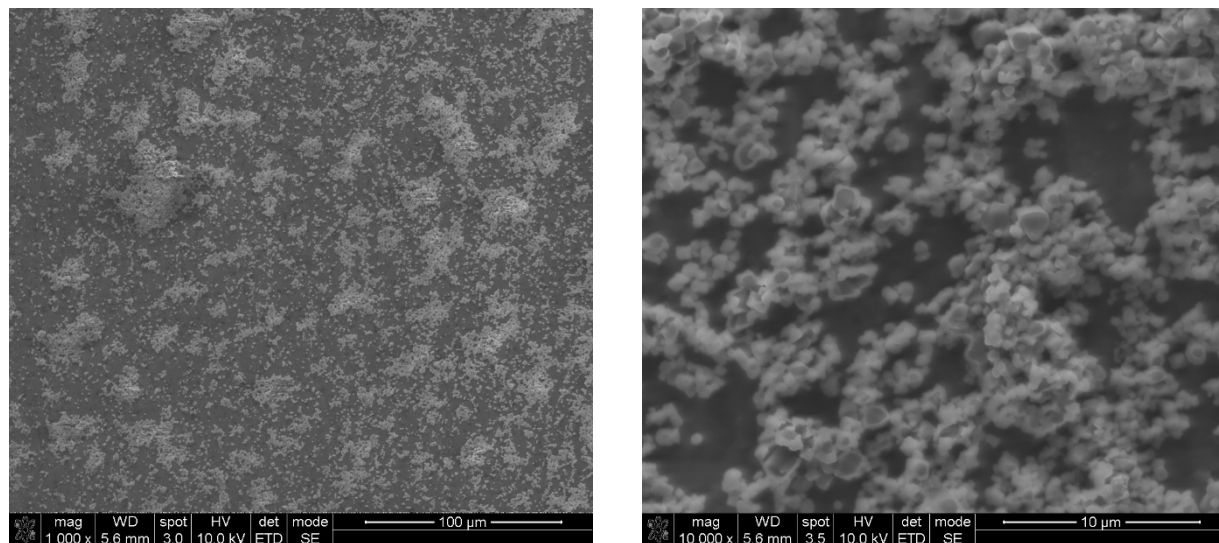


Figure S6.16 SEM images of LiMn_2O_4 electrode materials.

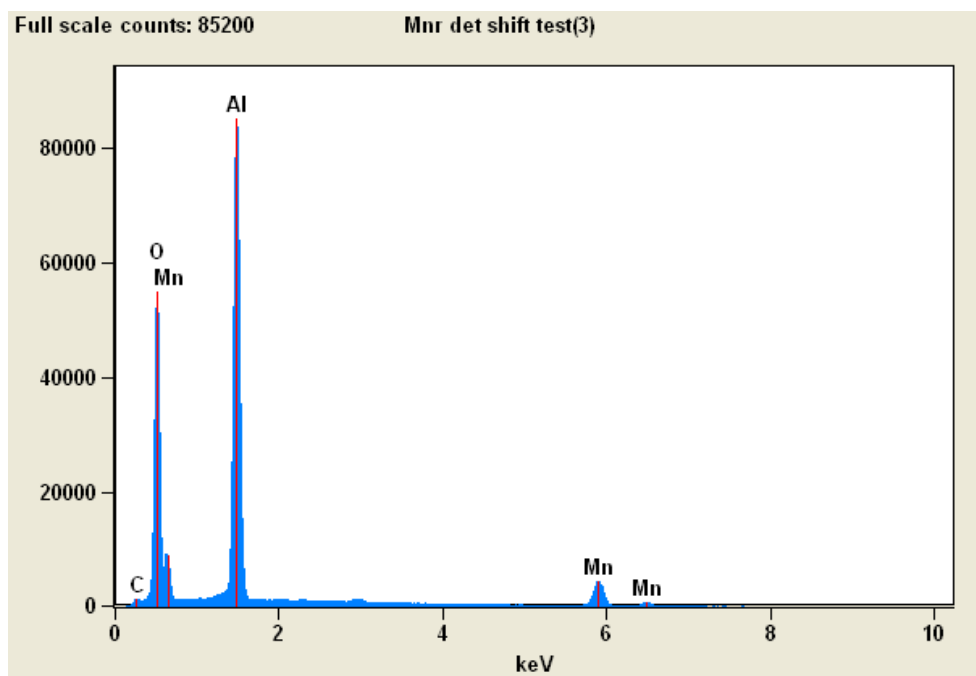


Figure S6.17 EDS spectrum of LiMn_2O_4 electrode materials.

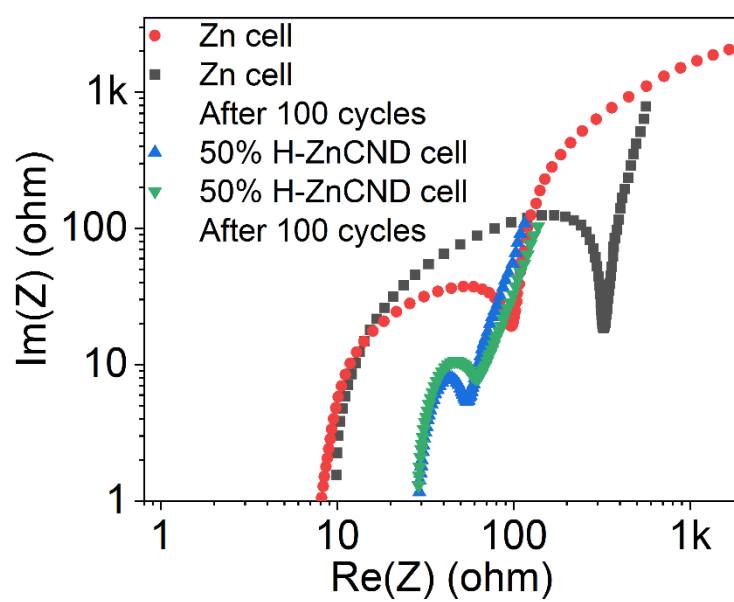


Figure S6.18 Nyquist plots of bare Zn||LiMn₂O₄ and 50%H-ZnCND@Zn||LiMn₂O₄ full cells before cycling and after 100 cycles at 1C rate.

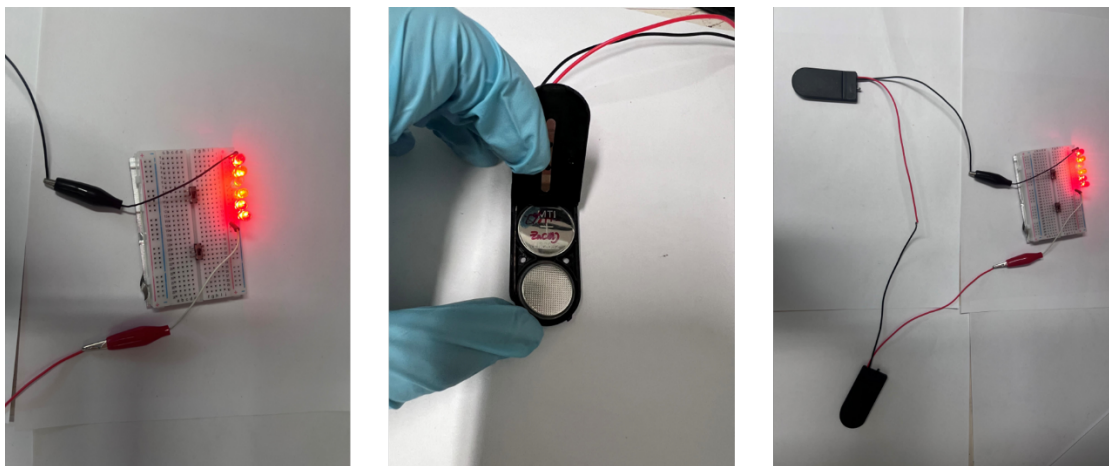


Figure S6.19 A pack of four-unit cells connected in series was used to power six 3 V red light emitting diodes (LEDs) connected in parallel.

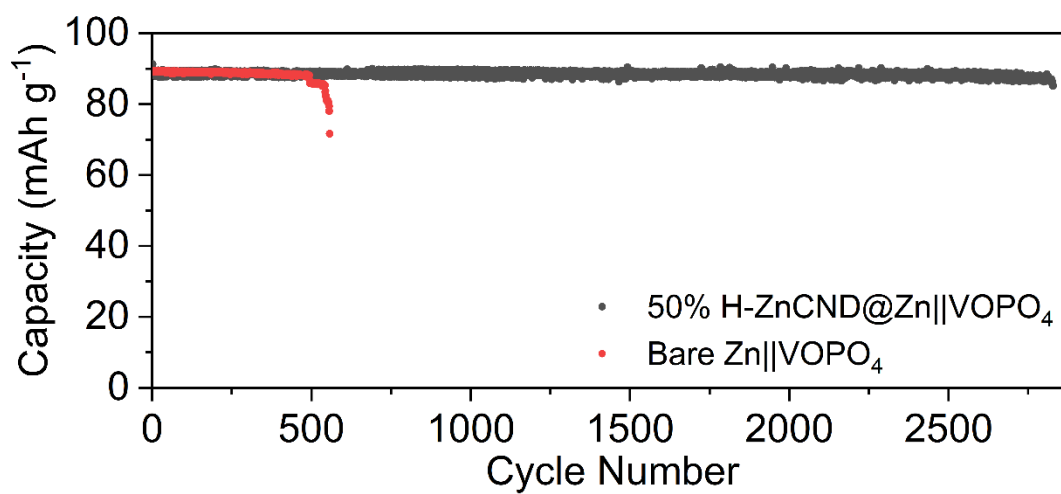


Figure S6.20 Cycling performance of 50% $\text{H-ZnCND@Zn||VOPO}_4$ and bare Zn||VOPO_4 at 1 A g^{-1}

1.

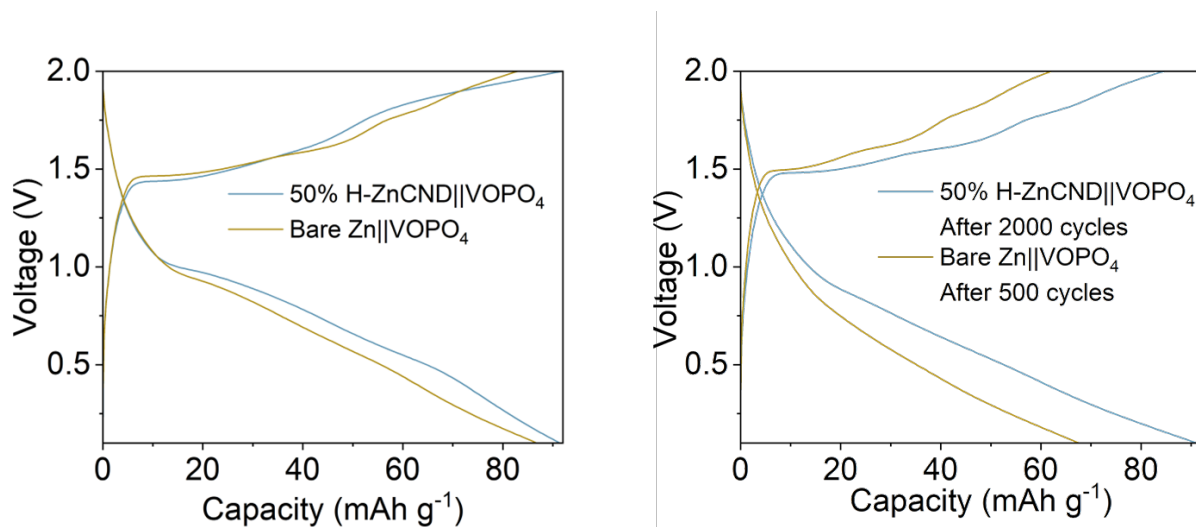


Figure S6.21 GCD profiles of 50% $\text{H-ZnCND@Zn||VOPO}_4$ and bare Zn||VOPO_4 at 1 A g^{-1} before cycling (left) and after cycling (right).

Atomic Percentage	CND	ZnCND	50% H-ZnCND	100% H-ZnCND
Carbon	75.69%	65.86%	58.29%	57.77%
Nitrogen	N/A	N/A	8.69%	14.25%
Oxygen	24.31%	25.27%	21.48%	15.06%
Zinc	N/A	8.47%	11.54%	12.92%

Table S1 Atomic percentage of individual elements in CND, ZnCND, 50%H-ZnCND and 100H-ZnCND based on peak intergration in XPS survey spectra.

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CHAPTER 7. LARGE-CAPACITY ZN METAL ANODES USING AN ELASTIC FLUORINATED INTERPHASE FOR HIGH REVERSIBILITY

"Adapted from a manuscript written by Wang C, Sung K, Zhu JZ, Qu S, Bao J, Chang X, Katsuyama Y, Yang Z, Zhang, El-kady MF, Kaner RB.

7.1 INTRODUCTION

Global energy independence can only be achieved with reliable, inexpensive energy storage, such as rechargeable batteries. In response to up-scaling stationary storage using green energy, large-volumetric-capacities batteries are desirable, which were enabled by multivalent cation batteries.¹ Meanwhile, batteries must show fast charging rates (high power density), which aqueous batteries can readily achieve.² Zinc batteries meet the two demands above, possessing a theoretical volumetric capacity of 5,851 Ah L⁻¹ (compared to 2060 Ah L⁻¹ for lithium metal) and a specific power of up to 800 W kg⁻¹ (compared to an average of 400 W kg⁻¹ in 783 commercial lithium-ion batteries).³ Thus, they are promised to be the ideal candidates for renewable electricity storage and beyond, considering further advantages of zinc batteries, such as plentiful metal supplies, non-toxic electrolytes, and minimal battery maintenance. However, zinc metal anodes exhibit unfavorable irreversibility due to their low reduction potential (0.76 V versus the standard hydrogen electrode).⁵ The emergence of hydrogen evolution causes a local pH rise leading to the side products such as ZnO, and Zn₄(OH)₆SO₄·xH₂O (ZHS). The repetitive consumption of zinc metal and electrolyte has a major impact on cycle life and Coulombic efficiency (CE). Another unsolved issue negatively affecting the lifespan is the mossy and non-planar dendrites formation during the zinc plating, which are attributed to uneven mass transport or electrical field distribution.¹⁰ Recurrent dendrite formation produces detached "dead zinc" that is non-

rechargeable and may short-circuit the cells. A well-formed SEI solves both issues and stabilizes the electrode and electrolyte interface over cycles. Such SEIs are compact and stiff to prevent detachment or protrusion, as well as mechanically elastic to conformally cover Zn anodes and accommodate volume variations that occur during cycling.¹¹ Also they should show high zinc ion affinity for fast de-solvation of ions in the electrolyte medium in order to achieve low overpotentials and minimize the side reactions. The SEI qualities are especially critical in commercial-grade zinc anodes, where a modest negative to positive (N/P) areal capacity ratio is used to maximize the pack-level energy density, implying that high depths of discharge (DOD) of zinc anodes are preferable.¹² As at a high DOD the zinc anodes experience greater lateral and vertical stress, a mechanically robust and elastic SEI that maintains structural integrity is significant to create high-CE and long-cycling zinc batteries with high capacities.

All these properties of SEI are dictated by the chemical composition and spatial arrangement of the SEIs in both lateral and vertical directions. Therefore, protect zinc anode from dendrite growth and irreversible side reactions, promoting high coulombic efficiency and long lifespans during repetitive plating and stripping. For example, a ZnF₂-rich SEI based on the hydrophobic anion trifluoromethanesulfonate (OTF) increased the cycle life of a Zn anode from 200 to 6000 cycles with a Coulombic efficiency close to 100%. The improvement can be applied to all zinc batteries, including Zn-MnO₂, Zn-O₂, and zinc redox flow batteries.⁹

Ideally, SEIs should be compact and smooth, exhibiting both mechanical robustness and elasticity and high ionic conductivity almost only to zinc ion. Besides these characteristics should maintain during cycling to prevent detachment or protrusion, as well as elastic enough to conformally cover Zn anodes and accommodate volume variations that occur during cycling.¹¹ This mechanical consideration is critical in commercial-grade zinc anodes. To realize zinc batteries with energy

densities close to their theoretical value, a modest negative to positive (N/P) areal capacity ratio is required at the cell level, implying that thin Zn chips are preferable to large metal reservoirs.¹² Anodes with a high depth of discharge (DOD) experience significant lateral and vertical stress. A mechanically robust and elastic SEI that maintains structural integrity is needed to create high-CE and long-cycling zinc batteries with a low N/P ratio.

As the properties such as mechanical robustness and elasticity of SEIs are dependent on the chemical composition and spatial arrangement in both lateral and vertical directions, in this work, we aim to develop an engineerable approach to ZF-based SEI.

As a result, the design of the Zn SEI should be mechanically robust enough to prevent detachment or protrusion, as well as elastic enough to conformally cover Zn anodes and accommodate volume variations that occur during cycling.¹¹ This mechanical consideration is critical in commercial-grade zinc anodes. To realize zinc batteries with energy densities close to their theoretical value, a modest negative to positive (N/P) areal capacity ratio is required at the cell level, implying that thin Zn chips are preferable to large metal reservoirs.¹² Anodes with a high depth of discharge (DOD) experience significant lateral and vertical stress. A mechanically robust and elastic SEI that maintains structural integrity is needed to create high-CE and long-cycling zinc batteries with a low N/P ratio.

Here a scalable solvothermal deposition method was used to carbonylate the fluorinated SEI. The formed (CO)-ZF layer demonstrates higher elasticity and zinc affinity than the pristine fluorinated SEI. The interface is passivated while retaining intact structures for a long working life. Atomic force microscopy (AFM) based nanoindentation was used to monitor the elastic modulus evolution over the electrodeposition cycles. Along with other morphological and chemical analyses, a clear

correlation is found between the enhanced elasticity and a well-regulated deposition process. Theoretical studies confirm the higher adsorption affinity to Zn^{2+} and a low diffusion energy barrier for Zn adatoms on the (CO)-ZF layer that suppresses side reactions and avoids dendritic depositions. Benefiting from these properties, the (CO)-ZF@Zn exhibits a cycle life of over 6900 at 1 mA cm^{-2} in symmetric cells and an unprecedentedly high cumulative capacity of 6000 mAh cm^{-2} at a DOD of 71.4%. The elastic (CO)-ZF enabled full cell (CO)-ZF@Zn||LMO shows a high capacity retention of 99.3% for 800 cycles at 1 C. At a low N/P ratio of 2.01, the (CO)-ZF@Zn||LMO full cell provides 94 mAh g^{-1} after 120 cycles and a competitive cumulative capacity density of 19.7 mAh cm^{-2} , which exceeds the reported values of commercial lithium-ion batteries. This work highlights a new mechanical perspective to realize reversible Zn-based batteries, suggesting an innovative direction for stabilizing metal anodes through structural design.

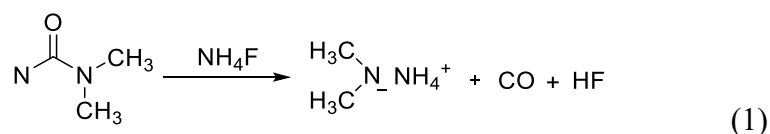
7.2 SYNTHESIS, CHARACTERIZATIONS, AND MECHANICAL PROPERTIES OF ELASTICATED (CO)-ZF INTERFACES

The elastic (CO)-ZF layer was deposited on Zn foil using a facile and scalable solvothermal method. The as-obtained (CO)-ZF was imaged in a field-emission scanning electron microscope (FE-SEM) and optical camera, showing a well-defined coating with smooth surfaces (**Figure 7.1a** and S7.1), compared with thermally deposited ZF layers where cracks are readily detected on the surface (**Figure 7.1b** and S7.1). The AFM image of carbonyl ZF shows a smoother surface after introducing CO ligands (**Figure 7.1c** and S2). The cross-sectional SEM image shows an average thickness of the (CO)-ZF of roughly $9 \text{ }\mu\text{m}$ (**Figure 7.1d**, the dash lines indicate the borders of the (CO)-ZF layer). The thickness of thermally deposited ZF layers was also measured using SEM. By tuning the reaction time, the ZF was prepared at a similar thickness ($\sim 10 \text{ }\mu\text{m}$) for further comparisons (**Figure S7.3**). Energy-dispersive X-ray spectroscopy (EDS) mapping shows the

homogeneous distribution of elemental Zn, F, C, and O in (CO)-ZF (**Figure 7.e-h**). In the X-ray diffraction (XRD) pattern (**Figure 7.1i**), the (110) and (100) planes of ZnF_2 (PDF #00-001-0661) are detected at 24.9° and 32.3° , respectively.¹³ These peaks show larger FWHMs in the carbonylated ZF, indicating an amorphous and disordered microstructure for (CO)-ZF (**Figure S7.4**). The derivative thermal gravitational analysis of carbonyl ZF displays a peak at 173.5°C , which can be assigned to carbonyl decomposition and metal oxides' formation (**Figure 7.1k**). Analysis of Fourier transform infrared (FTIR) spectroscopy reveals typical vibrational peaks at 1627, 1363, and 1319 cm^{-1} , which can be attributed to asymmetric and symmetric stretching of carbonyl groups from (CO)-ZF (**Figure 7.1j**).¹⁴ The carbonyl coordinated unsaturated Zn was also seen in ESR spectra as the (CO) content grows (**Figure 7.1l**). The g tensor parameter is 1.998. The high symmetry of intensity and shape in the ESR signal indicates that it can be assigned to the unpaired electron from the s orbital of Zn^{d^+} ($0 < d < 2$).^{15,16} The compositional ratios of (CO) and F were tuned by adding various amounts of NH_4F in the dimethylformamide (DMF) as indicated in EDS spectra (**Figure S7.5**). The carbonyl fluorinated interphase coated zinc foil using a lower NH_4F concentration was denoted as 2(CO)-ZF. The signals corresponding to (CO) are relatively stronger in EDS, TGA, and ESR patterns (**Figure S7.5 and S7.6**), indicating a higher carbonyl content was achieved. It was also found that in 2(CO)-ZF, where a higher carbonyl content is presented, the surface is smoother than (CO)-ZF (**Figure S7.2**). The ZnF_2 peaks in the XRD pattern of 2(CO)-ZF also show a more amorphous feature (**Figure S7.4**).

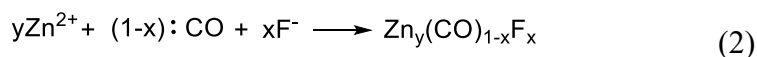
The X-ray photoelectron spectroscopy (XPS) depth profiles and deconvolution of each core spectrum indicate the evolution of chemical compositions and bonding at various thicknesses in (CO)-ZF (**Figure 7.2b**). The O 1s peak at 530.77 eV and C 1s peaks at 287.2 eV can be attributed to the carbonyl groups, showing Zn-(CO) as one of the predominant substances on the surface.¹⁷ Closer to the Zn foil, a small amount of ZnO arises and suggests a homogeneous coating. The peak intensities for F 1s fade, while intensities for Zn 2p grow throughout the etching depth suggesting a smooth compositional transition that ensures good adhesion as it minimizes residual stress resulting from the distinct phase boundary between zinc and zinc fluoride. The atomic percentages of each element present are shown by etching time in **Figure 7.2a**, where both C and O ratios are constant for 30-90 s before dropping off. Accordingly, based on the aliovalent-doped rhombohedral model,¹⁸ the chemical formula was determined to be $\text{Zn}_{0.48}(\text{CO})_{0.67}\text{F}_{0.33}$.

Consequently, the process below can explain the formation of (CO)-ZF. Carbonyl radicals form due to the thermal decomposition of DMF using NH_4F as a base, as shown in Equation 1:¹⁹



Via thermal activation, Zn is first converted to Zn^{2+} on the surface and then diffuses into the strong polar solvent under the influence of accelerated mass transport. Because of the lower standard reduction potential of O radical in an organic solvent generated from the decomposition of DMF,²⁰

ZnO is preferably produced at the solvent/metal interface. As the EDS mapping and XPS depth profile indicate, this stage may be accompanied by a sharp decrease in fluorine content and increased C=O bonding to ~38 nm. Under the etching of formed trace amounts of HF from the DMF solvent, $Zn_y(CO)_x F_{1-x}$ coordination complexes eventually formed when fluorine and carbonyl were gradually substituted into the oxide anions, as indicated by Equation 2.



After introducing the carbonyl groups, the inert fluorinated SEI demonstrated a high elasticity. The force versus displacement curves of the three artificial SEIs were obtained by AFM-based nanoindentation tests, which allowed for deliberate analysis of the elasticity in fluorinated SEI layers at different carbonylation levels.²¹ The different slopes of the loading and unloading curves and the largest yielding under an applied force within the indentation length (indentation < 0) indicates that pure Zn exhibits high plasticity (**Figure 7.2c**).²² In contrast, the same slope between the approaching and withdrawing curves was observed in the cases of carbonyl-rich (CO)-ZF and ZF demonstrating their higher moduli (**Figure 7.2d, e**). A more observable hysteresis yielding under the imposed load was also demonstrated by (CO)-ZF, demonstrating its higher elasticity.²³ Whereas a minimum hysteresis in ZF demonstrates a brittleness and rigidity of the SEI. High-performance batteries benefit more from carbonyl fluorinated SEI's excellent flexibility and homogeneity. Additionally, the mild acidic $ZnSO_4$ electrolyte does not irreversibly react with the modified Zn anodes at high capacities compared to the pure Zn anodes.

7.3 SUPPRESSED DENDRITE FORMATION AND CORROSION ON ELASTICIZED (CO)-ZF INTERFACES

The effectiveness of elastic (CO)-ZF in avoiding dendrite formation was examined by morphological and electrochemical analysis over the deposition capacity up to 20 mAh cm⁻² to simulate the plating

behaviors at high DOD charge/discharging processes. *Ex situ* SEM showed a structural evolution during the Zn electrodeposition from 1 mAh cm⁻² to 20 mAh cm⁻². The growing deposition layer on pure Zn foil has dense upright Zn flakes, random Zn clusters, and adhering glass fibers (which speed up dendrite formation and can even cause a short circuit) (**Figure 7.3a**). However, the deposition layer on (CO)-ZF@Zn exhibits nearly the same morphology as the original state, displaying the properties of a smooth surface with Zn deposition at small flake sizes on the surface (**Figure 7.3b**). Throughout the Zn plating/stripping process at a high DOD, the average roughness variation of the Zn metal surface is substantially higher than that of the (CO)-ZF layer. After cycling, the SEM image shows that the surface of (CO)-ZF@Zn is flatter than that of bare Zn. After 50 and 200 deep plating/stripping cycles at 10 mAh cm⁻², the porous, non-planar deposition was captured on the surface of pure Zn foils. These large dendrites will likely form so-called ‘dead’ and/or ‘orphaned’ zinc. The accumulated metal deposits bridge the interelectrode space to short-circuit the cell. However, relative smoothness was maintained at the surface of (CO)-ZF@Zn, corresponding to better cycling stability.

The regulated Zn nucleation behavior and growth process were also shown in chronoamperometry (CA) and deposition at various current densities (**Figure 7.3d**). The steadily rising current of bare Zn implies a 2D diffusion process in which lateral diffusion produces dendrites from absorbed Zn²⁺ aggregates.²⁴ (CO)-ZF, in contrast, shows the independence of the current from time following a transiently initial Zn nucleation. This behavior relates to a constant 3D diffusion process, demonstrating that significant (CO)-ZF adsorption prevents dendrite development by

impeding lateral Zn^{2+} diffusion.⁸ ZF demonstrated a particular promotion of 2D diffusion but was less significant than (CO)-ZF due to the inelastic ZF being less accommodating to large volume changes. The smaller nucleation potential at all current densities of (CO)-ZF compared with pure Zn and ZF also signified a more planar deposition surface and faster kinetics (**Figure 7.3c**). The exchange current (I_0) was calculated, and (CO)-ZF is the smallest of all three, indicating that an elastic protection layer prevents the growth of nuclei into dendrites.²⁵

Density functional theory (DFT) was used to optimize the crystal structures of these materials (**Figure 7.3e**). The climbing-image nudged elastic band approach was applied to determine Zn^{2+} diffusion between the most stable adsorption sites. **Figure 7.3e** shows the appropriate site transition during Zn^{2+} diffusion on the surface of pure Zn, ZnF_2 , and (CO)-ZF. Diffusion energy barriers for Zn^{2+} on (CO)-ZF is thus substantially lower at 0.099 eV than for other anode surfaces (pure Zn, 0.141 eV and ZnF_2 , 0.148 eV). The quick transit of Zn^{2+} and the homogeneous distribution of Zn^{2+} would benefit from the low energy barrier, especially at high current density. In this instance, the homogeneous Zn growth laterally will be advantageous instead of dendritic formation.

The electrostatic shielding effect of the elastic (CO)-ZF layer was investigated using finite element analysis (FEA). **Figure 7.3g-j**) depicts the current density and ion distribution of Zn^{2+} deposition in pure Zn cells and cells adopting a (CO)-ZF protection layer, respectively. The current density at the tip of the Zn dendrite of a pure Zn anode was higher than elsewhere, indicating a remarkably uneven localized electric field with intensity increasing at surface protuberance sites, which is significantly more uniform in the (CO)-ZF@Zn anodes. The (CO)-ZF forms a highly ionic conductive layer, resulting in an even distribution of Zn^{2+} on the interface. As a result, a uniform current density distribution was also induced because of the low electronic conductivity of the

protection layer. The ion diffusion condition was further shown by the simulated electric fields reflecting the spread of the Zn^{2+} concentration field as deposition progressed. A considerable number of Zn^{2+} ions rapidly congregated at the tips of the protrusions on the pure Zn anodes during the transitional stage of plating. However, the neighboring domains and bottom of the protrusions displayed low Zn^{2+} concentrations. As a result, Zn^{2+} convergence occurs near the top of the Zn dendrites, exacerbating their growth. Profiling the Zn^{2+} concentration along the electrode direction of the (CO)-ZF@Zn anodes, on the other hand, shows an even distribution resulting in a more homogeneous surface concentration distribution. The simulated diffusion period was subsequently increased to 20 min to demonstrate the redistribution of Zn^{2+} under high deposition capacity. This significant difference is attributable to the robust protection of the elastic (CO)-ZF layer on the tip of the Zn protrusions. This creates a strong electrostatic shield effect on Zn^{2+} , allowing Zn^{2+} to deposit on nearby domains.²⁶

In situ optical microscopy also tracked the Zn deposition's dynamic behavior. On the bare Zn surface (**Figure 7.4b**), H_2 bubbles developed as the deposition capacity increased, and zinc dendrites progressively formed. In contrast, (CO)-ZF maintained a dendrite-free (**Figure 47.a**), uniform morphology throughout the whole Zn electroplating process with no bubbles developing, revealing the (CO)-ZF layer's ability to inhibit dendritic formation and HER dramatically. One crucial factor to consider when evaluating a metal's corrosion resistance is the corrosion potential (E_c).²⁷ To explore the corrosion behavior of the Zn anode, the corrosion polarization measurement in 1 M H_2SO_4 solution was carried out based on Tafel extrapolation. **Figure 7.4f** demonstrates that the E_c of (CO)-ZF@Zn is less negative than that of bare Zn (-1.09 V vs. Ag^+/AgCl), indicating that (CO)-ZF has a smaller corrosion propensity. Additionally, (CO)-ZF@Zn has a lower corrosion rate than its equivalent without (CO)-ZF ($107.15 \text{ mA cm}^{-2}$) based on the corresponding corrosion

current density (I_c), which is substantially lower at that of ZHS linear scanning voltammetry (LSV) curves measured in 2M ZnSO_4 electrolyte in 7.4g, consistent with the findings of the Tafel test, show the ability of (CO)-ZF to inhibit HER in assembled symmetric cells.

Furthermore, incorporating the carbonyl group into the interfaces favors the promotion of Zn^{2+} desolvation and transport, further preventing side reactions such as hydrogen evolution (HER) and corrosion of the Zn anode.²⁸ *In situ* Raman spectroscopy measurements were used to visualize changes in the Zn ions at the electrode/electrolyte interface during Zn deposition, with the Raman beam focused on the neighborhood of the Zn surface, as shown in **Figure 7.4c** and 7.4d. The Raman signal at 980 cm^{-1} has significant intensity from SO_4^{2-} ,²⁹ and can be utilized to assess local variations in the Zn^{2+} concentration. The interface of the deposits/electrolyte gradually travels along the Zn deposit direction during Zn plating, allowing the observation of Raman signal variations corresponding to ion concentration changes. In **Figure 7.4d**, the pure Zn anode shows a considerable and quick decline of spectrum intensity with Zn plating, indicating the inhomogeneity of Zn ions along the electrode/electrolyte interface. However, as demonstrated in **Figure 7.4c**, the practically constant strength of the Raman signal in the CPE shows consistency and uniformity of the Zn ion distribution at the electrolyte and electrode interface during Zn plating.³⁰ This provides strong evidence that the (CO)-ZF can efficiently manage the migration movement of the ion flux to achieve homogeneous Zn^{2+} distribution, which adds significantly to the major improvements in Zn anode performance.

The behavior of the Zn-atom's electron redistribution on various substrates can be revealed by charge density difference analysis using DFT calculations. The poor affinity for Zn atoms is clearly demonstrated by the almost complete absence of charge transfer between the Zn metal surface and the Zn atoms (**Figure 7.4e**). In contrast, in ZF and (CO)-ZF, the electron density around the Zn

atoms observably moves to the fluoride and carbonyl sites. The predicted adsorption energies for Zn metal, ZF, and (CO)-ZF toward Zn^{2+} are quantitatively 0, -0.189, and -2.872 eV, respectively. Negative adsorption energy is much more prominent in (CO)-ZF than in the pure Zn and ZF, most likely due to the abundance of zincophilic carbonyl sites. As a result, Zn^{2+} is particularly prone to be adsorbed by (CO)-ZF, which prevents HER side reactions at the interface and makes Zn homogeneously nucleate and deposit.

Ex situ XRD experiments were carried out to investigate the corrosion process. Throughout the deposition process, the electrode without the (CO)-ZF layer progressively acquired the distinctive $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot 5\text{H}_2\text{O}$ (ZHS) (ICSD:61141) peaks at roughly 8.07° and 16.22° due to the local pH raise(**Figure S7.2**).³¹ Notably, the peaks continue to exist during the process of stripping, indicating that the corrosion processes that results in loose and unstable ZHS are irreversible. However, no noticeable ZHS characteristic peaks were seen on the surface of the electrode that had been modified by (CO)-ZF (**Figure S7.3**). Additionally, the unprotected electrode's Raman spectrum (**Figure S7.4**) shows a prominent band at 2633 cm^{-1} that corresponds to the O-H stretching vibration of ZHS after cycling.³² As the corrosion progresses, the usual peak of the O-H group is maintained and enhanced, which strongly supports the theory that the buildup of hydroxyl ions speeds up the creation of ZHS. Comparatively, the (CO)-ZF electrode has no evident peak at 2633 cm^{-1} , demonstrating that the hydroxide ion concentration at the electrode surface does not vary considerably (**Figure S7.4**). The XPS S 2p spectra also show that the (CO)-ZF@Zn surface has nearly no corrosion byproducts. (**Figure S7.5**). The enhanced kinetics and suppressed side reactions in the (CO)-ZF interface is ascribed to the higher wettability and Zn^{2+} transference number introduced by carbonyl motifs.

As shown in **Figure S7.6**, contact angle experiments with 2.0 M ZnSO₄ electrolyte were used to assess the wettability of various electrodes. Because carbonyl-rich 2(CO)-ZF had a substantially smaller contact angle (37.5°) than bare Zn (88.7°), ZF (78.1°), or less carbonyl modified (CO)-ZF (56.9°), it is considered more hydrophilic. The improved wettability and transference properties of (CO)-ZF favors the electrolyte's permeability and, as a result, encourage the solid-state diffusion process. In summary, *in situ* and *ex situ* investigations show that the (CO)-ZF layer may effectively provide faster ion kinetics reducing side reaction processes, including corrosion and hydrogen evolution.³³

7.4 REVERSIBLE ZN PLATING/STRIPPING OF ELASTICIZED (CO)-ZF AT A HIGH UTILIZATION RATE

Due to the enhanced elastic properties and high Zn²⁺ affinity, it is envisioned that (CO)-ZF will exhibit significantly improved cycling stability. As anticipated, the (CO)-ZF symmetric battery has a greatly extended cycle life of over 6900 hours at 1 mA cm⁻² with 1 mAh cm⁻², roughly 200 times longer than the lifespan of pure Zn (Figure S7.8). Even at the elevated current density of 20 mA cm⁻², the advantage of high Zn²⁺ conductivity of CO-ZF is demonstrated. The (CO)-ZF continues to operate reliably for over 130 h, while the ZF cell experiences a major voltage expansion after 60 h indicating a soft short-circuit (Figure 7.5a). In contrast, the bare Zn exhibits severe voltage fluctuations and an abrupt and rapid decrease in voltage after 5.74 hours, which can be attributed to uncontrollable short circuits caused by dendrite growth. Meanwhile, the overpotential of (CO)-ZF (154 mV) is significantly lower than that of ZF (307 mV) and bare Zn (423 mV) as a result of the speedy Zn²⁺ migration. Under an increased capacity of 10 mAh cm⁻² and DOD of 35.7%, the (CO)-ZF symmetric battery exhibited a longer cycle life of over 180 h compared to the Zn symmetric battery (41 h) (Figure 7.5b). Even when the Zn deposition capacity

was increased to 10 mAh cm^{-2} and a DOD of 71.4 %, the (CO)-ZF symmetric battery demonstrated over ten times enhancement of cycling stability compared to the Zn symmetric battery (Figure 7.5c). In addition, (CO)-ZF exhibited a low impedance even after 300 hours of deep cycling, demonstrating excellent reversibility at a high Zn utilization rate (Figure S7.9). Clearly, (CO)-ZF demonstrates a significantly lower voltage hysteresis than the other two control electrodes at varying current densities (Figure 7.5e). Meager ion migration resistance is responsible for exceptional rate performance in (CO)-ZF@Zn (Figure 7.5d). A 60-hour shelf-life test confirms the anti-corrosion ability of fluorinated SEI, enabling better cycling stability.

Compared to previously reported Zn anodes, the cycling time (6900 h) and cumulative capacity (6907 mAh cm^{-2}) of the Zn anodes presented in this study are highly competitive. As shown in Figure 7.5f, the (CO)-ZF protection layer demonstrates the best performance when compared to SEIs containing ZnO, ZnS, ZnSe, ZnF_2 , and $\text{Zn}_3(\text{PO}_4)_2$.^{34–47}

The electrochemical reversibility of asymmetric cells using treated pre-activated Cu foils as the working electrode, rather than Zn foils, was also evaluated to demonstrate the high CEs after cycling using (CO)-ZF. The Cu foils was first electrodeposited in a flooded cell using Zn as counter electrode, 2 M ZnSO_4 as electrolyte at 10 mAh cm^{-2} using a 1 mA cm^{-2} current. A uniform zinc layer at an average thickness of $\sim 60 \text{ }\mu\text{m}$ was deposited on the Cu foil and underwent the carbonyl fluorination processing. At a moderately high density of 10 mA cm^{-2} and moderate DOD (35.7%), the Cu||(CO)-ZF asymmetric cells have an average CE of 99.13% and satisfactory stability over 100 cycles (100 hours) (**Figure 7.5g**). In contrast, the Cu||Zn CE fluctuates dramatically and decreases, providing only 17 cycles. Cu||Zn demonstrates an initial CE of 95.6% during the first cycle when the DOD increases to ultrahigh values of 71.4% (**Figure 7.5h**). After that, the CE fluctuates drastically and decreases after five cycles. On the other hand, (CO)-ZF displays an initial

CE of 97.9%, which rapidly increased to 99.9% after five cycles and remained at 99.65% throughout 50 cycles. In addition, the plating/stripping overpotential of Cu||(CO)-ZF is only 87.5 mV at 10 mA cm⁻², which is lower than that of Cu||Zn (109.2 mV). The results confirm that (CO)-ZF increases reaction kinetics and reduces side reactions. When the reversible capacity and current density were increased to 20 mAh cm⁻² and 10 mA cm⁻², respectively, Cu||(CO)-ZF maintained a high average CE of 99.7% for more than 200 cycles (**Figure 7.5g**). In contrast, Cu||Zn showed a precipitous decline in CE after only 40 cycles. In addition, Cu||(CO)-ZF exhibited a lower overpotential of 58.5 mV compared to Cu||Zn (91.6 mV).

7.5 PRACTICAL VALIDATION OF A (CO)-ZF ANODE IN LOW N/P RATIO ZN BATTERIES

The performances of full cells employing LiMn₂O₄ (LMO) as the cathode material (associated XRD pattern EDS and SEM pictures are displayed in **Figures S7.11**, **S7.12**, and **S7.13**) were analyzed to demonstrate the viability of practical applications of (CO)-ZF anodes in aqueous Zn metal batteries. Due to the enhanced elastic properties of (CO)-ZF, there is no discernible capacity degradation over 800 cycles of charge/discharge in the full cell employing (CO)-ZF as the anode primarily due to the compressed formation of dead Zn (**Figure 7.6a**). In contrast, the capacity of a ZF-based full cell was reduced from 111 mAh g⁻¹ to 93.1 mAh g⁻¹ until the 437th cycle and experienced a short circuit after that. Both anodes expanded the life spans of Zn batteries considering that a pure Zn-based full cell only has a stable cycle life of ~200 cycles and largely compromised capacity retention. A study on the morphological evolution of cycled Zn anodes was conducted to determine the mechanisms of performance enhancement of (CO)-ZF over ZF. The rigid and brittle ZF collapses and fails to protect the Zn anode, as numerous protrusions emerge on the surface of the cycled ZF@Zn electrode. In sharp contrast, a homogeneous surface can be

found on the (CO)-ZF@Zn anode. Thus, the uniform Zn deposition facilitated by elastic-interface modulation is likely responsible for the increased storage performance of aqueous Zn-ion batteries.

Besides the improved elasticity, (CO)-ZF also suppressed self-discharge relative to pure Zn-based cells. After a 48-hour rest, the whole cell utilizing (CO)-ZF@Zn retained 98.9% of its initial capacity, which is significantly higher than that using bare Zn (80.5 %) (Figure 7.5c,d), indicating the (CO)-ZF layer's superior performance in suppressing side reactions. Figure 7.5e depicts the charge/discharge curves of bare Zn||LMO cells and (CO)-ZF@Zn||LMO cells at different cycle numbers, the voltage hysteresis of the (CO)-ZF@Zn||LMO cell is slightly lower than that of the pure Zn||LMO cell. The impedance spectra revealed that the R_{ct} of the (CO)-ZF@Zn||LMO cell is significantly lower than that of the pure Zn||LMO cell (Figure S7.10), showing better Zn^{2+} transport for quick redox reactions, which is compatible with its lower polarization. In slow CV scans (Figure 7.5f), the (CO)-ZF@Zn||LMO battery has a substantially narrower peak separation than the pure Zn||LMO, indicating that it has the best electrochemical kinetics and the lowest polarization. The rate performance of (CO)-ZF@Zn||LMO, ZF@Zn||LMO, and pure Zn||LMO cells is shown in **Figure 7.5g**. This better rate capacity is due to the low polarization and charge transfer resistance created by the (CO)-ZF@Zn||LMO anode.

To increase battery energy density further, (CO)-ZF||LMO full cells were assembled with a high cathode loading mass and a low N/P ratio (Figure 7.5h). When the N/P ratio was decreased to ~2.01:1, the (CO)-ZF@Zn||LMO full cell (cathode loading = 16.6 mg cm⁻²) demonstrated a competitive capacity of 107.6 mAh g⁻¹ at 1 C. The long-term cycling stability of the full cell was examined at 1 C and is shown in Figure 7.5g. After 120 cycles, the (CO)-ZF@Zn still has a high discharge capacity of 94 mA h g⁻¹ and an average CE of >99.5%. At the same N/P ratio, the full cell cycling stabilities for bare Zn and ZF are poor due to severe Zn dendrite formation and side

reactions at a high Zn utilization rate. The (CO)-ZF@Zn||LMO full cells provided energy densities of 16.7, 15.4, 14.2, and 12.8 Wh kg⁻¹ at 2.01, 4.75, 7.94, 10.27 N/P ratios, respectively, as shown in the graph in Figure S7.14. The energy densities are close to those of commercial lithium-ion batteries confirming the practical application of (CO)-ZF anodes. This work stands out when compared to previously reported cells with low N/P ratios because of the highest cumulative capacity (up to 19.7 mAh cm⁻²) and the lowest N/P ratio (2.01), indicating promising utilization for practical aqueous zinc ion batteries, as shown in **Figure S7.15**.^{35,48–56} All of these findings above show that the elastic (CO)-ZF protective layer proposed in this study can greatly improve the stability of Zn metal anodes.

7.6 CONCLUSIONS

An artificial fluorinated SEI (CO)-ZF was developed in a scalable solvothermal deposition by adding carbonyl ligands to the cationic coordination spheres of zinc fluoride. Because of its excellent homogeneity and flexibility, this SEI can not only effectively passivate the electrode surface but also buffer the volume expansion of electrode materials and maintain the structural integrity of the SEI during cycling. Additionally, the (CO)-ZF surface has strong Zn affinity due to the presence of enhanced Zn-F and Zn-CO zincophilic sites, as revealed by FEA and DFT calculations and orientated Zn deposition during plating. The mechanical and chemical suppression of irreversible reactions in (CO)-ZF@Zn renders it a more durable anode than the widely reported inert fluorinated SEI, ZF. As a result, the resulting (CO)-ZF@Zn symmetric cell has an ultra-long life of over 6900 h at 1 mA cm⁻². At a high DOD of 71.4%, the cell shows an ultrahigh cumulative capacity of 6000 mAh cm⁻². Furthermore, the (CO)-ZF@Zn||LMO battery has outstanding capacity retention of 99.3% after 800 cycles at 1 C. At a commercial-level of N/P ratio of 2.01, the (CO)-ZF@Zn||LMO cells have a superior reversible capacity of 94 mAh g⁻¹ after

120 cycles at 1 C and a cumulative capacity density of 19.7 mAh cm^{-2} with a high mass loading of 16.6 mg cm^{-2} , demonstrating their broad application potential to replace lithium-ion batteries in large-scale energy storage.^{57,58} The mechanical property reengineering used in this work to produce the elastic (CO)-ZF layer can provide critical insights into rationally designing improved metal-based batteries, such as sodium and potassium batteries.

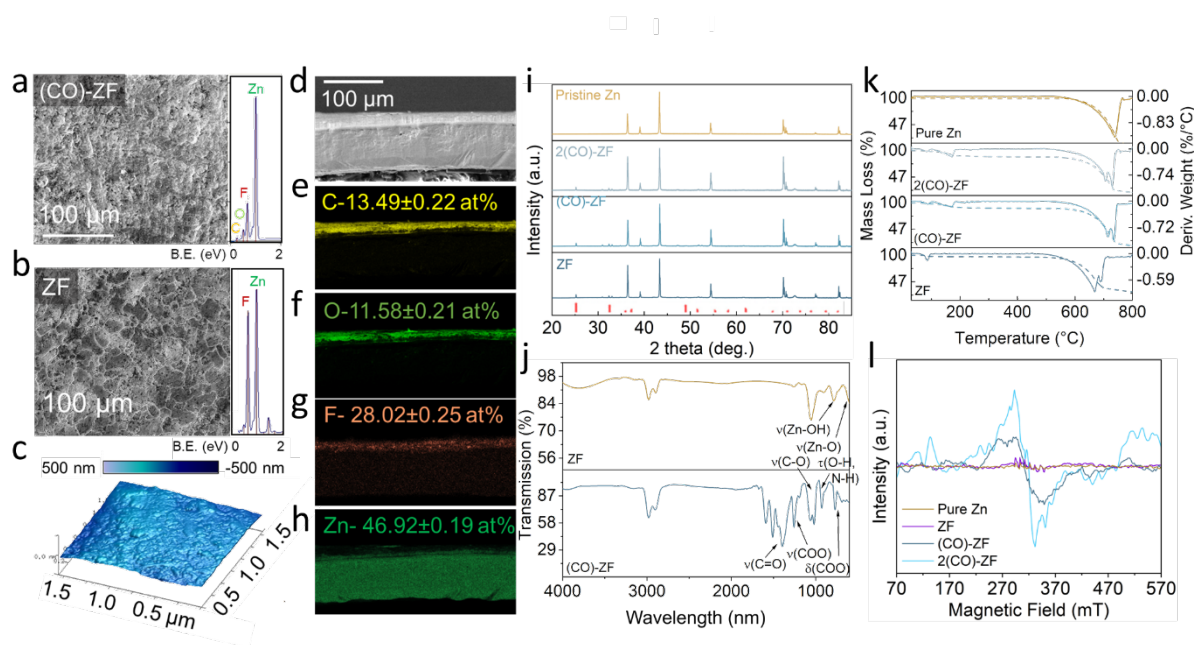


Figure 7.1 Typical SEM (top view) image and cumulative EDS spectra of a) (CO)-ZF@Zn, b) ZF@Zn. c) Typical AFM image of (CO)-ZF@Zn. d) Cross-sectional SEM images (CO)-ZF@Zn, and the corresponding EDX mapping images (e-h). i) XRD patterns (Bottom line is the characteristic peak position and intensity of standard ZnF_2 , PDF# 091-087-0713, k) TGA curves and differential thermal analysis of pristine Zn, ZF, (CO)-ZF and 2(CO)-ZF. j) FTIR spectra of scrapping powder from ZF and (CO)-ZF samples. l) EPR spectra of pure Zn, ZF, (CO)-ZF, and 2(CO)-ZF.

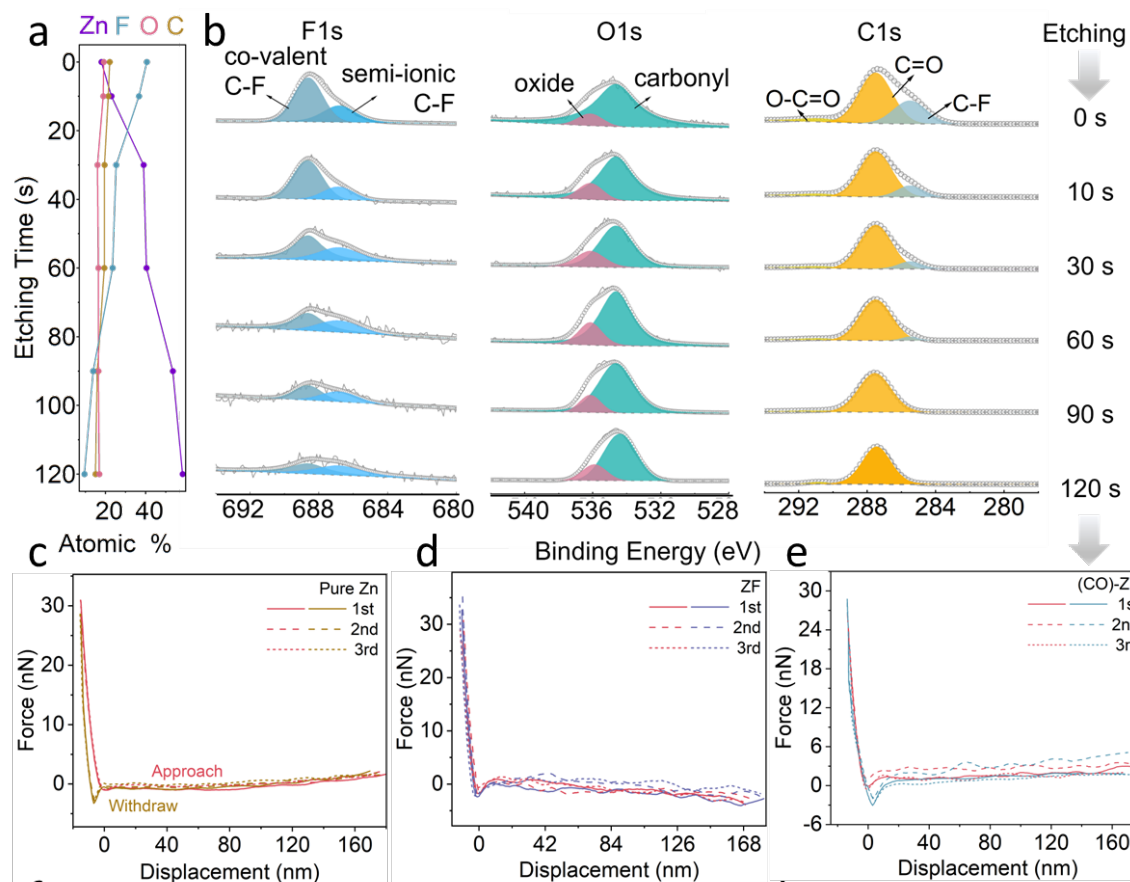


Figure 7.2 a) Atomic ratio variation of (CO)-ZF with Ar^+ etching time calculated from XPS spectra. b) XPS depth profile of (CO)-ZF. Force-displacement curves of c) pure Zn, d) pristine ZF, and e) (CO)-ZF.

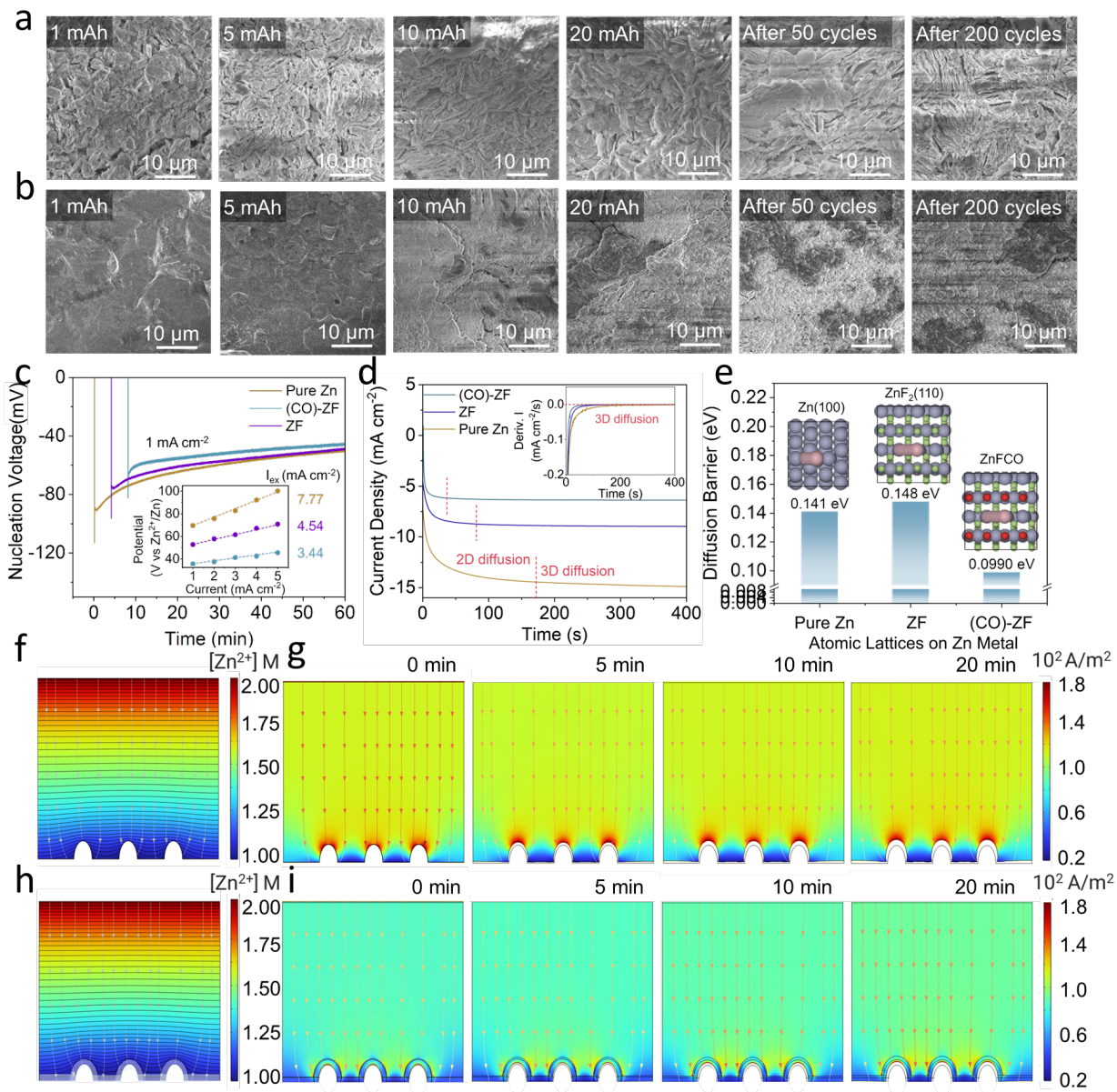


Figure 7.3 a) *Ex situ* SEM images of plated Zn in 2.0 M ZnSO₄ at different cumulative capacities and cycles. b) *Ex situ* SEM images of plated (CO)-ZF@Zn in 2.0 M ZnSO₄ at different cumulative capacities and cycles. c) *Ex situ* XRD patterns of plated Zn and (CO)-ZF@Zn. d) CA curves at an overpotential of -150 mV. Inset: first-order derivative of the curves. The region where the first order derivative is close to zero indicates a 2D and 3D diffusion process for Zn²⁺. e) Diffusion

barrier calculated based on DFT of pure Zn, ZF, (CO)-ZF. FEA dual-field simulations reveal that during the electrodeposition a redistribution of Zn^{2+} concentration in f) pure Zn anode, h) (CO)-ZF@Zn anode, and current density field distribution of g) pure Zn anode, i) (CO)-ZF@Zn anode.

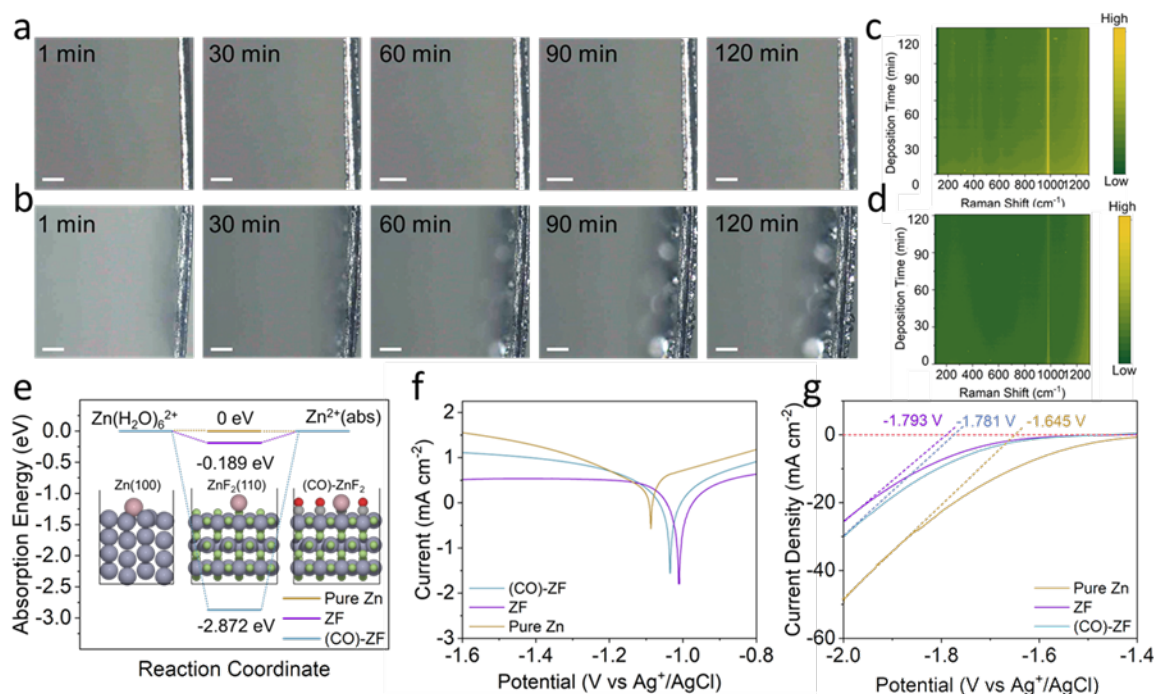


Figure 7.4 *In situ* optical microscopy photos of the Zn^{2+} plating processes for a) a (CO)-ZF@Zn anode and b) a pure Zn anode. *In situ* Raman spectra evolution over electrodeposition time for c) a (CO)-ZF@Zn anode and d) a pure Zn anode. e) Absorption energy calculated based on DFT of pure Zn, ZF, (CO)-ZF. f) Tafel plots in 1.0 M H₂SO₄, g) LSV curves in 2.0 M ZnSO₄ of pure Zn, ZF@Zn and (CO)-ZF@Zn.

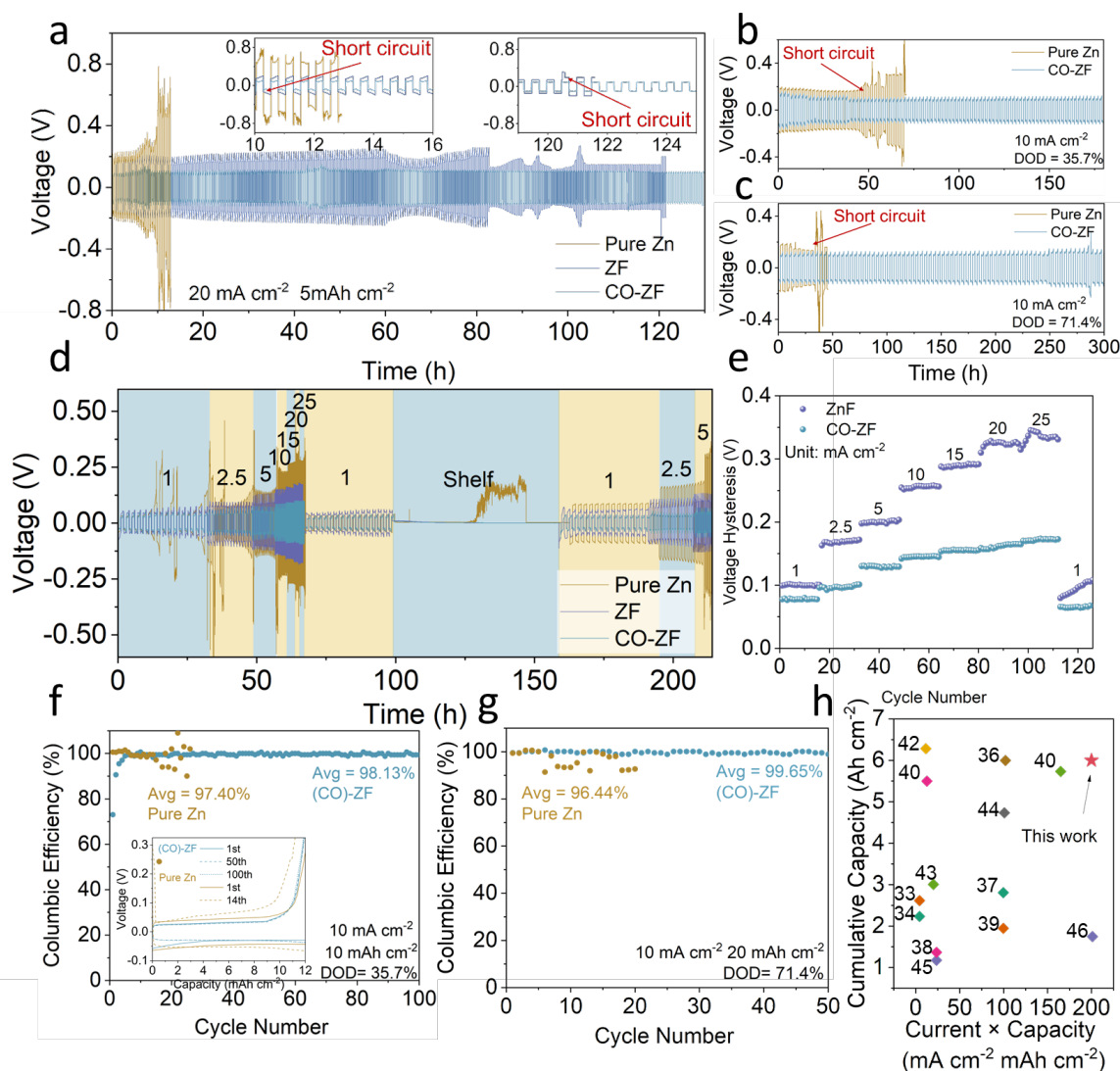


Figure 7.5 Symmetric cell cycle performance of pure Zn, ZF@Zn, and (CO)-ZF@Zn electrodes at the conditions of a) 20 mA cm^{-2} , 5 mA h cm^{-2} ; b) 10 mA cm^{-2} , DOD of 35.7%; and c) 10 mA cm^{-2} , DOD of 71.4%. d) Rate performance of the symmetric cells at current densities of 1, 2.5, 5, 10, 15, 20, and 25 mA cm^{-2} and areal capacities of 1 mA h cm^{-2} and a shelf-life test, as well as e) corresponding voltage hysteresis. Coulombic efficiency of Cu//Zn half cells using pure Zn, ZF@Zn, and (CO)-ZF@Zn electrodes under the conditions of f) 10 mA cm^{-2} , DOD of 35.7% (inset is the GCD profile); and g) 10 mA cm^{-2} , DOD of 71.4%. h) The comparison of cycling performance between this work and other previous reports.

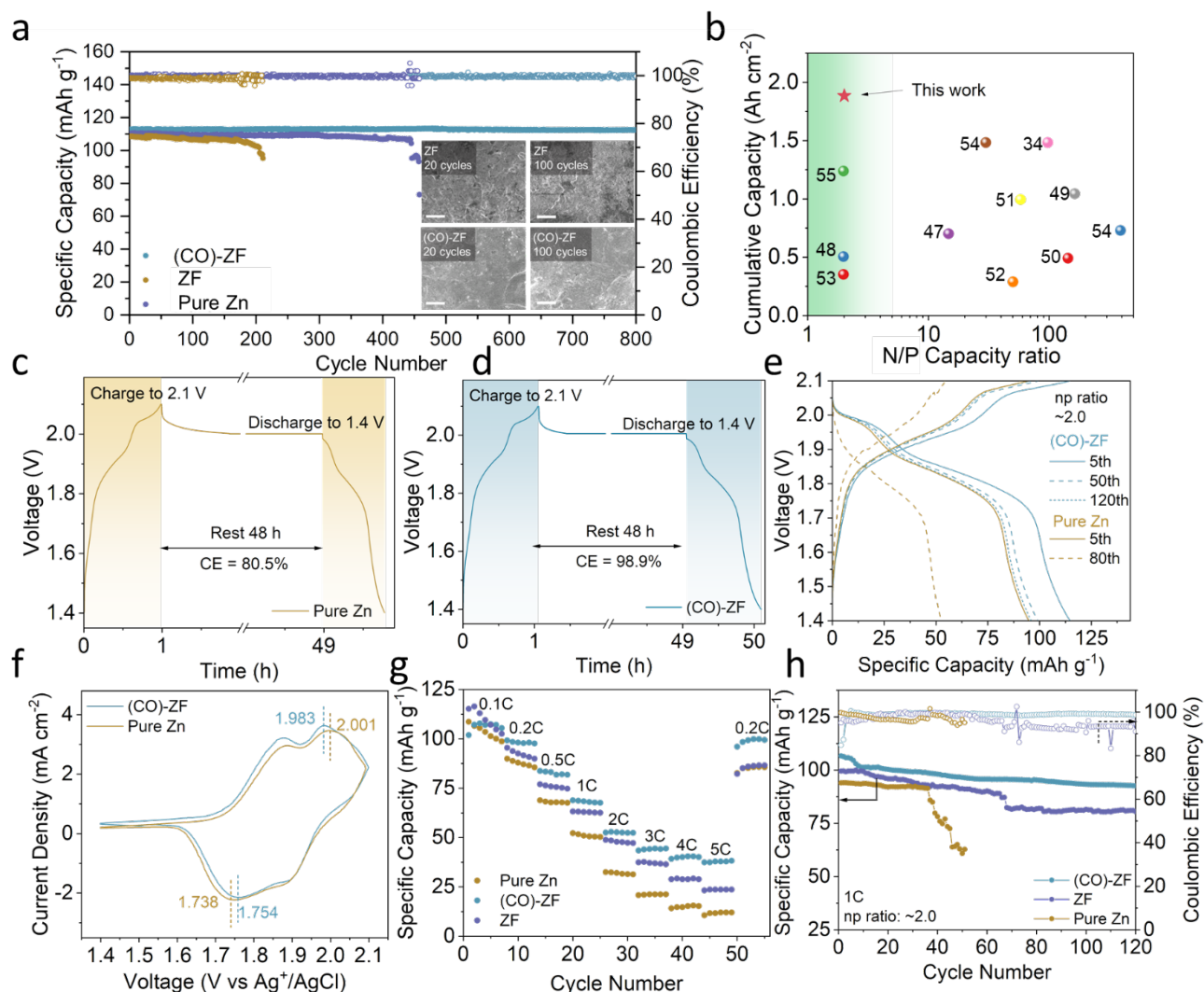


Figure 7.6 The electrochemical performance of Zn||LMO full cells. a) cycling performance and CEs at 1C (inset is the SEM (top view) images of cycled ZF@Zn and (CO)-ZF@Zn anode at different cycle numbers) c,d) GCD profiles during self-discharge tests of the full cells after a rest of 48 h. e) GCD profile at different cycle numbers f) CV profiles. g) rate performance. h) Cycling performance and CEs of the full cells with a negative/positive electrode capacity (N/P) ratio of 2.01 and an electrolyte/capacity (E/C) ratio of $10 \mu\text{L mAh}^{-1}$. b) Comparison of our performance with the previously reported low N.P ratio Zn ion batteries.

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7.7 EXPERIMENTAL SECTION

Preparation of elastic fluorinated artificial SEI on zinc anodes ((CO)-ZF@Zn): All chemicals were used as received without further purification. The as-purchased Zn foil (MTE, 0.1 μm in thickness) was first polished with abrasive paper to remove the native passivation oxide layer after cutting it into a 4 cm $\times$ 4 cm square sheet. The foil was rinsed with ethanol and acetone before the reaction. A mixture of 3.7 g NH_4F (Sigma Aldrich, >98%) and 50 mL anhydrous N, N-Dimethylformamide (Supelco) was prepared to deposit (CO)-ZF. A mixture of 1.85 g NH_4F

and 50 mL anhydrous N, N-Dimethylformamide was prepared to deposit 2(CO)-ZF. Zinc foil was added to the mixture, degassing and filling with nitrogen. Reflux was set up at 160 °C for a time ranging from 2 hours. After thermal heating, the zinc foil was retrieved and washed with methanol and ethanol. The obtained Zn foil was dried at room temperature in a vacuum. The modified Zn and bare Zn foils were punched into a disc (Φ 10 mm) to be directly used as Zn anodes without further treatment.

Preparation of pristine fluorinated artificial SEI on zinc anodes (ZF@Zn): The preparation was modified based on a previously reported method.¹ The polished zinc foil was cut into rectangles that were 1.8 cm by 9 cm to fit within the corundum crucible. The Zn foil was then placed on top and covered with a glass slide to be fixed. 1 g of NH₄F was added uniformly to the crucible. The system was then moved into a tube furnace and ran for two hours with an Ar gas flow. Thermal treatment was conducted with a heating rate of 3 °C min⁻¹ up to 210 °C (the temperature at which NH₄F decomposes) and maintained at that temperature for 2 hours. The fluorinated artificial SEI-coated Zn foil was obtained after being washed thoroughly with methanol and ethanol, and the (CO)-ZF@Zn was dried at room temperature in a vacuum.

Synthesis of LMO Cathodes: The LMO cathode material was prepared by mixing 70 wt% LiMn₂O₄ (Lib-LMO, MTI), 20 wt% conductive carbon (KS-6, MTI), and 10 wt% PVDF in N-Methylpyrrolidone (Sigma-Aldrich), and the slurry mixture was then coated on a graphite paper and dried in a vacuum oven at 60 °C for 1 day. The specific capacity of the LMO cathode was

calculated based on the weight of the active materials. The mass loading of LMO under unconstrained testing conditions was $\approx 16.7 \text{ mg cm}^{-2}$.

Electrochemical Measurements: To assemble the symmetric cells, 2032-type coin cells were assembled with two identical Zn or x(CO)-ZF@Zn electrodes with a thickness of 100 μm . 150 mL ZnSO_4 (2 mol L^{-1} , Sigma Aldrich, 98%) aqueous solution was used as the electrolyte. The Zn||Cu was assembled similarly, replacing one side of the electrode with a Cu disc ($\Phi 10 \text{ mm}$). Linear polarization measurements were conducted in a three-electrode configuration with bare Zn and x(CO)-ZF@Zn foils used as the working electrode, Zn foil as the counter electrode, and a leakless Ag/AgCl electrode (sat. KCl, 0.197 V vs. SHE) as the reference electrode. The corrosion potentials were calculated from the Tafel fit software included in the electrochemical workstation. CA curves of symmetrical Zn||Zn cells using bare Zn or x(CO)-ZF@Zn were tested at a constant potential (-150 mV). The Zn^{2+} transference number was measured based on the method from Zou et al.² For the measurements of full coin cells, LMO cathodes with a diameter of 1 cm were paired with (CO)-ZF and bare Zn anodes (thickness: 100 μm) employing 150 μL ZnSO_4 (2 mol L^{-1}) and Li_2SO_4 (1 mol L^{-1}) aqueous solution. All Zn from the anode was discharged to the cathode before cycling. The N/P ratio was controlled by comparing the cathode loading mass with the mass of anode chips as follows. When the cathode loading mass is 45.77 mg, the N/P ratio is 2.01:1. When the cathode loading mass is 19.37 mg; the N/P ratio is 4.75:1. When the cathode loading mass is 11.59 mg, the N/P ratio is 7.94:1. When the cathode loading mass is 8.96 mg, the N/P ratio is 10.27:1.

Galvanostatic cycling tests were also carried out at room temperature using a 63000 mA, up to 5V potentiostat (MTI, BST 8-3). The cycling condition, C rate, was calculated based on the reported theoretical capacity of LiMn_2O_4 is 148 mAh g^{-1} . For example, the current density of 1C is 148 mA g^{-1} . Moreover, EIS tests were performed using a CHI 660e electrochemical workstation (BioLogic, VMP-3) between 0.01 Hz and 100 kHz. Cyclic voltammetry curves at scan rates of 5 mV/s over the range of 1.4–2.05 V were also recorded with the VMP-3 electrochemical workstation. In situ Raman spectra of cells were acquired using a Renishaw InVia Raman microscope with an excitation length of 633 nm, where all spectra were acquired individually. The setting time was 60 s, and the exposure time was 10 s at intervals over an electrodeposition time in the first 2 hr. Typically, the PITT-In situ EIS are potentiostatic charged and discharged in the voltage range of 1.4-2.0 V with a step size of 50 mV and a working time of 15 min. The ESI analysis is tested at the corresponding voltages.

Zinc cation transference number

The Zn^{2+} transference number of the LZ-Zn and bare Zn electrode was evaluated in symmetrical cells by recording the EIS before and after chronoamperometry measurements with applied voltage polarization at 5 mV for 1000 seconds. The following equation calculates the transference number:

$$T = \frac{I_s(\Delta V - I_0 R_0)}{I_0(\Delta V - I_s R_s)}$$

where ΔV is the voltage polarization applied, I_0 and R_0 are the initial current and resistance, I_s and R_s are the steady-state current and resistance, respectively.

Coulombic efficiency in Cu//Zn cells (CE)

In specific, asymmetric cells such as Cu//Zn cells based on different Zn samples, i.e., bare Zn, pure- and LZ-Zn, were first conditioned by plating (1 mA cm^{-2} , 1 mAh cm^{-2}) and stripping Zn by charging to 0.5 V during the first cycle. Then, a Zn reservoir was built on the Cu electrode with a 21 mAh cm^{-2} (Q_t) capacity for the following cycling. During the subsequent 9 cycles, the current density at 1 mA cm^{-2} was applied for stripping and plating Zn with the capacity of 1 mAh cm^{-2} (Q_c) was plated or stripped in each cycle. In the last step, the final capacity (Q_s) was observed when plated Zn was stripped by charging 0.5 V. The Zn plating/stripping CE was calculated in the equation as follows:

$$CE = (9Q_c + Q_s) / (9Q_c + Q_t)$$

The utilization rate or the degree of discharge of Zn (DOD_{Zn}) was calculated as following,

$$DOD = \frac{2m_{Zn}}{C_{T,areal}}$$

Where $C_{T,areal}$ is the areal capacity of Zn plating/stripping.

Calculation of Energy Density of Full Cells: The energy density (Wh kg^{-1}) was calculated by the following equations:

$$E = \frac{C \times V \times 100}{m}$$

where C was the discharge capacity (Ah) of the first cycle at 1 C, V was the average operating voltage (V), and m was the total mass (g) of the active materials based on the anode and cathode electrodes.

7.8 SUPPORTING INFORMATION AND FIGURES

General characterization

A Jasco FT/IR-4100 with a single reflection ATR unit was used for FT-IR spectroscopy.

Bruker's D8 Discover powder X-ray diffractometer recorded CuK α radiation ($\lambda = 1.5406 \text{ \AA}$)

XRD patterns. A Renishaw InVia Raman Microscope with a 633 nm laser captured Raman

spectra in individual spectral or mapping mode. Single Lorentzian functions with R²-values of

0.99 fit Raman spectra peak fitting. Fluorescence baseline subtraction and Lorentz peak centers

deconvolved the powder Raman spectra. Peak positions were determined via Raman spectra of

several materials. Contact angle measurements were acquired on Kruss DSA10 (Germany). The

in-situ optical images were obtained on an optical microscope (Zeiss). SEM images were

captured using JEOL JSM-6700F FE-SEM. Elemental mapping analyses of the samples were

obtained using an energy-dispersive X-ray spectrometer (EDS, as an attachment to an SEM

instrument). Al or Cu foil substrates were used to support samples. A 120 kV FEI T12 TEM was

performed TEM. A 5 μL ethanol-diluted powder dispersions were drop cast over Lacey-carbon

supported TEM grids to produce TEM samples. A Kratos Axis Ultra DLD spectrometer with a

monochromatic Al K α X-ray source ($h\nu = 1486.6 \text{ eV}$) produced XPS spectra. XPS depth

profiling was conducted using the instrument's Ar⁺ ion source operated at 4kV, 50uA, and

mastered over a 3x3 mm area for 4 minutes. The atomic composition was determined based on

photoelectron peak areas and the relative sensitivity factors provided in CasaXPS. Carbon tape

(Ted Pella) was used to calibrate high-resolution spectra. CasaXPS processed raw data (version 2.3.16). C 1s spectra were fit using Gaussian–Lorentzian line shapes for all spectral components except the sp^2 C component, which was fitted with an asymmetric line shape to reflect the metallic nature of the samples. All samples used FWHM and position limitations for consistency. The electron paramagnetic resonance was recorded by Bruker EMXplus with a frequency of 9.8 GHz. Thermal gravimetric analysis (TGA) was tested using a thermogravimetric analyzer (TGA/SDTA 851, Mettler Toledo, Switzerland) in the air with a heating rate of 10 °C min⁻¹. Ultraviolet–visible–near infrared spectrometer (UV–VIS–NIR, Perkin Elmer, Lambda 950) was used to measure the absorption spectra.

Small-load nanoindentation and determination of Young's modulus

In order to collect as many force-displacement data points as feasible while retaining the SEI's deformation in the elastic zone, the maximum force for the first test was set at 100 nN. Under ambient conditions, PF-QNM measurements were done with silicon probes (TAP525A, Bruker). A probe was chosen for measuring both the stiff and soft portions of the SEI layer. The deflection sensitivity of the cantilever was measured on a clean sapphire sample to calibrate the probe. A nominal spring constant was used, and then the tip radius was calibrated using a reference sample (highly ordered pyrolytic graphite, Bruker) with a known elastic modulus (18 GPa). The tip radius was adjusted until the observed modulus data matched the known modulus value. After calibrating the probe, topology and elastic modulus images were collected over a $2 \times 2 \mu\text{m}^2$ area at a resolution of 259 pixels $\times$ 256 pixels. The line scanning rate was set to 0.9 Hz. Each set of Young's modulus measurements on the sample is based on 256×256 force-

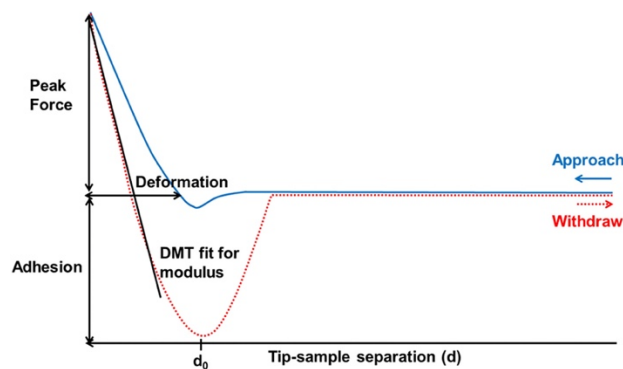
separation curves. To prevent damage to the SEI layer formed on the surface of the sample, the 50-100 nN tip force was set to acquire the elastic modulus map for the scratched area. The PF-QNM measurement was performed in three different regions of the sample. The Young's modulus of the SEI layer was determined by fitting the Derjaguin-Muller-Toporov (DMT) model to the retracting curves of the obtained force-separation curves, as shown in Fig. 1. According to the DMT model, the force that describes the tip-surface interaction behavior can be expressed as:

$$F - F_{\text{adh}} = \frac{4}{3E^* \sqrt{R(d-d_0)^3}}$$

where F is the tip-sample interaction force, F_{adh} is the adhesion force during the contact, E^* is the reduced elastic modulus obtained from the DMT fit, R is the tip-end radius and $d - d_0$ is the deformation of the sample. The Young's modulus of the sample can be derived using the equation:

$$E^* = \left[(1 - \nu_s^2) / E_s + (1 - \nu_{\text{tip}}^2) / E_{\text{tip}} \right]^{-1}$$

where E_s is Young's modulus of the sample, ν_s is the Poisson's ratio of the sample, the tip is the Poisson's ratio of the probe, and E_{tip} is Young's modulus of the probe. In the PF-QNM measurement, the second term of the above equation was neglected, based on the assumption that $E_s \ll E_{\text{tip}}$. The Poisson's ratio of the sample was assumed to be equal to 0.3. The maps obtained using these methods were post-processed with NanoScope Analysis software (Bruker).



Large-load nanoindentation and determination of elastic strain limit

In order to deliberately break the SEI and collect data on its elastic strain limit, the second test's maximum loading force was set to 1500 nN. Since only elastic deformation is needed for a stable zinc battery, the elastic strain limit is a crucial factor in determining the deformability of the SEI. After the external loading force has been eliminated, elastic deformation can entirely recover. Plastic deformation, on the other hand, is a permanent distortion that cannot be undone when external pressures are no longer present. In the battery industry, it is hypothesized that plastic deformation without fracture still poses a threat to the battery's cyclic stability.¹ The deformation behavior of a metal anode during cycling is significant at high DOD of zinc anodes. Only the elastically deformed SEI is able to completely return to its pre-cycle condition, maintaining a steady electrochemical behavior at each cycle. Contrarily, plastically deformed SEIs are unable to recover all of their deformation after charging, leading to gaps and voids between the current collector and the SEI, even though no cracks are visible. These holes cause uneven metal deposition during the subsequent discharge cycle in addition to raising the cell's resistance. With

each cycle, these harmful consequences of plastic deformation will increase, impairing cell function over time.

The primary stresses along the y-axis in zinc anode SEI layers are provided by for pure Hertz contact.

$$\begin{aligned}\sigma_r = \sigma_\theta &= -p_0(1 + \nu) \left\{ 1 - \left(\frac{y}{b} \right) \tan^{-1} \left(\frac{b}{y} \right) \right\} + \frac{1}{2} p_0 \left(1 + \frac{y^2}{b^2} \right)^{-1}, \\ \sigma_y &= -p_0 \left(1 + \frac{y^2}{b^2} \right)^{-1},\end{aligned}$$

where b is the contact radius and $p_0 = \frac{3}{2} \left(\frac{F}{A} \right) = \frac{3F}{2\pi R d}$. The maximum shear stress in the contact stress field of two solids of revolution occurs beneath the surface on the axis of symmetry. Yielding of most ductile material is usually taken to be governed by von Mises' shear strain-energy criterion:

$$J_2 \equiv \frac{1}{6} \{ (\sigma_y - \sigma_r)^2 + (\sigma_y - \sigma_\theta)^2 + (\sigma_\theta - \sigma_r)^2 \} = k^2 = \frac{Y^2}{3}$$

or by Tresca's maximum shear stress criterion:

$$\max\{|\sigma_y - \sigma_r|, |\sigma_y - \sigma_\theta|, |\sigma_\theta - \sigma_r|\} = 2k = Y$$

in which k and Y denote the values of yield stress of the softer material in simple shear and simple tension (or compression), respectively. The maximum value of $|\sigma_y - \sigma_r|$, for $\nu = 0.3$, is $0.62p_0$. By both the Tresca criterion and the von Mises criterion, the value of p_0 at yield is calculated to be:

$$p_0 = 1.6Y$$

Thus, the load to initiate yielding becomes:

$$F_Y = \frac{\pi^3 R^2}{6 E_r^{*2}} (1.6Y)^3$$

$$Y = \frac{1}{1.6\pi} \left(\frac{6F_Y E_r^{*2}}{R^2} \right)^{\frac{1}{3}}$$

where

and $E_r^* = \left(\frac{1-\nu_{tip}^2}{E_{tip}} + \frac{1-\nu^2}{E} \right)^{-1}$ is the Young's modulus of SEI after eliminating the substrate influence,

and the value of F_Y is the force value corresponding to deflection point (b) or the elastic limit.

The assumption for this treatment is that the SEI exhibits elastic-plastic behavior and the substrate effect on the value of F_Y is negligible due to the transmissibility of the force. The elastic strain limit ε_Y is then obtained by:

COMSOL simulations

A Finite Element Analysis (FEA) model was created utilizing the "Tertiary Current Distribution" and "Phase Field" modules of the COMSOL Multiphysics 5.6 program to simulate the dynamic Zn deposition on electrodes in mild alkaline electrolytes. The complete two-dimensional model's size was set to $2.0 \times 2.0 \mu\text{m}$ for the investigation of the dispersion of the electric field. In a space filled with electrolyte, the process was transiently simulated. The plating/stripping process was simulated using the phase field approach with a current density of 1 mA cm^{-2} .

The Zn^{2+} transfers by the concentration diffusion in the model follow Fick's law, as shown in equations:

$$N_i = J_i = -D_i \nabla c_i$$

$$\frac{\partial c_i}{\partial t} + \nabla \cdot J_i = R_{i,tot}$$

Where J_i is the ion flux, D_i is the diffusion coefficient of electrolytes ($D_{Zn} = 1.0 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$

For $\text{ZnSO}_4\text{-H}_2\text{O}$ electrolytes), c_i is the ion concentration of electrolytes ($c_i = 2000 \text{ mol m}^{-3}$), ∇c_i is the concentration gradient.

The Nernst-Einstein equation (below) governs the relationship between the diffusion coefficient and electric mobility.

$$N_i = -D_i \nabla c_i - z_i u_{m,i} F c_i \nabla \phi_i + u c_i = J_i + u c_i$$

Where z_i is the transfer number ($z_{Zn} = 2$), $u_{m,i}$ is the electric mobility coefficient, F is the Faraday constant (96485 C mol^{-1}), ϕ is the electrolyte potential.

The equilibrium potential of the electrode surface was described by the Nernst equations below.

$$E_{eq} = -\frac{\Delta G}{nF}$$

$$E_{eq} = E_{eq,ref} - \frac{RT}{nF} \ln \prod_i \left(\frac{a_i}{a_{i,ref}} \right)^{v_i}$$

Where E_{eq} is the electrode potential, $E_{eq,ref}$ is the standard electrode potential, ΔG is the Gibbs free energy, R is the ideal gas constant, T is the temperature ($T = 298 \text{ K}$), n is the transfer electron number of the reaction, α_i is the (electrode reactive ion concentration), $\alpha_{i,ref}$ is the (standard electrode reactive ion concentration), v_i is the reaction stoichiometric number.

The kinetics of electrode reaction was described by the Butler-Volmer equation below.

$$i_{loc} = i_0 \left(\exp\left(\frac{\alpha_a F \eta}{RT}\right) - \exp\left(\frac{-\alpha_c F \eta}{RT}\right) \right)$$

Where i_{loc} is the local current density at the electrode/electrolyte interface, i_0 is the exchange current density ($i_0 = 1.0 \text{ A m}^{-2}$), α_a and α_c are the cathodic and anodic charge transfer coefficients ($\alpha_a = 0.5$, $\alpha_c = 1.5$), η is the activation overpotential.

Density functional theory (DFT) calculations

The zinc metal surface is modeled by a $4 \times 4 \times 4$ slab of the (100) termination, with XY dimensions of $10.46 \text{ \AA} \times 9.75 \text{ \AA}$. The zinc fluoride surface is modeled by a $4 \times 4 \times 4$ slab of the F-terminated (110) termination, with XY dimensions of $13.30 \text{ \AA} \times 12.53 \text{ \AA}$. The ZnFCO surface is constructed by replacing all terminal F of the ZnF2(110) with CO. The bottom two layers of all slab models are constrained to represent bulk behavior. A vacuum layer of $15 \text{ \AA}$ thickness is added to each model to eliminate artifact interactions among neighboring images under the periodic boundary conditions.

The DFT calculations are performed with the PBE functional³ and PBE_PAW pseudopotentials⁴ using the VASP program (version 5.4.4).⁵⁻⁸ Solvation effects are treated implicitly using the VASPsol code.⁹ The convergence criteria for electronic and force minimization are set to 10^{-5} eV and $0.05 \text{ eV/\AA}$ during the geometry optimization. Γ -centered $2 \times 2 \times 1$ k-points are sampled in the reciprocal space of the Brillouin zone throughout, and the cutoff energy for the kinetic energy of the plane waves was 400 eV . The transition states (TS) are located using climbing image nudged

elastic band (CI-NEB) method¹⁰ with image-dependent pair potential (IDPP) interpolation.¹¹

Each TS geometry has been confirmed to have only one imaginary mode.



Figure S7.1 The photograph of pure Zn, ZF, and (CO)-ZF.

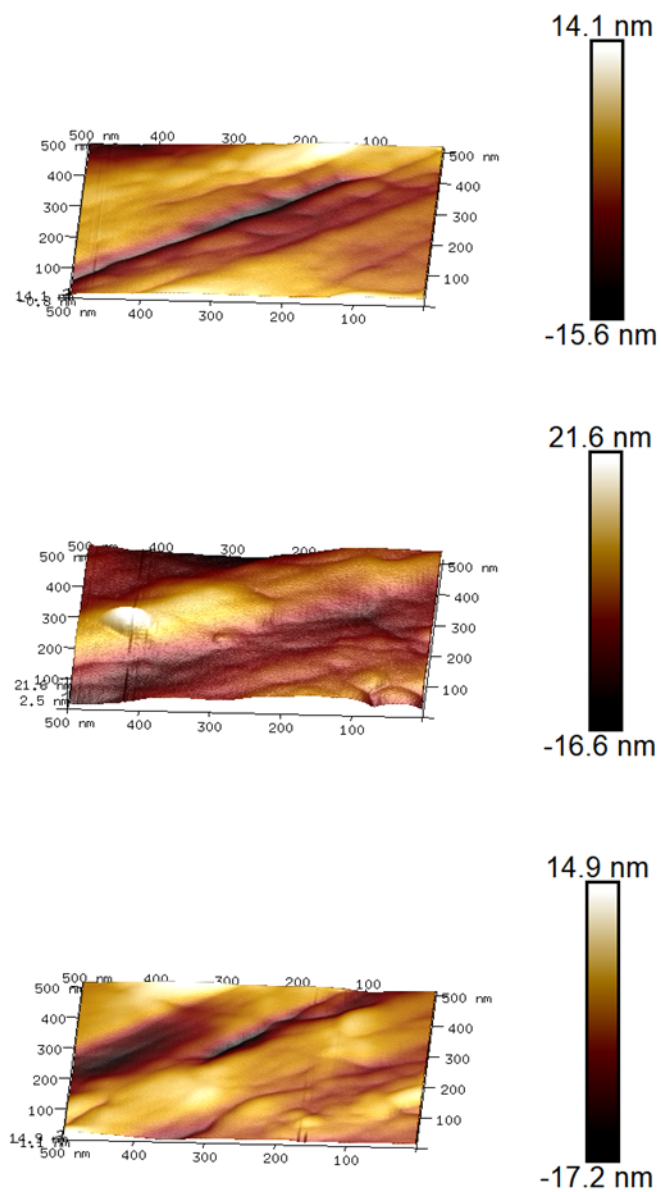


Figure S7.2 The AFM images of pure Zn (top), ZF (middle), and 2(CO)-ZF (bottom).

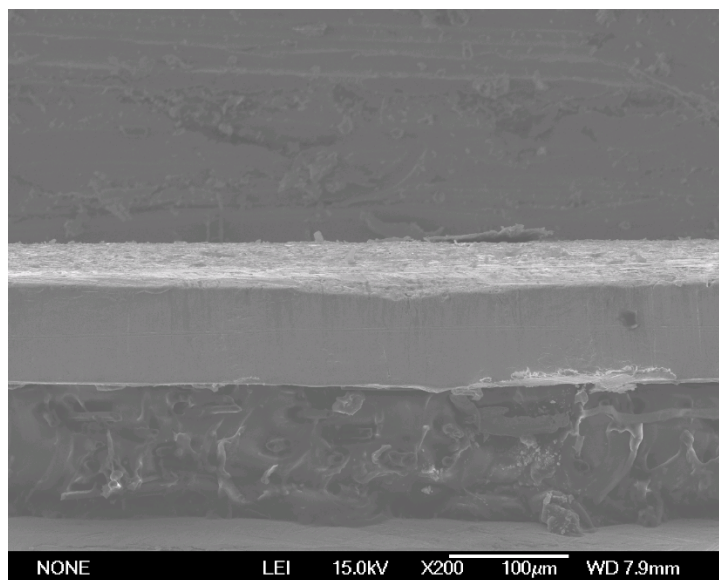


Figure S7.3 The cross-sectional SEM image of ZF.

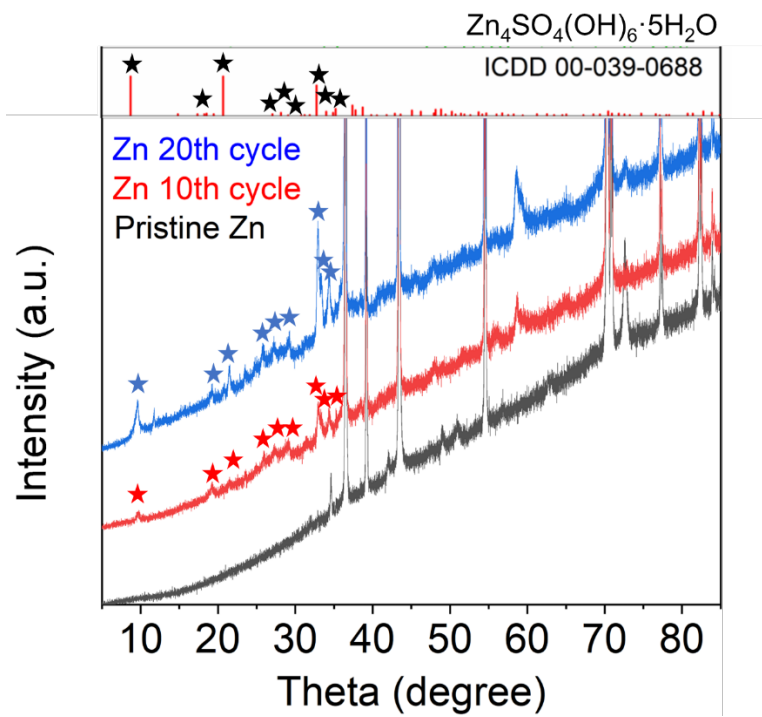


Figure S7.4 XRD patterns of cycled pure Zn anodes.

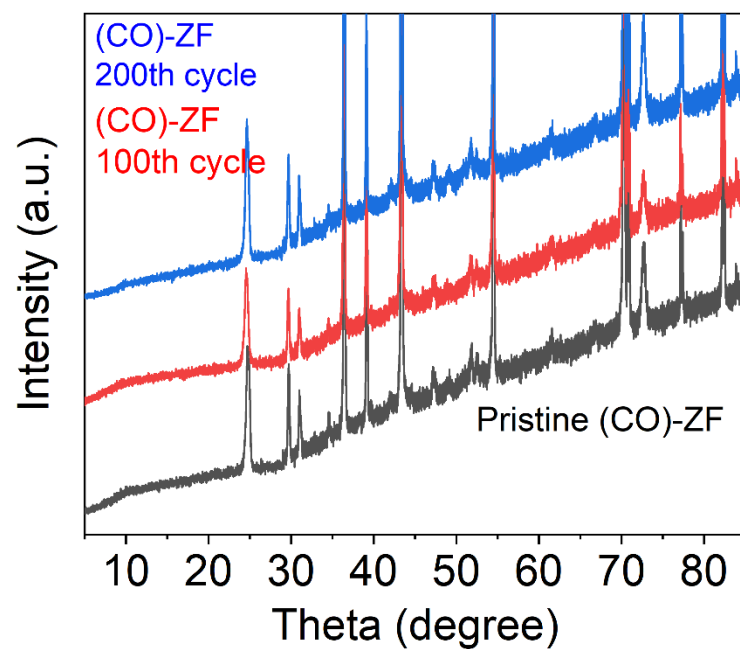


Figure S7.5 XRD patterns of cycled (CO)-ZF@Zn anodes.

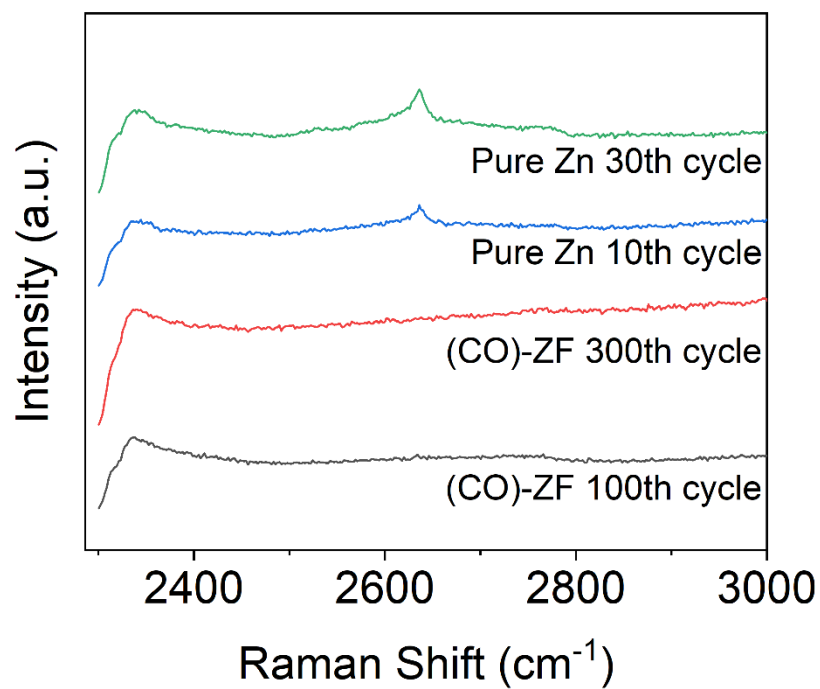


Figure S7.6 Raman spectra of cycled pure Zn and (CO)-ZF anodes.

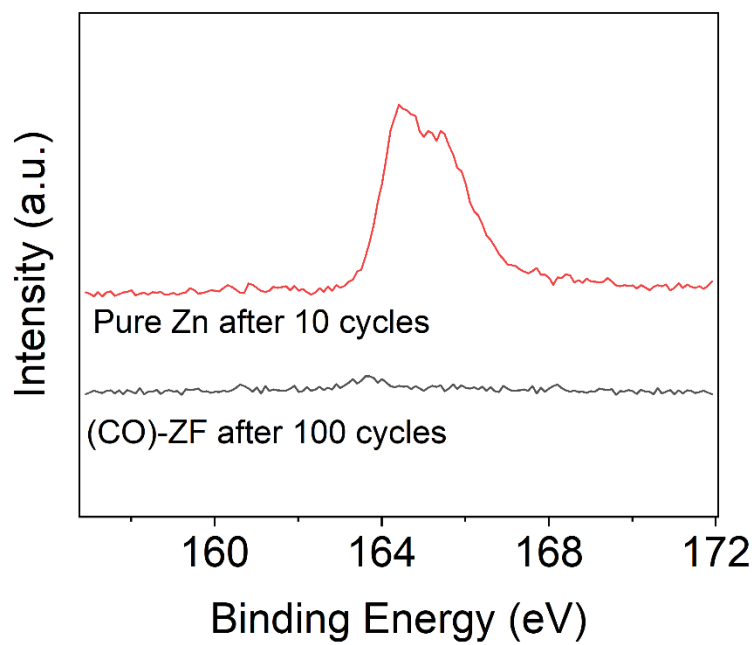


Figure S7.7 The core spectra of sulfur 2p of cycled bare Zn and (CO)-ZF electrodes.

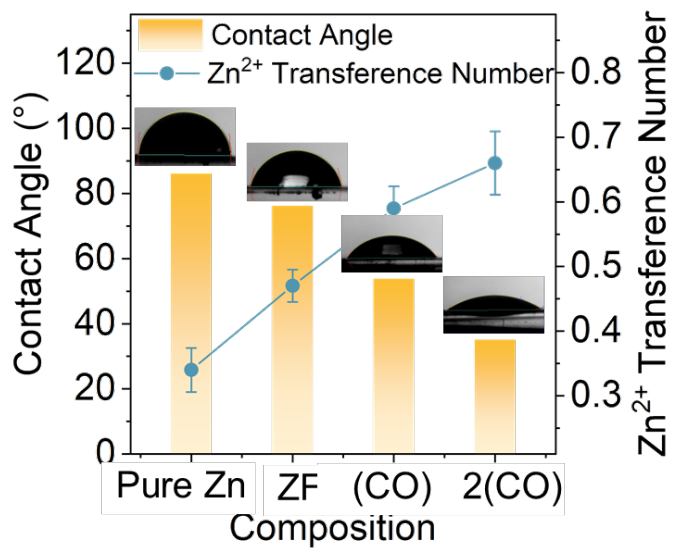


Figure S7.8 The water contact angle and transference number of pure Zn, ZF, (CO)-ZF, and 2(CO)-ZF

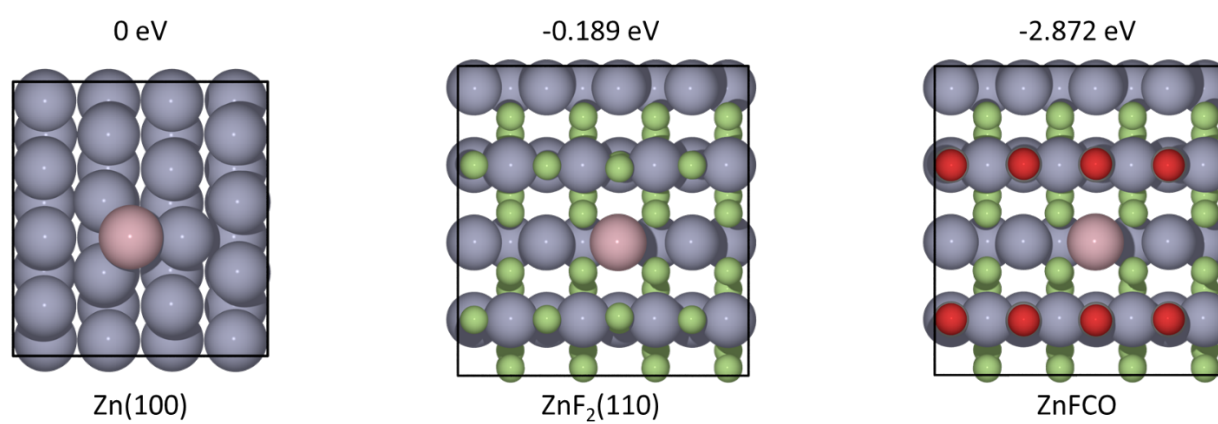


Figure S7.9 Rendered models (top view) of Zn²⁺ absorption energy on pure Zn, ZF, and (CO)-ZF.

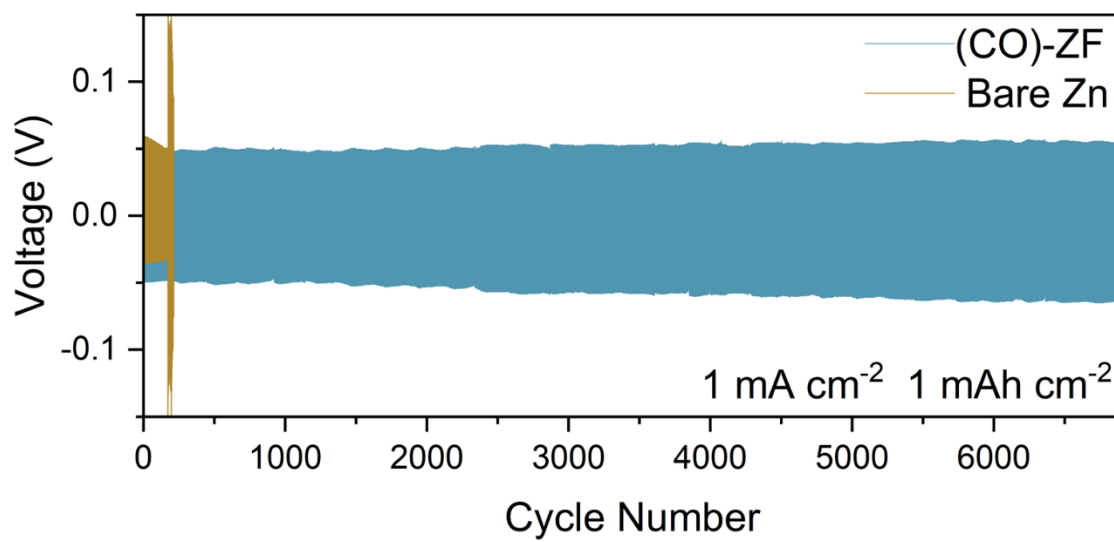


Figure S7.10 Symmetric cell performance of bare Zn and (CO)-ZF at 1 mA cm⁻² and 1 mAh cm⁻².

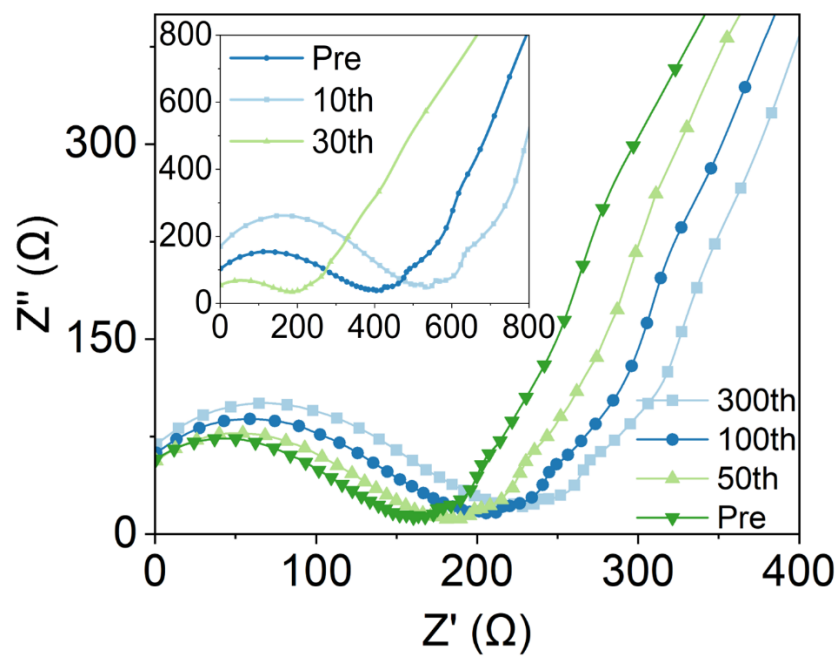


Figure S7.11 EIS of the symmetric cell of bare Zn and (CO)-ZF after cycles.

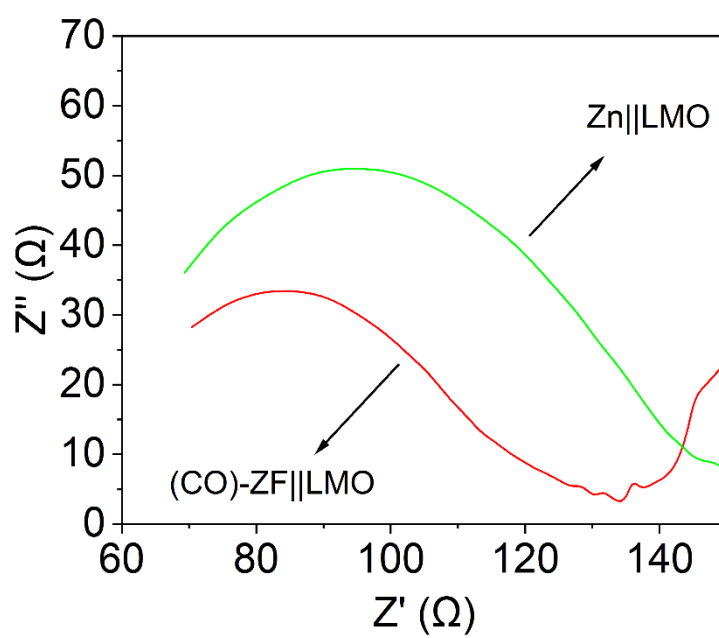


Figure S7.12 EIS of the full cell of bare Zn||LMO and (CO)-ZF||LMO after cycles.

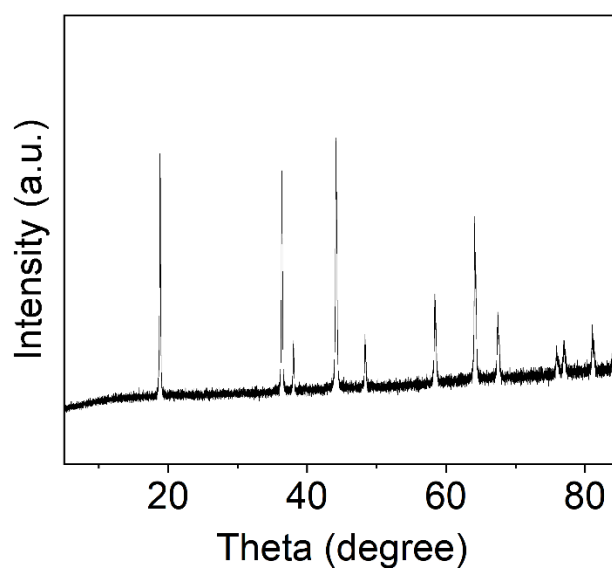


Figure S7.13 The XRD pattern of LiMn_2O_4 cathode materials.

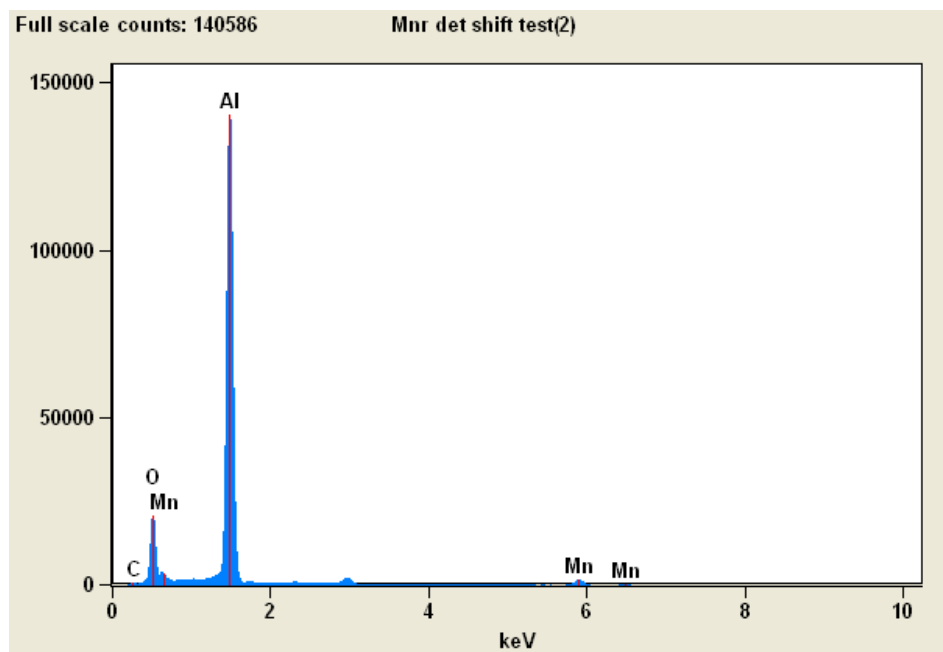


Figure S7.14 The EDS spectrum of LiMn_2O_4 cathode materials deposited on aluminum foil.

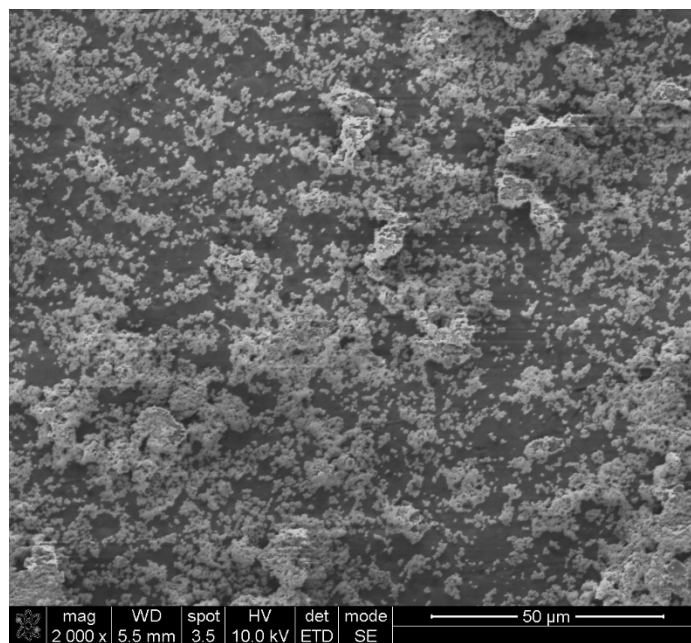


Figure S7.15 The SEM image of LiMn_2O_4 cathode materials.

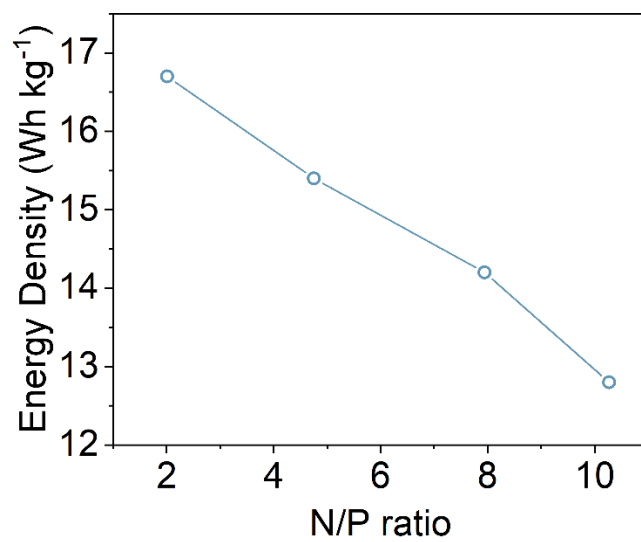


Figure S7.16 The energy density of full cell (CO)-ZF||LMO at various N/P ratios.

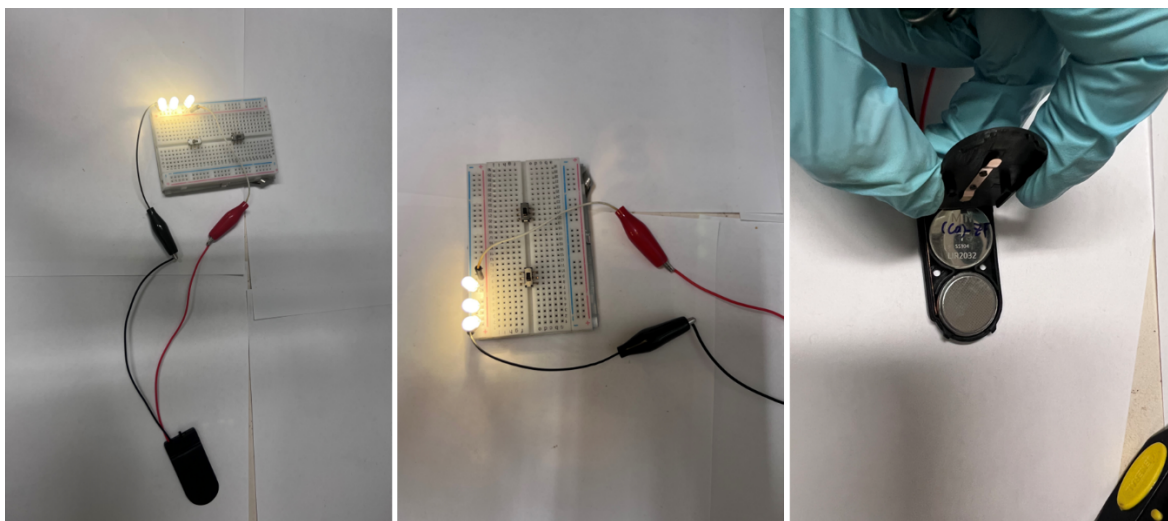


Figure S7.17 The photograph of LED light charged by two (CO)-ZF||LMO coin cells.

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