

Review

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# 3D-printed conductive hydrogels for flexible electrochemical energy storage: mechanisms, fabrication, and applications

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## Abstract

Conductive hydrogels have emerged as crucial components for sophisticated flexible energy storage devices, such as batteries and supercapacitors, because of their customizable microstructures, mechanical versatility, and integrated electronic/ionic conductivity. Conventional fabrication methods face persistent challenges in balancing electrical performance with mechanical durability and constructing complex three-dimensional (3D) geometries. Three-dimensional-Printed addresses these limitations by enabling precise spatial control over material deposition and structural design. This review comprehensively analyses three critical aspects of 3D-printed conductive hydrogels: (1) Fundamental conduction mechanisms in electronic, ionic, and composite hydrogels, focusing on material optimization through nanoscale dispersion control and dynamic network design; (2) Advanced manufacturing methods including photopolymerization and direct ink writing, analyzing critical parameters including rheological behavior, printing resolution, and structural-functional synergy; (3) Groundbreaking applications in flexible energy storage, particularly supercapacitors with geometrically enhanced electrodes and batteries featuring self-healing zinc anodes. Persistent challenges in material compatibility, scalability trade-offs between resolution and speed, and interfacial stability are critically assessed. Future research directions focus on multifunctional ink development, multiscale structural engineering, and reliability optimization to enable



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customized, commercially viable flexible energy storage technologies.

**Keywords:** 3D printing, conductive hydrogels, supercapacitors, batteries, electrochemical performance, mechanical flexibility

## INTRODUCTION

In recent years, electrochemical energy storage devices, such as batteries and supercapacitors (SCs), have been extensively employed as primary power sources for everyday applications<sup>[1,2]</sup>. Hydrogels, characterized by water-filled cross-linked hydrophilic polymer networks<sup>[3]</sup>, have become a very promising substitute for traditional electrolytes. Their exceptional water retention capacity and inherent softness make them well-suited to the essential requirements of flexible energy storage devices<sup>[4]</sup>. Conductive hydrogels are often classified as electronically conductive hydrogels<sup>[5]</sup>, ionically conductive hydrogels<sup>[6]</sup>, and composite conductive hydrogels<sup>[7]</sup>, based on their distinct conduction mechanisms. Among them, electronically conductive hydrogels, especially those derived from conductive polymer hydrogels (CPHs), combine the electrical conductivity and pseudocapacitance of conductive polymers with the tunable mechanical flexibility of hydrogels, positioning them as outstanding candidates for electrode materials for flexible, high-capacity energy storage devices<sup>[8]</sup>. However, while increasing the filler density of conductive additives improves the conductivity of hydrogels, excessive filling can induce phase separation between the hydrogel matrix and the fillers, severely compromising their stretchability. This trade-off presents a challenge in achieving both high toughness and high conductivity in conductive hydrogels<sup>[9]</sup>. Similarly, in ionically conductive hydrogels, there is often an inverse relationship between ionic conductivity and their mechanical strength. While increasing cross-linking density enhances the mechanical property and elasticity, the resistance to ionic migration also increases, making it challenging to simultaneously achieve both superior mechanical strength and high ionic conductivity<sup>[10]</sup>.

Traditional template-based fabrication methods have limited the hydrogel electrolyte preparation to templated approaches, often resulting in predominantly two-dimensional (2D) or simplistic three-dimensional (3D) structural configurations. Due to this limitation, they cannot be used to create energy storage devices with complex geometries and cutting-edge topologies<sup>[3]</sup>, as shown in the comparison in Table 1.

In recent years, hydrogels have shown great promise as feedstocks for 3D printing, facilitating the fabrication of fiber scaffolds with micro- and submicron-scale resolution. Advanced 3D printing inks and printable hydrogel formulations have been the focus of increasing research efforts. For instance, Zhu *et al.*<sup>[19]</sup> looked into the basic ideas behind 3D printing inks along with the developments and difficulties of flexible electrochemical energy storage devices such as SCs and batteries. Additionally, silk fibroin-based hydrogels have been developed, showing considerable potential as 3D printing materials for various applications<sup>[20]</sup>. Moreover, an effective gelation strategy has been developed using dual-addition-induced physical cross-linking, enhancing the extrusion-based 3D printing performance of Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT: PSS) hydrogels<sup>[21]</sup>. These creative studies demonstrate how well hydrogel materials and 3D printing technologies work together.

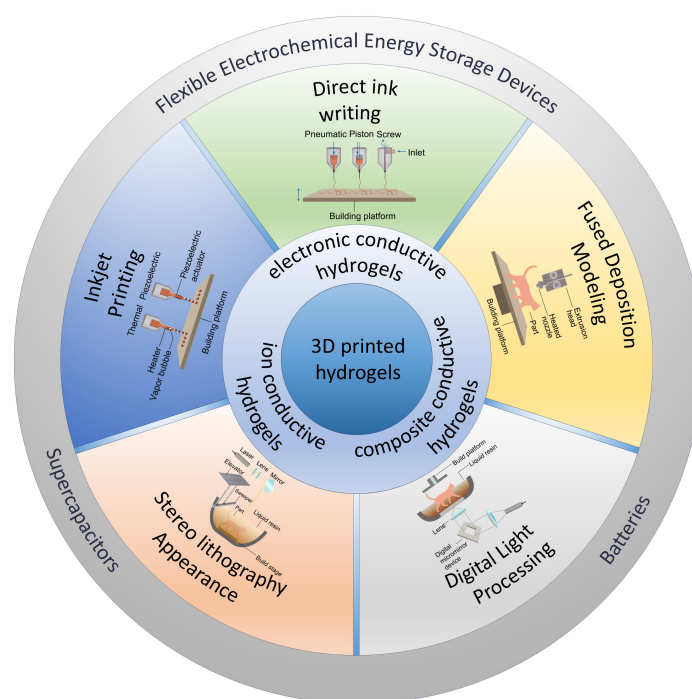
The field of flexible energy storage devices utilizing 3D-printed hydrogels represents a highly promising frontier for research and innovation, as illustrated in Figure 1. Numerous studies have delved into the advancements, applications, and transformative potential of this emerging field. These cutting-edge advanced fabrication technologies are revolutionizing the production of 3D-structured electrochemical



**Table 1. Comparison between 3D printing and traditional methods for hydrogel fabrication**

|                                         | Conventional methods                                                                         | 3D printing                                                                     | Ref.    |
|-----------------------------------------|----------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------|---------|
| Process principle                       | Depending on the mold, formed by casting or pressing                                         | Based on a digital model, materials are deposited layer by layer                | [11]    |
| Forming freedom                         | Difficult to prepare complex structures due to mold limitations                              | Complex 3D structures can be designed                                           | [12,13] |
| Material utilization rate               | May generate excess waste                                                                    | Allocation on demand, utilization rate > 90%                                    | [14]    |
| Resolution                              | Limited by molds (typically > 100 $\mu\text{m}$ ); difficult to achieve micro-scale features | High precision, 50-510 $\mu\text{m}$                                            | [11]    |
| Cost                                    | Mold development costs are high, suitable for mass production                                | High equipment investment, but flexible for single-piece/small-batch production | [15]    |
| Multi-material integration capabilities | Challenging; requires post-assembly; limited material compatibility                          | Printable multi-material composite structures                                   | [16-18] |

3D: Three-dimensional.



**Figure 1.** An overview of the application of different 3D printing techniques in the fabrication of hydrogels with distinct three-dimensional configurations for flexible electrochemical energy storage devices<sup>[22-27]</sup>. 3D: Three-dimensional.

energy storage devices, bridging the gap between the macro and nanoscales<sup>[28]</sup>. Significant gains in energy and power densities are made possible by the unmatched ability of 3D printing technology to accurately regulate the spatial geometry and architecture of devices<sup>[29]</sup>. Furthermore, the additive nature of 3D printing enables the creation of complex designs through a streamlined and cost-effective process<sup>[30]</sup>. Evolving from rapid prototyping, 3D printing is an advanced fabrication technique that constructs 3D objects with intricate geometries directly from programmed designs through layer-by-layer material deposition<sup>[31]</sup>. Leveraging its unique ability to manipulate materials in both spatial and temporal dimensions, high-resolution fabrication of intricate structures is made possible, which also makes it easier to combine several materials in one process. The creation of electrochemical energy storage systems with optimally designed architectures is made possible by this capacity<sup>[32]</sup>.

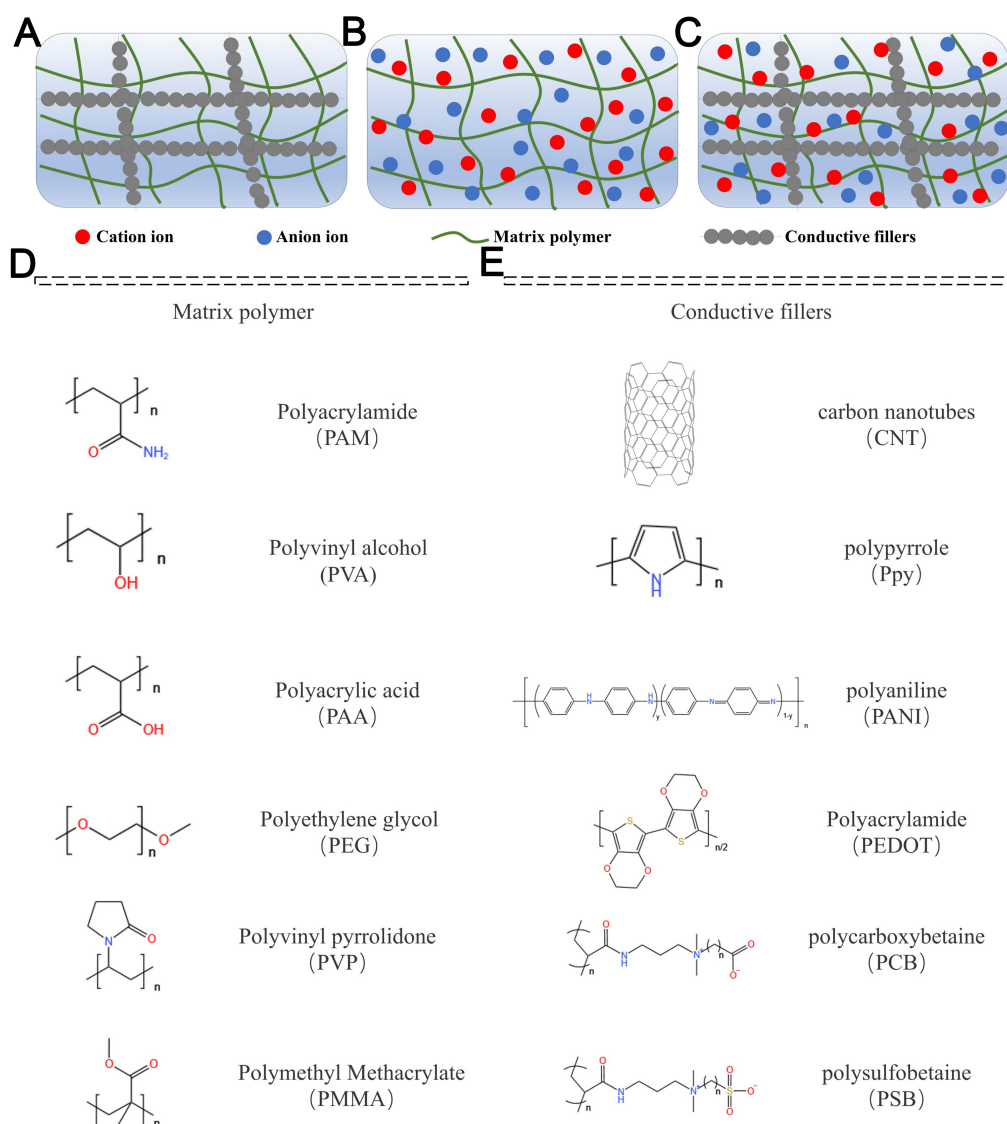
In light of the rapid advancements in novel hydrogel materials, innovative hydrogel ink formulation techniques, and state-of-the-art 3D printing technologies, a comprehensive and critical review is both timely and imperative. This review systematically consolidates and critically analyzes the latest advancements in 3D-printed hydrogels specifically designed for flexible electrochemical energy storage devices. Initially, we provide an in-depth summary of the classification, conduction mechanisms, and intrinsic characteristics of conductive hydrogels. Following this, we delve into the integration of 3D printing technologies in hydrogel fabrication, highlighting the categorization of fabrication methods, fundamental principles, and unique material characteristics. Furthermore, we investigate the applications of 3D-printed hydrogels in flexible energy storage systems, with a particular focus on recent advancements and technological breakthroughs. Furthermore, the applications of 3D-printed hydrogels in flexible energy storage systems, with a particular emphasis on recent advancements and technological breakthroughs, were systematically summarized. Finally, we provide a critical evaluation of the impact of 3D printing on electrochemical performance, exploring its compatibility with hydrogels, strategies for enhancing electrochemical properties, and the ongoing challenges that remain in the field. This review aims to facilitate further innovation in flexible electrochemical energy storage devices, expanding the potential of 3D-printable hydrogel materials and fabrication methodologies while positioning them as pivotal candidates for the next generation of flexible energy storage technologies.

## FUNDAMENTALS OF CONDUCTIVE HYDROGELS

Powering wearable electronics demands flexible energy storage systems capable of enduring continuous bending, stretching, and twisting. Among these, SCs and batteries emerge as the most promising candidates, necessitating a balance between electrochemical stability and mechanical robustness<sup>[33]</sup>. Hydrogels are soft, moisture-rich materials with a 3D porous network structure, enabling them to absorb and retain substantial water content while preserving their semi-solid integrity [Figure 2A-C]<sup>[34,35]</sup>. The incorporation of conductive materials into the hydrogel matrix transforms hydrogels into conductive materials. An extensive variety of conductive agents, such as conductive polymers<sup>[36]</sup>, metallic nanoparticles/nanowires<sup>[37]</sup>, liquid metals (LMs)<sup>[38]</sup>, carbon-based nanomaterials<sup>[39]</sup>, and ionic liquids<sup>[40]</sup>, have been integrated into hydrogel matrices to engineer conductive hydrogels, as illustrated in Figure 2D and E<sup>[41]</sup>. Typically, the conductivity of hydrogels is improved through the incorporation of increased amounts of conductive materials or the doping of conductive polymers. Based on their conduction mechanisms, these enhanced hydrogels are categorized into electronically conductive hydrogels, ionically conductive hydrogels, and composite conductive hydrogels. Conductive hydrogels synergize the distinctive benefits of conductive materials and hydrogels, offering outstanding electronic properties, adjustable mechanical flexibility, and facile processability<sup>[42]</sup>.

### Electronically conductive hydrogels

Electronically conductive hydrogels represent a unique category of hydrogel materials that enable electrical conductivity via electron transport mechanisms, predominantly driven by the free electrons of metals or the delocalized  $\pi$ -electrons of conjugated systems. The conductive fillers integrated into these hydrogels are generally classified into metal-based, carbon-based, and conductive polymer-based, *etc.*<sup>[43]</sup>. Metal-based conductive hydrogels seamlessly integrate the exceptional electrical conductivity of metals with the inherent flexibility of hydrogels. Typical metal fillers include gold and silver nanoparticles or nanowires, and LMs. While metal nanoparticles offer excellent conductive properties, their propensity to aggregate within the hydrogel matrix poses challenges. Furthermore, the mechanical disparity between rigid metallic fillers and the soft, elastomeric hydrogel matrix often results in stress concentration at the hydrogel-filler interface, thereby restricting scalability and undermining long-term durability<sup>[44]</sup>. Additionally, LMs represent a novel class of alloys that uniquely combine the superior electrical conductivity of traditional metals with the remarkable fluidity characteristic of liquids at or near ambient conditions<sup>[45]</sup>. Soft LMs endow hydrogels



**Figure 2.** Classification of different conductive hydrogels, including (A) electronically conductive hydrogels<sup>[35]</sup>, (B) ion conductive hydrogels<sup>[35]</sup>, and (C) composite conductive hydrogels<sup>[41]</sup>. Molecular structures of (D) matrix polymers<sup>[41]</sup> and (E) conductive fillers commonly utilized in conductive hydrogel formulations<sup>[41]</sup>.

with exceptional conductivity and deformability. However, challenges such as poor interfacial compatibility between LMs and the polymer matrix hinder mechanical performance, while the susceptibility of LMs to oxidation further limits their long-term stability<sup>[46]</sup>. Toward this, Wu *et al.*<sup>[47]</sup> addressed these challenges by stabilizing LM emulsions via strong electrostatic interactions. This enabled the polymerization of acrylic acid (AA) within the stabilized emulsions, yielding a LM-polyacrylic acid (PAA) hydrogel with exceptional conductivity ( $1.54 \text{ S m}^{-1}$ ), superior tensile strength, notable elongation at break, self-adhesion, and rapid self-healing capabilities.

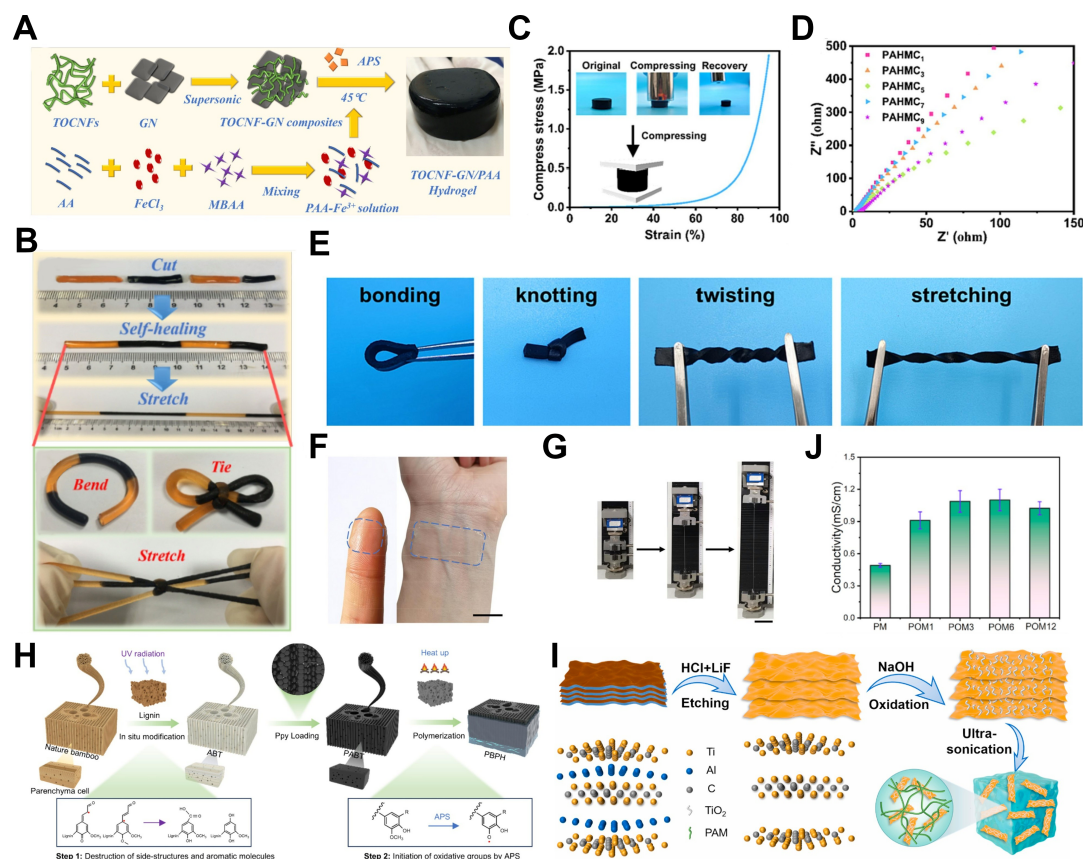
Carbon-based materials, including graphene (GN)<sup>[48]</sup> and carbon nanotubes (CNTs)<sup>[49]</sup>, offer remarkable advantages, such as high surface area, exceptional electron mobility, and outstanding mechanical flexibility<sup>[50]</sup>. However, the inherent hydrophobicity of GN and CNTs often results in aggregation within aqueous media, posing significant challenges to achieving uniform dispersion<sup>[51]</sup>. To overcome this

challenge, Zheng *et al.*<sup>[52]</sup> developed a highly stretchy, durable, and self-healing hydrogel created by using both physical and chemical cross-linking to disperse 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-oxidized cellulose nanofibers-GN nanocomposites into PAA (TOCNFs-GN/PAA) composite hydrogel [Figure 3A and B]. The multifunctional TOCNFs act as both an eco-friendly dispersant for GN, enhancing its dispersion in water, and as a reinforcing nanofiller, facilitating the formation of a conductive GN network within the PAA matrix. Xie *et al.*<sup>[53]</sup> also designed a double-network hydrogel incorporating a dynamic cross-linked rigid network of carboxymethyl chitosan, a covalently cross-linked soft network of polyacrylamide-co-hydroxyethyl acrylate (PAM-co-HEA), and a homogeneous conductive network of carboxylated CNTs. This hydrogel demonstrated exceptional mechanical strength (475.4 kPa), impressive compressive ability (1.9 MPa, Figure 3C), and ultra-high conductivity ( $0.19 \text{ S cm}^{-1}$ , Figure 3D) and good flexibility [Figure 3E]. Other researchers have integrated diverse materials to enhance performance. For instance, Sun *et al.*<sup>[54]</sup> introduced multi-walled CNT-bridged LM composites (LM/CNT), overcoming traditional hydrogel limitations. This LM/CNT hydrogel exhibited impressive properties, including rapid self-healing (20 min), high conductivity ( $94 \text{ S m}^{-1}$ ), high transparency (93%, Figure 3F), and exceptional stretchability (2,200%, Figure 3G).

Conductive polymer-based hydrogels typically incorporate conductive polymers such as polypyrrole (PPy)<sup>[55]</sup>, polyaniline (PANI)<sup>[56]</sup>, and poly(3,4-ethylenedioxythiophene) (PEDOT)<sup>[57]</sup>. Unlike other conductive fillers, CPHs maintain structural uniformity between the hydrogel matrix and the conductive material, eliminating the interfacial issues typical in organic-inorganic composites. This normally results in more consistent and adaptable electronic conductivity<sup>[58]</sup>. However, these hydrogels often suffer from low mechanical strength, primarily due to the inherent brittleness of conductive polymers, which makes it challenging to incorporate toughening agents without compromising the conductive network<sup>[59]</sup>. Zhou *et al.*<sup>[60]</sup> introduced a dual-continuous CPH (BC-CPH) that integrates high conductivity ( $> 11 \text{ S cm}^{-1}$ ), superior fracture toughness ( $> 3,300 \text{ J m}^{-2}$ ), and exceptional stretchability ( $> 400\%$ ). This hydrogel is appropriate for sophisticated fabrication processes such as 3D printing since it is made from phase-separated inks that include hydrophilic polyurethane for improved mechanical qualities and PEDOT:PSS for electrical conductivity. In addition, Bai *et al.*<sup>[61]</sup> developed an anisotropic bamboo template (ABT) via ultraviolet (UV)-assisted catalytic oxidation, onto which PPy and flexible polyacrylamide (PAM) were integrated to form a 3D hydrogel network [Figure 3H], exhibiting excellent electrochemical performance, high mechanical strength (104.82 MPa), and toughness ( $1.95 \text{ MJ m}^{-3}$ ).

Since the successful exploration of 2D transition metal carbides/nitrides (MXene) in 2011, they have garnered significant attention in research, with their integration into hydrogel systems notably enhancing performance<sup>[62]</sup>. However, the abundance of polar groups on MXenes leads to their tendency to aggregate during hydrogel formation. To address this, Zhang *et al.*<sup>[63]</sup> employed oxidation treatment to prepare oxidized MXene (OM) to adjust its nanostructure. The oxidation products were embedded within the MXene layers, improving their dispersion in the hydrogel matrix. A composite hydrogel was synthesized by combining OM with PAM [Figure 3I]. The nanostructural modification of MXene improved its dispersion in the composite hydrogel, leading to the PAM/OM (POM) hydrogel exhibiting superior conductivity, enhanced transparency, mechanical strength, and sensitivity compared to the PAM/MXene (PM) hydrogel [Figure 3J]. A high loading of conductive fillers is essential for establishing efficient conductive networks. However, their poor hydrophilicity and strong interactions with the hydrogel matrix often lead to aggregation, undermining the mechanical integrity of the composite<sup>[64,65]</sup>. Therefore, striking an optimal balance between conductivity and mechanical performance remains a formidable challenge.

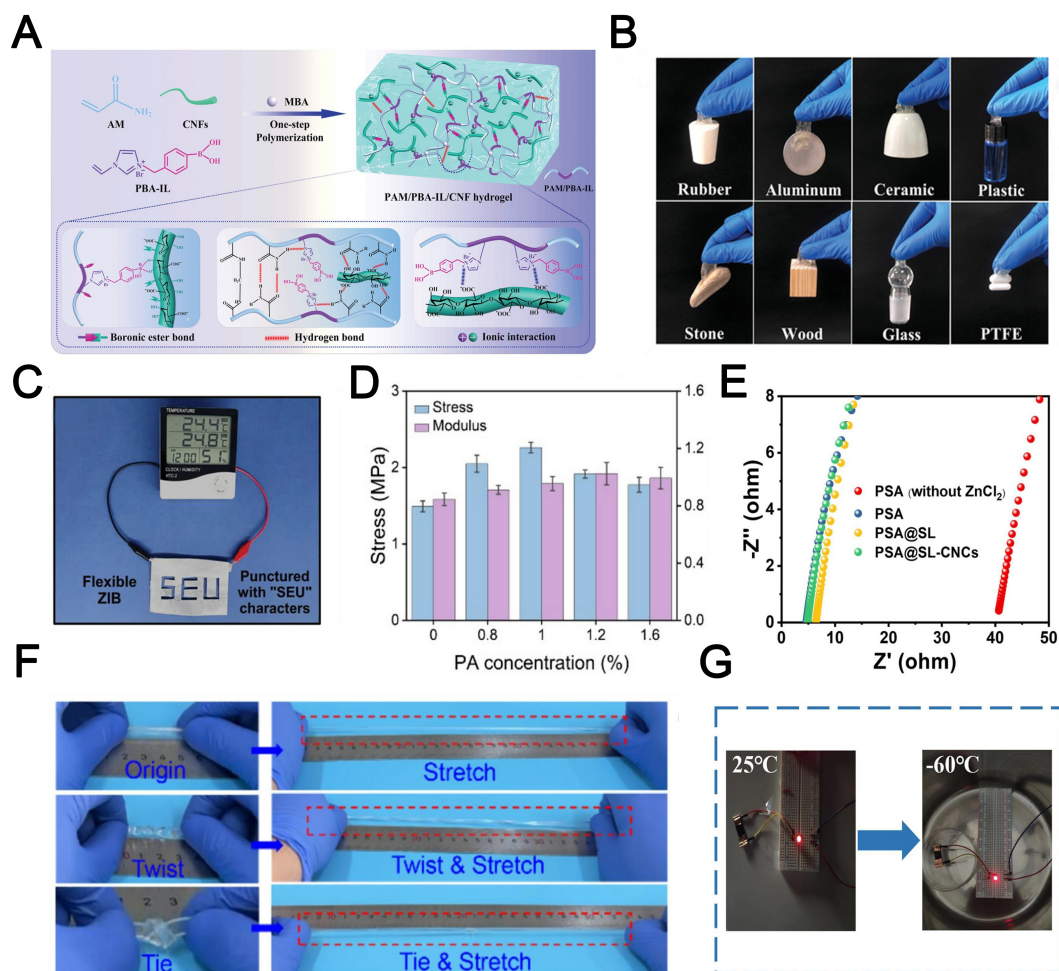




**Figure 3.** (A) Preparation of the TOCNF-GN/PAA composite hydrogels<sup>[52]</sup>; (B) Demonstration of the excellent self-healing ability, stretchability, and flexibility of the hydrogels<sup>[52]</sup>; (C) Compressive stress-strain curve of the PAM-co-HEA hydrogel<sup>[53]</sup>; (D) EIS spectra of the hydrogels with varying CNT content<sup>[53]</sup>; (E) Photographs of the hydrogel under bending, knotting, twisting, and stretching conditions<sup>[53]</sup>; (F) Photographs of the LM/CNT hydrogel applied to the finger pulp and wrist<sup>[54]</sup>; (G) Photographs of the LM/CNT hydrogel before and after stretching<sup>[54]</sup>; (H) Schematic of the synthesis process for anisotropic bamboo template (ABT) and polypyrrole (PPy) bamboo-based/polyacrylamide hydrogel (PBPH)<sup>[61]</sup>; (I) Schematic synthesis of the composite hydrogels<sup>[63]</sup>; (J) Conductivity of the PAM/OM composite hydrogels<sup>[63]</sup>. TOCNFs-GN/PAA: 2,2,6,6-tetramethylpiperidine-1-oxyl radical-oxidized cellulose nanofibers-GN nanocomposites into PAA; PAM-co-HEA: polyacrylamide-co-hydroxyethyl acrylate; PAA: polyacrylic acid; CNT: carbon nanotube; LM: liquid metal; OM: oxidized MXene; EIS: electrochemical impedance spectroscopy.

### Ion conductive hydrogels

Ion-conductive hydrogels (ICHs) are typically synthesized by integrating salt solutions<sup>[66]</sup>, polyelectrolytes<sup>[67]</sup>, or ionic liquids<sup>[68]</sup> into the hydrogel matrix. The 3D network of the hydrogel provides channels to facilitate ion transport, endowing the material with enhanced conductivity. Because of their superior ionic conductivity and chemical durability, ICHs are extensively used in flexible electronics, electrochemical energy storage, catalytic transistors, and other applications<sup>[69]</sup>. However, their brittle mechanical properties and limited moldability still seriously hinder their broader applications<sup>[70]</sup>. To address this, Cui *et al.*<sup>[71]</sup> demonstrated the synergistic effects of cations and anions in toughening the mechanical properties of ICHs, offering new perspectives for network design and functional optimization. In addition, Yao *et al.*<sup>[72]</sup> developed a multifunctional ICH using a phenylboronic acid-ionic liquid (PBA-IL)-based system, enhancing its application potential. This semi-interpenetrating network hydrogel was synthesized by integrating cellulose nanofibrils (CNF) into a PBA-IL/acrylamide cross-linked network through a straightforward one-step process [Figure 4A]. Ingeniously, the dynamic borate ester bonds, along with hydrogen and electrostatic interactions within the cross-linked network, imparted the hydrogels with remarkable stretchability ( $1,810 \pm 38\%$ ), self-healing efficiency ( $92 \pm 2\%$ ), and adhesion [Figure 4B]. The



**Figure 4.** (A) Fabrication mechanism and dynamic networks of the PAM/PBA-IL/CNF hydrogel<sup>[72]</sup>; (B) Adhesive properties of the PAM/PBA-IL/CNF hydrogel<sup>[72]</sup>; (C) A flexible Zn ion battery with "SEU" characters punctured, capable of powering the thermo-hygrometer<sup>[73]</sup>; (D) Profile of stress and elastic modulus of PVA/PA hydrogels with different contents of PA<sup>[67]</sup>; (E) EIS spectra of PAD@SC<sup>[76]</sup>; (F) Photographs of the POIG hydrogel under stretching, torsion stretching, and knot stretching states<sup>[78]</sup>; (G) LED brightness with the PGI20M0.65G hydrogel as the conductor at room temperature and after freezing at  $-60^\circ\text{C}$ <sup>[79]</sup>. PAM: Polyacrylamide; PBA-IL: phenylboronic acid-ionic liquid; CNF: cellulose nanofibrils; PVA: polyvinyl alcohol; PAD@SC: poly (acrylic acid-co- 3-dimethyl (methacryloyloxyethyl) ammonium propane sulfonate) hydrogel incorporated with sodium lignosulfonate and cellulose nanocrystals; PA: phytic acid; EIS: electrochemical impedance spectroscopy; POIG: polymeric organic-ionic gel; LED: light emitting diode.

incorporation of CNF effectively synergized the enhancement of both mechanical strength and ionic conductivity.

To improve their ionic conductivity, water-based hydrogels are usually swelled with saline solutions. However, this often hinders their intimate interaction with electrodes and diminishes their mechanical characteristics. To address this, Xia *et al.*<sup>[73]</sup> developed a zinc-ion conductive hydrogel electrolyte by incorporating a PAM network with a pseudo-polyurethane structure. At ambient temperature, this hydrogel electrolyte demonstrated an ionic conductivity of  $22.4\text{ mS cm}^{-1}$ , a high  $\text{Zn}^{2+}$  transference number of 0.923, and can power a hygrometer [Figure 4C]. In addition to their mechanical properties, hydrogels face limitations in operating across a broad temperature range due to issues such as severe dehydration, deionization, and freezing, *etc.*<sup>[74]</sup>. For instance, Zhu *et al.*<sup>[67]</sup> developed a self-assembled 3D polysaccharide network with different contents of phytic acid (PA) to improve the mechanical properties of conductive



hydrogels, enhancing freeze resistance and water retention. PA acted as a multifunctional cross-linker, forming a robust network through ion-dipole interactions and hydrogen bonding, addressing the brittleness and low conductivity of glycerol-solvent hydrogels. The hydrogel exhibited impressive mechanical performance with a maximum stress of 2.26 MPa, 0.95 MPa modulus, and  $3.59 \text{ S m}^{-1}$  conductivity [Figure 4D]. Moreover, it demonstrated a wide operational temperature range down to  $-48^\circ\text{C}$  and maintained flexibility for 7 days.

In addition, constructing ICHs with ionic group-containing polymers is a promising strategy. Notably, zwitterionic hydrogels excel in ion transport dynamics, offering high migration numbers and conductivity through their rapid anion-cation channels<sup>[75]</sup>. Liu *et al.*<sup>[76]</sup> developed self-adhesive hydrogel electrolytes (PAD@SC) by copolymerizing AA with the zwitterionic monomer sulfonated betaine. The incorporation of bio-based lignosulfonate and nanocellulose facilitated the reconstruction of a robust non-covalent hydrogen bond network, significantly enhancing mechanical properties. The resulting PAD@SC hydrogel exhibited a remarkably high  $\text{Zn}^{2+}$  transference number ( $t_{\text{Zn}^{2+}} = 0.87$ ) and ionic conductivity of  $43.2 \text{ mS cm}^{-1}$  [Figure 4E].

In addition to utilizing salt solutions and ionic group-containing polymers, ionic liquids, which are low-melting organic salts, present a promising approach for fabricating ICHs. Ionic liquids are distinguished by their remarkable properties, including high ionic conductivity, robust electrochemical stability, an expansive electrochemical potential window, and potent antibacterial properties<sup>[77]</sup>. For instance, Zhang *et al.*<sup>[78]</sup> developed an innovative polymeric organic-ionic gel (POIG), combining a polyvinyl alcohol (PVA)/ethylene glycol (EG) dual-polymer network with ionic liquids. This gel has remarkable extensibility (820%) [Figure 4F] and tensile strength (3.01 MPa). POIG outperforms commercial foams by five times in high-speed impacts ( $1.4 \text{ kJ m}^{-1}$ ) and dissipates over 90% of energy at low speeds, demonstrating superior performance in both low and high-speed impacts. The integration of ionic liquids ensures a stable, uniform conductive structure, resulting in rapid response times ( $\sim 10 \text{ ms}$ ), ultra-low strain responsiveness (0.2%), and excellent sensing capabilities. ICHs typically require high liquid content to attain superior conductivity, but this compromises their mechanical integrity. Conversely, reinforcing the hydrogel network to improve mechanical properties can impede ion migration. Finding the ideal balance between conductivity and mechanical strength remains a critical challenge.

### Electro-ionic composite conductive hydrogel

Besides electronic and ICHs, some studies have integrated both types to develop hydrogels with dual transport capabilities. For instance, Wan *et al.*<sup>[79]</sup> incorporated MXene and ionic liquids into a gelatin/PAM precursor solution. The flexible strain sensors, based on a PAM/gelatin/ILs/MXene/glycerol (PGIMG) hydrogel, utilized a dual electronic-ionic conductive network created through electrohydrodynamic printing and in-situ photopolymerization. Ionic liquids provided ionic conduction, while MXene nanosheets formed an interpenetrating network with gelatin and PAM, enhancing both mechanical and sensing performance. The PGIMG hydrogel exhibited a tensile strength of 0.21 MPa at 602.82% strain, high sensitivity (sensitivity factor = 4.17), and high conductivity of  $1.636 \times 10^{-3} \text{ S cm}^{-1}$ . Moreover, the glycerol further imparted excellent freeze resistance (at  $-60^\circ\text{C}$ ) and water retention [Figure 4G]. In addition, Zhao *et al.*<sup>[80]</sup> also developed a novel dual-network (DN) ICH system, combining poly(vinyl alcohol) (PMP DN ICH), MXene, and poly(ionic liquid) using freeze-thaw cycles and ionizing radiation. The ICH demonstrated remarkable ionic conductivity ( $63.89 \text{ mS cm}^{-1}$  at  $25^\circ\text{C}$ ), exceptional thermal stability ( $-60^\circ\text{C}$  to  $80^\circ\text{C}$ ), long-term durability (30 days at ambient temperature), and notable antioxidant and antibacterial properties, alongside superior mechanical strength and adhesion. The PMP DN ICH electrolyte demonstrated remarkable environmental adaptability when utilized in solid-state SCs, achieving an excellent areal capacitance of  $253.38 \text{ mF cm}^{-2}$  at  $1 \text{ mA cm}^{-2}$ .

In summary, composite conductive hydrogels often demonstrate conductivity several orders of magnitude higher than that of ICHs<sup>[81]</sup>. The integration of conductive fillers within the hydrogel matrix, coupled with advanced fabrication techniques and design strategies tailored to specific applications, plays a pivotal role in enhancing their conductivity, mechanical robustness, and other performance attributes.

Conductive hydrogels combine the unique advantages of conductive materials and water, giving them excellent electronic properties, adjustable mechanical flexibility, and easy processing characteristics. And many researchers are constantly optimizing the performance of conductive hydrogels and expanding the application scenarios of conductive hydrogels. However, due to their inherent properties, they still face many challenges in terms of conductivity, mechanical strength, stability and processing adaptability, such as the problem that hydrogels are easy to lose water in the air, insufficient chemical stability under actual working conditions such as alkalinity/acidity/high temperature, and the conflict between conductivity and mechanical properties. These problems seriously restrict their development. In order to solve the above problems, it is urgent to carry out systematic research in material design, structural optimization, and process control.

### 3D PRINTING TECHNOLOGY IN HYDROGEL PREPARATION

The technology, 3D printing, commonly known as additive manufacturing, is a process that constructs objects layer by layer from digital models. It enables the rapid, highly precise fabrication of complex structures, with exact control over design and production facilitated by advanced computer-aided design/manufacturing (CAD/CAM) systems<sup>[82]</sup>. In contrast to traditional manufacturing techniques, 3D printing offers superior operational ease, exacting structural precision, and cost efficiency. This method enables the creation of highly customized, intricate 3D structures with diverse functions and high resolution. Recent advancements in 3D-printed hydrogels have demonstrated considerable potential in applications such as SCs, batteries, and wearable electronics. Advancements in post-processing methods, printable materials, and structural design continuously enhance the performance of flexible electrochemical energy storage devices.

#### Preparation methods

The 3D printing technology has rapidly advanced in recent years, driven by its mold-free nature and versatile capabilities for customized structural design. Depending on material deposition methods, curing processes, and bonding mechanisms, there are seven different types of 3D printing: (i) Material extrusion [e.g., direct ink writing (DIW), fused deposition modeling (FDM)]; (ii) Material jetting [e.g., inkjet printing (IJP)]; (iii) Photopolymerization [e.g., stereolithography (SLA), digital light processing (DLP)]; (iv) Powder Bed Fusion [e.g., selective laser melting (SLM), selective laser sintering (SLS)]; (v) Sheet Lamination [e.g., laminated object manufacturing (LOM)], *etc.* Each of these 3D printing methods possesses unique characteristics and advantages, such as material options, speed, resolution, and cost, making them appropriate for a range of uses<sup>[83,84]</sup>. The successful 3D printing of conductive hydrogels has been well demonstrated by recent investigations employing cutting-edge methods including DIW, DLP, SLA, and FDM, with significant applications in areas such as flexible energy and electronics, biosensors, and soft robotics<sup>[35]</sup>. As shown in Table 2, a thorough analysis of the most recent developments in the 3D printing of conductive hydrogels was carried out in this section.

#### DIW

DIW, an extrusion-based 3D printing technique, employs a three-step fabrication process: (1) formulation of a viscoelastic ink system exhibiting well-defined yield stress properties; (2) controlled extrusion of the ink through micron-scale nozzles under precisely regulated pressure to generate continuous filaments; and (3)

**Table 2. Summary of 3D printing technologies for conductive hydrogel fabrication**

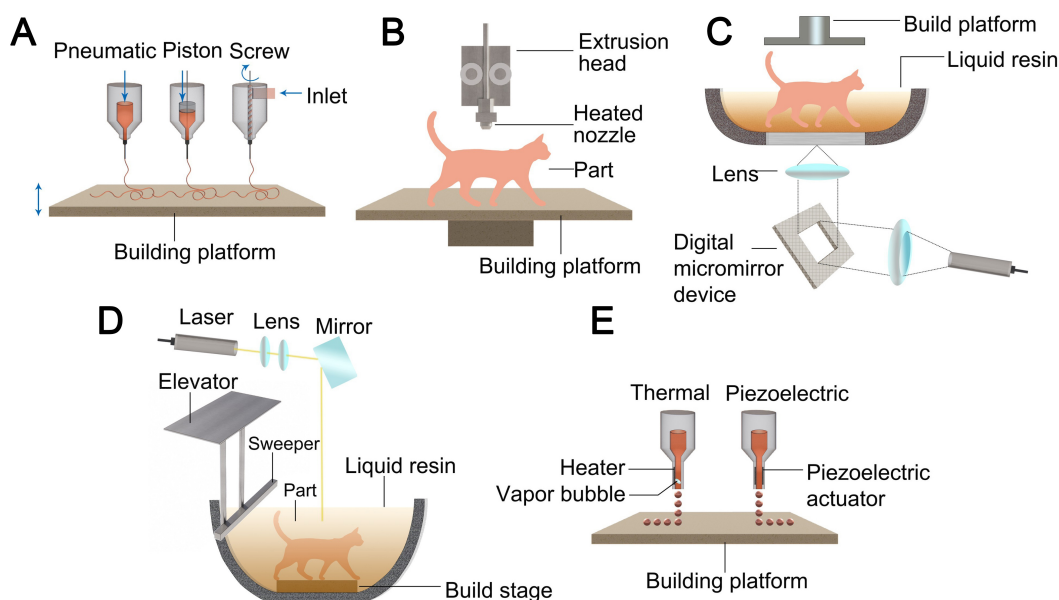
| 3D printing technology | Materials                                                        | Layer thickness ( $\mu\text{m}$ ) | Advantages                                       | Disadvantages                                      | Ref.        |
|------------------------|------------------------------------------------------------------|-----------------------------------|--------------------------------------------------|----------------------------------------------------|-------------|
| DIW                    | Ceramics, composites, polymers, tissues                          | 50-300                            | Fast, adaptable, and devoid of support materials | Low resolution, postprocess                        | [85-87]     |
| FDM                    | Thermosets, glass, metals                                        | 50-200                            | Fast, affordable, simple, versatile              | Poor mechanical strength, limited materials        | [88,89]     |
| IJP                    | Ceramics, metals, polymers                                       | 1-200                             | Fast printing, large-scale printing              | Low resolution, poor adhesion between layers       | [90]        |
| SLA                    | UV-curing resins or photopolymers with ceramics & nanocomposites | 1-50                              | Microscale resolution, high structural fidelity  | Limited supplies, sluggish printing, and expensive | [91,92]     |
| DLP                    | Photosensitive resin, photopolymers                              | 1-50                              | Microscale resolution, high structural fidelity  | Limited supplies, sluggish printing, and expensive | [81,93, 94] |

3D: Three-dimensional; DIW: direct ink writing; FDM: fused deposition modeling; IJP: inkjet printing; SLA: stereolithography; DLP: digital light processing; UV: via ultraviolet.

layer-by-layer deposition of 3D architectures guided by CAD/CAM systems [Figure 5A]. The manufacturing process involves coordinated motion control, where the printhead executes programmed trajectories in the XY plane while the build platform undergoes controlled displacement along the Z-axis, enabling the sequential construction of complex 3D structures<sup>[95]</sup>.

The printing resolution of this technology is primarily determined by three key factors: nozzle geometry, extrusion pressure, and the rheological properties of the ink. Among these, the rheological behavior of the ink plays a critical role in influencing printing outcomes, with essential parameters including yield stress ( $\sigma_y$ ), storage modulus ( $G'$ ), loss modulus ( $G''$ ), and apparent viscosity ( $\eta$ ). Yield stress, in particular, serves as a pivotal indicator, regulating both the extrusion flow rate and the structural stability of the printed material, and thus directly determining the material's printability. When the applied stress is below  $\sigma_y$ , the ink exhibits solid-like elastic behavior; once this critical threshold is exceeded, a solid-to-liquid transition occurs, enabling controlled flow. The ink's viscosity ( $\eta = \tau / \dot{\gamma}$ ) defined as the ratio of shear stress ( $\tau$ ) to shear rate ( $\dot{\gamma}$ ) reflects its internal flow resistance dominated by intermolecular interactions. Studies have shown that excessively low viscosity ( $< 10^4$  mPa·s) can result in filament breakage and structural instability, whereas excessively high viscosity ( $> 10^8$  mPa·s) may cause nozzle clogging and significantly increase energy consumption. Therefore, an ideal DIW ink should possess three essential rheological characteristics: a moderate yield stress (10-1,000 Pa) to ensure shape retention, pronounced shear-thinning behavior (viscosity decreasing with shear rate) to facilitate extrusion, and excellent thixotropy (enabling rapid structural recovery upon cessation of shear) for post-printing stability<sup>[95]</sup>.

DIW technology exhibits significant advantages in the fabrication of functional materials. First, its material utilization efficiency exceeds 95%, markedly outperforming traditional subtractive manufacturing methods. Second, it enables the construction of composite systems incorporating diverse functional components, such as nano-conductive particles, carbon-based fibers, and ionic hydrogels. Third, the equipment costs associated with DIW are approximately 30%-50% lower than those of other 3D printing technologies. By precisely regulating the viscoelastic properties of precursor solutions and controlling curing kinetics, DIW facilitates the fabrication of functional hydrogels with complex 3D topological structures<sup>[14]</sup>. Nevertheless, a major technical bottleneck remains: the development of functional inks that can simultaneously satisfy stringent criteria, including high solid content ( $> 20$  wt%), well-controlled rheological behavior (viscosity in the range of  $10^6$ - $10^8$  cP), and stable extrusion performance<sup>[95]</sup>.



**Figure 5.** Schematic overview of the light- and ink-based 3D printing techniques. (A) DIW printing<sup>[22,27]</sup>; (B) FDM printing<sup>[22,27]</sup>; (C) DLP printing<sup>[23,27]</sup>; (D) SLA printing<sup>[25,27]</sup>; (E) Inkjet printing<sup>[26,27]</sup>. DIW: Direct ink writing; FDM: fused deposition modeling; DLP: digital light processing; SLA: selective laser sintering.

There have been recent developments in the creation of functional inks. Yu *et al.*<sup>[96]</sup> innovatively constructed a CPH system based on a PVA matrix. By integrating PEDOT: PSS conductive networks and ionic liquid plasticizers, they successfully formulated a multifunctional, 3D-printable ink. Benefiting from its unique structural design, the system demonstrates significantly enhanced performance: an electrical conductivity of  $1.2 \text{ S}\cdot\text{m}^{-1}$  (two orders of magnitude greater than traditional hydrogels), a reduced interfacial impedance of  $20 \text{ }\Omega$ , a fracture elongation reaching 349%, a toughness of  $109 \text{ kJ}\cdot\text{m}^{-3}$ , and an interfacial adhesion strength exceeding  $1 \text{ MPa}$ . Bioelectronic interface devices fabricated using DIW technology effectively overcome the technical limitations associated with conventional fabrication processes, achieving high micro-patterning precision ( $< 50 \text{ }\mu\text{m}$ ), high device integration levels ( $> 10$  layers), and enabling personalized customization. These developments offer promising solutions for the fabrication of next-generation implantable biosensors and wearable electronics.

### FDM

One of the most popular commercial 3D printing technologies is FDM, which is preferred due to its low cost, patent advantages, fast printing speed, and large-scale manufacturing capabilities. In order for FDM to work, thermoplastic filaments must be heated to a semi-molten state, extruded through a fine nozzle, and rapidly solidified on the build platform to achieve layer-by-layer construction of 3D structures<sup>[97]</sup> [Figure 5B]. Common materials for FDM include polylactic acid (PLA), acrylonitrile butadiene styrene (ABS), polycarbonate (PC), polyamide (PAM), and thermoplastic polyurethane (TPU), all of which must be fabricated into filaments of specific diameters. Although the limited material selection restricts FDM applications in fields such as battery electrode manufacturing, this challenge can be addressed by embedding active materials into thermoplastic matrices to produce composite filaments, thus broadening the application scope. In addition, FDM can be employed to print substrates, which can subsequently be functionalized by post-processing techniques such as electrode or electrolyte deposition. However, compared with DIW, FDM has limited throughput, less flexibility for integrating several materials, and a poorer printing resolution (usually between  $50$  and  $200 \text{ }\mu\text{m}$ ). Unlike DIW, which relies on the preparation

of printable inks, FDM fundamentally depends on the development and processing of composite thermoplastic filaments<sup>[95]</sup>.

### *Photopolymerization*

Photopolymerization-based 3D printing technologies mainly include SLA and DLP, both commonly employing photopolymerizable hydrogels as printing materials. In this approach, UV light initiates the polymerization of photosensitive polymers to form patterns in designated areas, enabling the layer-by-layer construction of 3D structures. SLA achieves complex geometries through point-by-point laser scanning, whereas DLP cures an entire layer simultaneously via digital projection. Despite the high cost, limited mechanical strength, and shrinkage risk associated with photopolymerizable hydrogels, SLA and DLP exhibit significant advantages in fabricating flexible electrochemical energy storage devices with intricate geometries, offering high resolution, rapid printing speeds, the elimination of support structures, and excellent surface quality. Moreover, photopolymer resins suitable for SLA are generally compatible with DLP technology<sup>[35]</sup>.

DLP is an advanced 3D printing technology that constructs 3D structures through the layer-by-layer cross-linking of photopolymerizable monomers [Figure 5C]. Unlike SLA, which uses a point laser, DLP employs a digital projector as the light source, significantly reducing printing time. The printability of DLP is primarily influenced by the photopolymer system, which typically consists of photopolymerizable monomers, photoinitiators, and additives such as light absorbers, pore-forming agents, and plasticizers. Commonly used biocompatible photopolymers, including polyethylene glycol diacrylate (PEGDA), have been successfully applied in DLP printing. PEGDA stands out due to its tunable mechanical and biological properties, with its concentration significantly affecting the fidelity, mechanical strength, and release characteristics of printed samples. The photoinitiator plays a crucial role in determining the wavelength of the photopolymerization reaction, thereby affecting printing efficiency. Light absorbers help delay the polymerization process, enhancing the printability of internal channels. Additionally, pore-forming agents such as polyethylene glycol (PEG) and NaCl promote drug release, while plasticizers such as glycerol improve the flexibility of the printed materials. Given the varying needs for external and internal structures, further investigation into the printability of these components is essential<sup>[98]</sup>. For example, Yin *et al.*<sup>[14]</sup> developed a light-polymerization-based 3D printing technique utilizing the tunable properties of PPAm-PEGDA hydrogel and DLP technology, successfully simplifying the manufacturing process of ionic hydrogel structures. This method offers high sensitivity and low detection limits, providing an efficient and flexible approach for fabricating microstructural devices and serving as a platform for the development of smart electronics and artificial intelligence technologies.

SLA is a photopolymerization-based 3D printing technology that uses UV laser to focus on the surface of a photosensitive resin, which solidifies layer by layer through a precise photochemical curing process to form a 3D model [Figure 5D]. This technique relies on the efficient combination of prepolymers and photoinitiators to ensure rapid curing of the resin under laser exposure, forming a cross-linked network. SLA offers high flexibility in resolution, enabling the production of intricate and detailed structures. However, its application is limited by material selection and cost factors. Despite these limitations, SLA remains highly favored due to its nozzle-free design, high precision, and versatility in industries such as automotive, aerospace, and biotechnology<sup>[95]</sup>. Using riboflavin as the photoinitiator and poly(ethylene glycol) dimethacrylate (PEGDMA) as the encapsulating polymer network, Karakurt *et al.*<sup>[98]</sup> created a unique water-soluble resin chemistry for SLA 3D printing. A viable route for the pharmaceutical industry to use non-toxic 3D printing materials for regulated and customizable drug release systems is provided by the system, which shows 3D-printed hydrogels with a variety of distinct geometries and their corresponding



ascorbic acid release rates.

### *IJP*

IJP, a non-contact extrusion-based technique [Figure 5E], utilizes nozzle-ejected droplets that are rapidly deposited onto substrates to fabricate pre-designed patterns. IJP technology primarily utilizes two distinct droplet generation methods: drop-on-demand (DOD) and continuous inkjet (CIJ) systems. In CIJ printing, a pressurized liquid jet exiting the nozzle undergoes controlled hydrodynamic instability, resulting in the formation of a monodisperse droplet stream. Selective electrostatic charging of individual droplets enables precise trajectory control while facilitating ink recovery and recirculation. However, exposure to the surrounding environment during recycling may lead to contamination of the ink. In DOD inkjet systems, discrete droplet ejection is achieved through precisely controlled pressure pulses generated either by piezoelectric actuator deformation or thermally induced vapor bubble nucleation. The DOD mode is more cost-effective and can produce smaller ink droplets (CIJ droplets range from 20–50  $\mu\text{m}$ , while DOD droplets are typically around 100  $\mu\text{m}$ ), which is highly advantageous for 3D printing manufacturing<sup>[97]</sup>.

IJP technology has proven to be a simple and efficient method for printing a wide variety of materials, including metals, polymers, and ceramics, offering excellent spatial resolution and uniformity for creating diverse geometries. The success of high-quality pattern printing heavily relies on the use of printable inks with specific characteristics, such as viscosity, surface tension, shear yield stress, shear elasticity, and loss modulus. These inks typically consist of active materials, solvents [such as water, N-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), dimethylformamide (DMF), and ethanol], and functional additives to optimize fluid behavior. Stable droplet generation requires careful matching of ejection parameters (velocity, nozzle geometry) with the ink's fluid characteristics to maintain optimal jetting performance<sup>[97]</sup>.

## **ADVANCEMENTS IN 3D PRINTING FOR FLEXIBLE ELECTROCHEMICAL ENERGY STORAGE DEVICES**

With the continuous growth in energy demand and the ongoing challenges in energy supply, efficient and functional flexible energy storage devices have become a major focus of current research. This is particularly true in fields such as wearable electronics and medical devices, where there is an increasing demand for flexible energy storage devices that offer fast charging, high energy density, power density, lightweight properties, and long-term stability. SCs and batteries, as typical representatives of flexible energy storage devices, have their performance significantly influenced by the properties of electrode and electrolyte materials. In this regard, hydrogels, with their exceptional electrical properties and mechanical performance, provide an ideal material foundation for the design of flexible electrochemical energy storage (FEES) devices<sup>[99]</sup>. The 3D printing technologies have recently enabled unprecedented expansion of hydrogel functionality and application scope. Through precise control over structure and function, 3D-printed hydrogels can achieve exceptional attributes such as stretchability, biocompatibility, sensitivity, adhesion, self-healing, and freeze resistance, thereby meeting the requirements of various application scenarios. This technology also increases the surface area, improving electrochemical reaction efficiency. This section delves into the advancements of 3D-printed hydrogels in SCs and batteries, highlighting their potential to create efficient, multifunctional FEES devices and exploring their broad prospects in the future of energy storage and conversion<sup>[83,84]</sup>.

### **Supercapacitors**

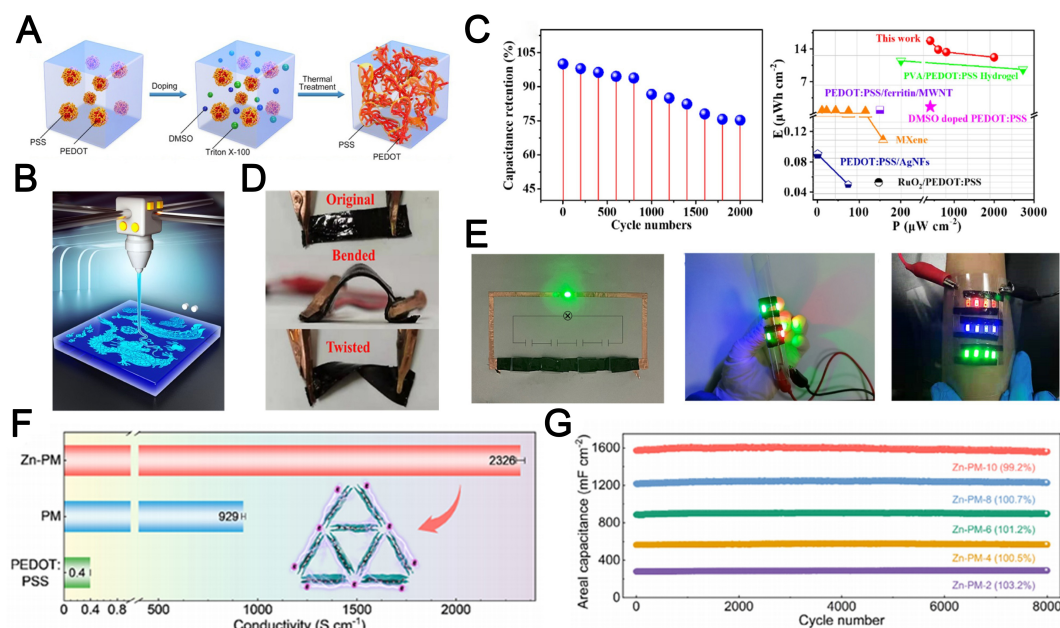
The rapid miniaturization, integration, and intelligence of electronic devices have significantly increased the demand for high-energy-density, exceptional power density, long cycle life, and customizable micro-supercapacitors<sup>[21]</sup>. SCs are typically classified into electric double-layer capacitors, which store charge

via electrostatic adsorption, and pseudocapacitors, which use fast, reversible redox reactions. While current flexible electrode materials and hydrogel electrolytes demonstrate promising mechanical properties, their electrochemical performance still requires optimization<sup>[100]</sup>. The fabrication and integration of electrodes and electrolytes play a pivotal role in enhancing the performance of flexible electrochemical energy storage devices, such as SCs and batteries. Conventional manufacturing techniques often face limitations in controlling the geometry and microstructure of these components, leading to performance inefficiencies. In contrast, 3D printing offers a revolutionary approach, enabling precise manipulation of device geometry, such as size, porosity, and morphology, which leads to substantial improvements in specific energy and power density. 3D printing can finely control the thickness of electrodes, streamlining production while minimizing costs. Moreover, the ability to integrate multiple nanomaterials within a single printed structure further enhances the multifunctionality and performance of flexible electrochemical energy storage devices, positioning 3D printing as a transformative technology in energy storage applications<sup>[2,101]</sup>.

### *3D printing of hydrogels for supercapacitor electrodes*

Nowadays, electrode materials based on metal oxides, conductive polymers, and electroactive carbon-based materials are used mainly in the fabrication of flexible SCs. When compared to metal oxides, conductive polymers, including PANI, PPY, and PEDOT: PSS, provide better conductivity and flexibility. Moreover, they can achieve higher capacitance and energy density than carbon-based materials due to their Faradaic pseudocapacitance. Conductive polymers are therefore frequently seen in flexible SCs. While conventional conductive polymers offer numerous advantages, their mechanical flexibility is inherently constrained by rigid  $\pi$ -conjugated backbones. More critically, these materials require exogenous structural support due to insufficient freestanding mechanical stability when deployed as flexible SC electrodes. Unfortunately, these substrates lack electrochemical activity and occupy significant volume and mass, reducing the overall specific capacitance and energy density and adding extra costs while complicating integration. Additionally, due to the mismatch in Young's modulus between the electrode materials and the substrate, the deformability of these SCs is severely limited by inevitable dislocations at the electrode-substrate interface. To construct high-capacity and highly deformable SCs, substrate-free SCs present a promising and feasible solution. The key challenge lies in developing independent electrode materials that exhibit both high conductivity and mechanical stretchability<sup>[21]</sup>.

Unlike traditional conductive polymers, CPHs achieve self-supporting capabilities and maintain mechanical deformation without the need for an external substrate, thanks to the gelation process. This renders CPHs highly suitable for developing standalone SCs with high capacity and mechanical deformability. For example, Cheng *et al.*<sup>[21]</sup> proposed a dual-additive gelation strategy for fabricating high-performance PEDOT: PSS hydrogels with intrinsic conductivity [Figure 6A]. By physically cross-linking the conductive PEDOT nanofibrils, these hydrogels exhibited enhanced conductivity ( $\approx 3,000 \text{ S}\cdot\text{m}^{-1}$ ), low Young's modulus ( $\approx 2.8 \text{ MPa}$ ), mechanical stretchability ( $\approx 55\%$ ), and 3D printability [Figure 6B]. Owing to their high conductivity, distinctive layered architecture, and outstanding mechanical performance, the PEDOT: PSS hydrogel-based SCs demonstrated excellent energy storage ( $\approx 15.7 \mu\text{Wh}\cdot\text{cm}^{-2}$  energy density,  $\approx 400 \mu\text{W}\cdot\text{cm}^{-2}$  power density) [Figure 6C], a high areal capacitance ( $\approx 177 \text{ mF}\cdot\text{cm}^{-2}$ ), and stable electrochemical performance after 1000 bending cycles [Figure 6D], showcasing exceptional deformability and elasticity [Figure 6E]. Additionally, Meng *et al.*<sup>[102]</sup> developed high-mass-loading  $\text{Zn}^{2+}$ -PEDOT: PSS/MXene (Zn-PM) gel electrodes for zinc-ion hybrid micro-supercapacitors (ZHMSCs) using DIW 3D printing. The synergistic interaction between PEDOT: PSS and MXene enabled printable inks with ultra-high mass loading ( $32.2 \text{ mg cm}^{-2}$ ) and excellent shape fidelity.  $\text{Zn}^{2+}$  coordination, MXene doping, and freeze-thaw treatment formed a continuous 3D conductive porous network with high conductivity ( $2,326 \text{ S cm}^{-1}$ ) [Figure 6F] and fast ion transport. The resulting quasi-solid-state ZHMSC delivered an areal capacitance of



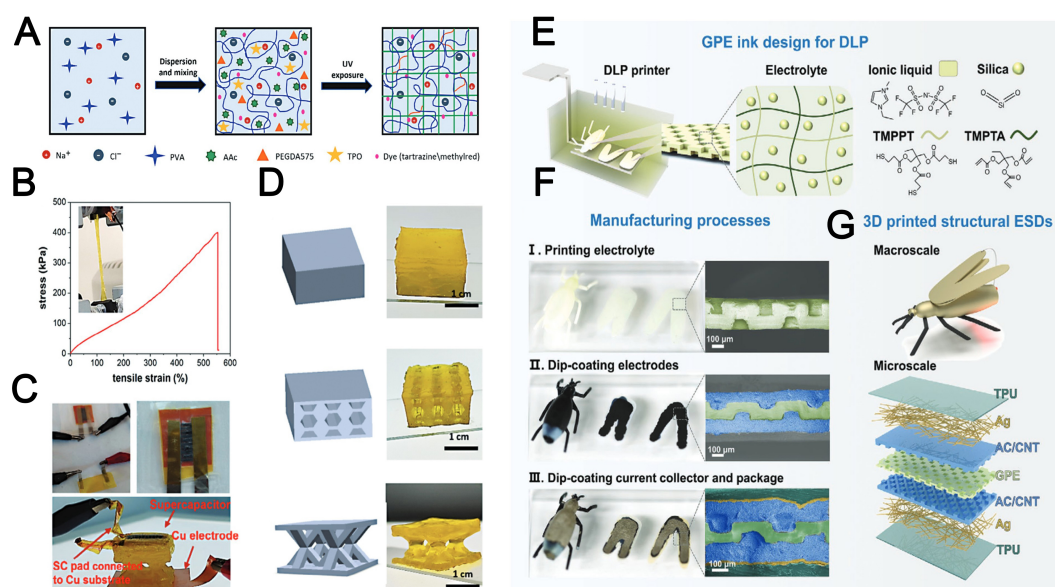
**Figure 6.** (A) Schematic illustration of the gelation mechanism for PEDOT:PSS hydrogels<sup>[21]</sup>; (B) Diagram of the extrusion-based 3D printing process<sup>[21]</sup>; (C) Cyclic stability and Ragone plot of supercapacitors based on PEDOT:PSS hydrogels<sup>[21]</sup>; (D) Photographs of the original, bent, and twisted supercapacitors<sup>[21]</sup>; (E) Wearable demonstrations of the supercapacitors based on PEDOT:PSS hydrogels connected in series<sup>[21]</sup>; (F) Electrical conductivity of PEDOT:PSS, PM gel composite, and Zn-PM gel composite<sup>[102]</sup>; (G) Cycling stability of Zn-PM ZHMSCs with different printing layers at  $20 \text{ mA cm}^{-2}$ <sup>[102]</sup>. PEDOT:PSS: Poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate); ZHMSCs: zinc-ion hybrid micro-supercapacitors.

$2,179 \text{ mF cm}^{-2}$  and energy density of  $333.6 \mu\text{Wh cm}^{-2}$ , and  $\approx 100\%$  capacitance retention after 8,000 cycles [Figure 6G].

### 3D printing hydrogels for supercapacitor electrolytes

As a key component of SCs, electrolytes critically determine the operating voltage window, which in turn governs the achievable energy density. Therefore, precise design and adjustment of the electrolyte are essential. Currently, the stable operating voltage of aqueous electrolytes is typically limited by the thermodynamic decomposition voltage of water ( $1.23 \text{ V}$ ). Organic electrolytes ( $\geq 2 \text{ V}$ ) and ionic liquids ( $\geq 3 \text{ V}$ ) offer higher voltage windows. While these expand the operating range, organic electrolytes present serious safety risks due to their high flammability and volatility, while ionic liquids suffer from high cost and low ionic conductivity, limiting their widespread use. As a result, ongoing research focuses on exploring novel electrolytes that provide superior performance compared to traditional alternatives<sup>[103]</sup>.

Mogli *et al.*<sup>[104]</sup> explored a photopolymerized hydrogel based on a semi-interpenetrating polymer network [Figure 7A] that demonstrates excellent sensitivity to mechanical deformation. This material demonstrates outstanding mechanical performance, including an ultimate tensile strain of  $550\%$  [Figure 7B], and has spontaneous self-healing capabilities [Figure 7C]. It can be used to 3D-print complex-shaped strain sensors [Figure 7D] with significantly enhanced mechanical stress sensitivity, achieving a special pressure detection limit below  $1 \text{ Pa}$ . The hydrogel was also utilized as an electrolyte in laser-induced GN-based SCs, forming a fully integrated, self-powered strain sensor system. Liu *et al.*<sup>[105]</sup> proposed a novel electrolyte-related 3D energy storage device (ESD) fabrication strategy, where an electrolyte template is first printed using DLP, followed by sequential coating of electrode, current collector, and encapsulation materials [Figure 7E]. This method enables customization of the device's external geometry and optimization of its internal structure



**Figure 7.** (A) Schematic illustration of the composition and fabrication process of the ionically conductive PVA/AAC/NaCl hydrogel<sup>[104]</sup>; (B) Tensile curve of 3D-printed dumbbell sample (at a tensile test velocity of 10 mm min<sup>-1</sup>)<sup>[104]</sup>; (C) Images of the integrated device featuring two different configurations. At the top, a pouch-sealed supercapacitor and sensor connected via electrical terminals (left), alongside a close-up view of the sealed LIG-hydrogel supercapacitor (right). At the bottom, the supercapacitor is encapsulated directly on the top electrode of the sensor<sup>[104]</sup>; (D) Printed compression specimens (bulk, honeycomb, stars) and their STL models<sup>[104]</sup>; (E) Schematic illustration of the GPE printing setup and its key compositional elements<sup>[105]</sup>; (F) Optical images and false-colored cross-sectional SEM micrographs of the samples captured at various stages of the dip-coating process<sup>[105]</sup>; (G) Schematic of customizable external geometry and internal 3D interdigitated architecture of 3D-printed EDLSCs<sup>[105]</sup>. PVA: Polyvinyl alcohol; 3D: three-dimensional; LIG: laser-induced graphene; STL: standard tessellation language; GPE: gel polymer electrolyte; SEM: scanning electron microscope; EDLSCs: electric double layer supercapacitors.

via 3D cross-sectional design. Using SCs as prototype devices, the internal 3D cross-configuration between the electrodes and electrolytes demonstrated a 3D-printed ESD with an areal capacitance of 282.7 mF cm<sup>-2</sup>, outperforming the reference device using a planar stacking configuration (205.5 mF cm<sup>-2</sup>) with the same mass loading. Thanks to the high customization capabilities of DLP printing and the conformal deposition characteristics of the dip-coating process, various 3D ESDs with customizable shapes have been proven to integrate with other electronic devices, enabling weight reduction and miniaturization [Figure 7F and G]. Kil *et al.*<sup>[106]</sup> developed a self-charging solid-state SC (SPSC) with an integrated microneedle glucose sensor. The SPSC uses a hydrogel electrolyte layer based on PVA and phosphoric acid, which not only provides an ion conduction channel but also gives the device good flexibility and mechanical stability, allowing it to maintain stable performance during repeated deformation. In an 11 mM glucose solution, the system achieved a power density of 0.62 mW/cm<sup>2</sup> and a high specific capacitance of 1,600 F/g. Pazhamalai *et al.*<sup>[107]</sup> designed a self-charging SC power supply unit (SCSPC) that integrates energy collection, conversion, and storage. It introduces a polyelectrolyte-type ICH, Nafion, as a solid electrolyte and diaphragm. Using its excellent ionic conductivity and piezo-ionic effect, it can generate an output voltage of up to 910 mV under mechanical stress, realizing the self-charging capability of the device (maximum self-charging voltage reaches 243 mV).

#### Design of 3D-printed supercapacitor configurations

In-plane solid-state SCs are considered promising candidates for fully printed solid-state energy devices, offering advantages such as fast charge/discharge rates, high-frequency response, long cycle life, operational stability in ambient conditions, and shape-factor-free fabrication. To date, various 3D-printable electrode



materials have been investigated primarily to enhance the energy density of vertically assembled SC devices. However, despite significant advancements in electrode materials, other component layers, such as metal current collectors and solid-state electrolytes, have seldom been reported as 3D-printable materials. Despite significant advances in 3D-printed electrode materials, realizing fully 3D-printed SC devices remains a considerable challenge. Fully 3D-printed SC devices have yet to be demonstrated in structures with arbitrary designs.

Chae *et al.*<sup>[108]</sup> developed a unique strategy for on-demand shaping of energy storage units through a 3D printing process involving nozzle-based metal current collectors, carbon electrodes, and ionic liquid electrolyte fluids. By combining 3D printing and 3D laser sintering techniques, they created Ni metal current collectors that can operate stably under high-voltage conditions (up to 3V). GN nanoplatelet-based electrode fluids and UV-curable ionic liquid-based electrolyte fluids were continuously printed onto the top of the 3D-structured current collectors. The results demonstrated that the fully 3D-printed micro SC devices exhibited energy densities ranging from 25.4  $\mu\text{Wh cm}^{-2}$  to 8.5  $\mu\text{Wh cm}^{-2}$  and power densities from 150  $\mu\text{Wh cm}^{-2}$  to 6,483  $\mu\text{W cm}^{-2}$ .

## Batteries

To improve the overall performance of batteries, including critical metrics such as energy density, volumetric energy density, power density, cycle life, and safety, it is essential to design and fabricate different battery modules, including cathodes, anodes, electrolytes, and separators. We will look at the existing printed battery modules from an architectural standpoint in this part. A single battery module requires specific characteristics, such as mechanical strength, high electronics, and ionic conductivity. Selecting and combining suitable 3D printing technologies and materials is essential to ensure they meet these requirements. The development of novel functional nanomaterials for electrochemical energy storage into printable materials for particular 3D printing technologies is unquestionably crucial for the growth of batteries and other energy storage technologies, given the rapid increase in the quantity of these materials<sup>[95]</sup>.

Rechargeable electrochemical batteries (REBs) play an essential role in energy storage and transmission by effectively converting electrical and chemical energy through electron and ion transfer in the electrodes. The electrochemical characteristics of the electrode materials and the macro/microstructure of the electrode/electrolyte interface are the main determinants of REB performance. In recent years, 3D printing technology has been widely used in the fabrication of REB electrodes and electrolytes. These materials can be categorized into lithium-based, sodium-based, metal-based, and carbon-based materials. For example, lithium-based materials such as  $\text{LiCoO}_2$  and  $\text{LiMn}_2\text{O}_4$ , and sodium-based materials such as  $\text{Na}_3\text{V}_2\text{P}_3\text{O}_{12}$  are widely used for 3D-printed electrodes, while carbon-based materials are widely applied as additives in various battery systems. Despite significant advancements in 3D-printed battery materials, traditional 2D coated electrodes have not fully exploited the potential of these materials<sup>[97]</sup>. Conventional planar electrodes typically lead to longer ion transport distances and smaller interface areas, which diminishes electrochemical performance. As a result, 3D-structured electrodes featuring porous microstructures have gained significant importance, providing shorter diffusion pathways and larger interface areas<sup>[1]</sup>. This highlights the importance of designing and fabricating 3D electrodes and electrolytes for the progress of battery technologies<sup>[109]</sup>.

### 3D printing hydrogels for battery electrodes

The emergence of flexible and stretchable electronics has created a need for stretchable electrodes that possess outstanding mechanical durability and consistent electrochemical performance. Numerous initiatives have been undertaken to achieve this goal. For example, Qu *et al.*<sup>[110]</sup> prepared stretchable metal



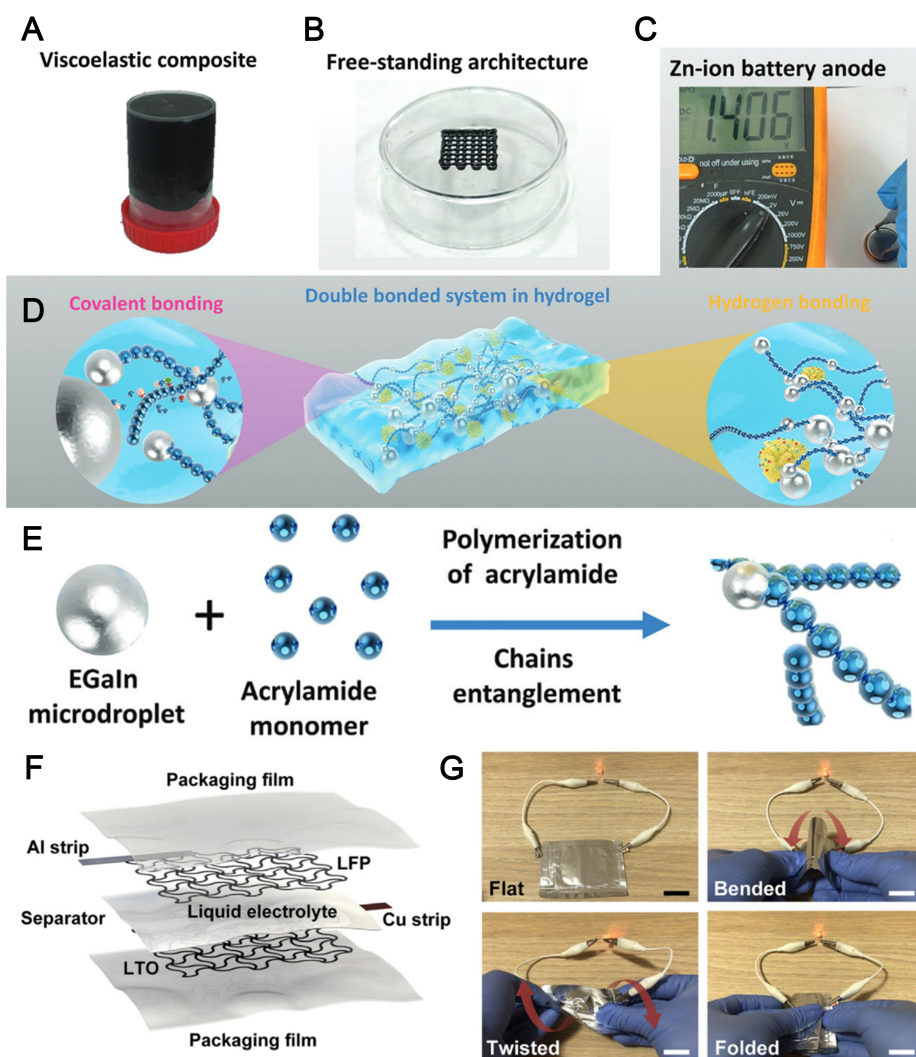
(zinc or nickel)-coated polyurethane sponge electrodes by a two-step deposition method, and Yu *et al.*<sup>[111]</sup> prepared ultra-stretchable CNT composite electrodes by coating CNT films and active material powders on a bidirectional pre-strained polydimethylsiloxane substrate. Compared with these methods, 3D printing technology can quickly and efficiently generate complex patterns in a plane or 3D space, and through appropriate geometric patterns, inherently hard and brittle materials can be made compliant and deformable. In addition, many studies have prepared 3D-printed conductive inks with various properties and stability, which provides us with a simple and effective solution for manufacturing stretchable electrodes.

Shi *et al.*<sup>[112]</sup> developed a PAM-hemicellulose/EGaIn microdroplet hydrogel [Figure 8A] for 3D printing scaffolds [Figure 8B] and self-healing anodes for zinc-ion batteries (ZIBs, Figure 8C). The hydrogel, initiated by LM, is a dual covalent hydrogen bonding system [Figure 8D] with self-healing and shear-thinning properties [Figure 8E], enabling extrusion-based 3D printing. It prevents short-circuiting by evenly distributing LM microdroplets while serving as a conductive matrix for stable Zn ion deposition during plating/stripping. Bao *et al.*<sup>[113]</sup> found 3D-printed  $\text{LiFePO}_4(\text{LFP})/\text{Li}_4\text{Ti}_5\text{O}_{12}$  (LTO) electrodes to exhibit sustained electrochemical functionality and robust mechanical integrity following multiple stretches. After 100 cycles, the half-cell with patterned LFP cathodes and LTO anodes retained 92% and 88% capacity, respectively. Cells featuring these electrodes demonstrated a robust  $120 \text{ mAh g}^{-1}$  discharge rate at 0.3 C and notable flexibility [Figure 8F]. Three-dimensional printing of these electrodes enables low-cost, high-performance, deformable electrode production [Figure 8G].

### 3D printing hydrogels for battery electrolytes

Traditional template manufacturing methods can only form hydrogel electrolytes with simple 2D or 3D structures. This limitation restricts their applicability in designing batteries with complex shapes and structures. Three-dimensional printing technology can quickly produce customized complex 3D structures. This method has the advantages of low loss, low cost, high throughput, and customization. However, the rheological characteristics of the produced inks must meet specific specifications set by 3D printing technology<sup>[114]</sup>. At present, the precursors of hydrogel electrolytes are usually low-viscosity liquids and are not suitable for 3D printing. Adding a thickener is the most popular way to make the ink more viscous. The hydrogel electrolyte structure's stability will be harmed by the addition of the thickener, which will also have a major impact on its mechanical and electrochemical characteristics. As a result, we must satisfy the viscosity requirements of 3D printing technology while also guaranteeing the hydrogel electrolyte's mechanical and electrochemical qualities.

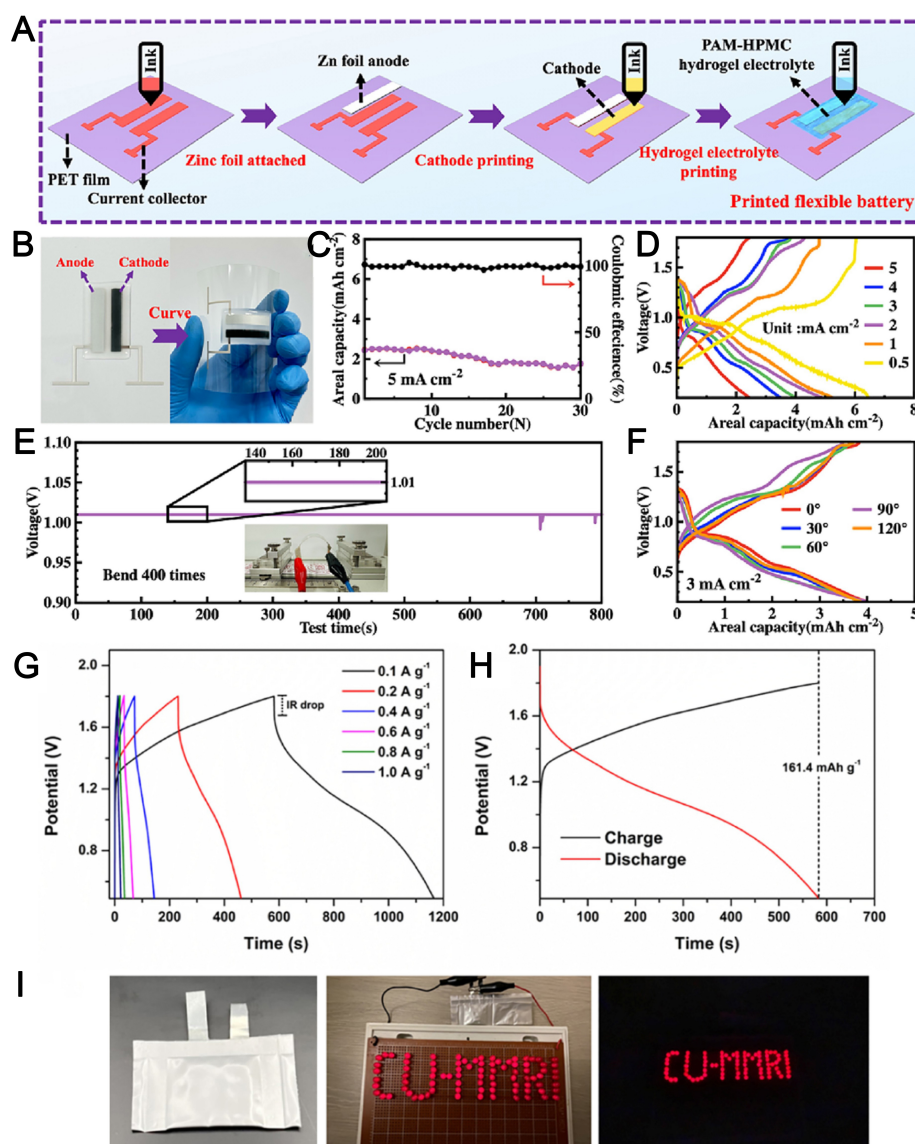
Lu *et al.*<sup>[3]</sup> designed a novel 3D-printable hydrogel electrolyte ink based on DN cross-linked PAM/hydroxypropyl methylcellulose (PHHE) [Figure 9A and B]. This PHHE material demonstrated exceptional electrochemical properties, including: (1) high ionic conductivity ( $31.72 \text{ mS cm}^{-1}$ ), (2) remarkable cycling stability (maintaining performance over 600 h at  $0.5 \text{ mA cm}^{-2}$  current density) [Figure 9C], and (3) a broad electrochemical stability window (0–2.3 V). By employing this PHHE electrolyte in 3D printing fabrication, the researchers successfully developed flexible zinc-ion micro batteries (FZIMBs) that achieved both high areal capacity ( $6.45 \text{ mAh cm}^{-2}$  at  $0.5 \text{ mA cm}^{-2}$  discharge current) [Figure 9D] and superior mechanical flexibility [Figure 9E and F]. These FZIMBs, integrated with pressure-sensing components, formed an interactive sensing system for practical use in flexible wearable devices. Poompiew *et al.*<sup>[115]</sup> fabricated a novel class of 3D-printable flexible hydrogel polymer electrolytes for ZIBs utilizing PAM as the hydrogel matrix. Through DLP 3D printing technology, the researchers engineered an optimized porous architecture specifically designed for ZIB applications. This advanced manufacturing approach enabled the direct fabrication of functional ZIB devices with tailored structural characteristics. The 40% porosity PAM



**Figure 8.** (A) Digital photos of the viscoelastic composite<sup>[112]</sup>; (B) 3D-printed hydrogel scaffold made of polyacrylamide, hemicellulose, and EGaIn microdroplets<sup>[112]</sup>; (C) The composite is used as the anode host in a Zn-ion battery<sup>[112]</sup>; (D) Schematic of the hydrogel containing covalent bonds and hydrogen bonds<sup>[112]</sup>; (E) The EGaIn LM microdroplets cause acrylamide monomers to undergo radical polymerization with the microdroplets<sup>[112]</sup>; (F) Diagram of the printed LTO/LFP electrodes in a complete pouch cell battery<sup>[113]</sup>; (G) A pouch cell with printed electrodes that illuminates an LED in its folded, twisted, bent, and flat configurations is demonstrated. There is a 1 cm scale bar<sup>[113]</sup>. 3D: Three-dimensional; LTO:  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ; LFP:  $\text{LiFePO}_4$ ; LED: light emitting diode.

hydrogel electrolyte produced via 3D DLP showed promising potential as a solid-state electrolyte for ZIBs, with excellent electrochemical performance [Figure 9G-I].

In summary, conductive hydrogels can be used as both electrodes and ionic electrolytes in energy storage systems, depending on their structural and compositional design. When used as electrodes, hydrogels are often embedded with conductive fillers and active materials to facilitate the transport of electrons and ions while maintaining mechanical flexibility. In contrast, hydrogel electrolytes mainly serve as ionic conductors and separators, providing a hydrated environment that enables ions to migrate between electrodes. For hydrogel-based electrodes, future research may focus on enhancing electronic conductivity and mechanical integrity. Strategies such as nanoconfinement of conductive networks (e.g., CNTs, MXenes), hierarchical porous structures, and dynamic cross-linking are expected to improve charge transfer, durability, and



**Figure 9.** The FZIMBs' electrochemical performance. (A) FZIMBs printing procedure<sup>[3]</sup>; (B) The FZIMBs' optical pictures<sup>[3]</sup>; (C) Performance of cycling at  $5 \text{ mA cm}^{-2}$ <sup>[3]</sup>; (D) GCD curve from  $0.5 \text{ mA cm}^{-2}$  to  $5 \text{ mA cm}^{-2}$ <sup>[3]</sup>; (E) Voltage variation during the battery bending process, with embedded test images<sup>[3]</sup>; (F) Battery GCD curves at various bending angles at  $3 \text{ mA cm}^{-2}$ <sup>[3]</sup>; Charge-discharge curves at (G) different current densities<sup>[115]</sup> and (H) at  $0.1 \text{ A g}^{-1}$  for 3D printed 40% porosity hydrogel electrolyte<sup>[115]</sup>, and (I) battery with 40% porosity hydrogel electrolyte connected with LED light<sup>[115]</sup>. FZIMBs: Flexible zinc-ion micro batteries; 3D: three-dimensional; GCD: galvanostatic charge-discharge.

structural adaptability. In addition, integrating pseudocapacitive or redox-active units into the hydrogel matrix can significantly improve energy density. On the other hand, hydrogel electrolytes need to improve ionic conductivity, long-term hydration stability, and chemical compatibility with a variety of electrode materials. The performance gap between commercially available flexible devices and 3D printing devices is shown in Tables 3 and 4.

## THE EFFECT OF 3D-PRINTED HYDROGELS ON ELECTROCHEMICAL PERFORMANCE

The main reasons for the creative use of 3D printing technology in electrochemical energy storage are its special benefits in material integration and structural design. Compared to traditional manufacturing

**Table 3. Performance comparison between commercial flexible supercapacitors and 3D-printed conductive hydrogel supercapacitors**

| Parameter                                 | Commercial flexible supercapacitors | 3D-printed conductive hydrogel supercapacitors | Ref.          |
|-------------------------------------------|-------------------------------------|------------------------------------------------|---------------|
| Areal capacitance ( $\text{mF cm}^{-2}$ ) | 500-2,600                           | 100-600                                        | [116]         |
| Energy density ( $\text{mWh cm}^{-2}$ )   | 0.1-0.5                             | 0.1-2                                          | [116]         |
| Power density ( $\text{mW cm}^{-2}$ )     | 1-50                                | 0.1-58                                         | [116,117]     |
| Cycle life (capacitance retention)        | 10,000-40,000 cycles (88%-98%)      | 5,000-10,000 cycles (83%-96%)                  | [116,118]     |
| Bending angle ( $^{\circ}$ )              | $90^{\circ}$ - $180^{\circ}$        | $150^{\circ}$ - $180^{\circ}$                  | [116,118,119] |
| Flexibility                               | Good                                | Excellent                                      | [116,119]     |

3D: Three-dimensional.

**Table 4. Performance comparison between commercial flexible batteries and 3D-printed conductive hydrogel batteries**

| Parameter                               | Commercial flexible supercapacitors | 3D-printed conductive hydrogel supercapacitors | Ref.        |
|-----------------------------------------|-------------------------------------|------------------------------------------------|-------------|
| Areal capacity ( $\text{mAh cm}^{-2}$ ) | 0.05-23                             | 0.5-10                                         | [3,120,121] |
| Energy density ( $\text{mWh cm}^{-2}$ ) | 0.5-20                              | 0.2-10                                         | [121,122]   |
| Power density ( $\text{mW cm}^{-2}$ )   | 1-10                                | 2-8                                            | [102,121]   |
| Cycle life (capacity retention)         | 500-3,000 cycles (> 80%)            | 100-2,000 cycles (> 80%)                       | [120-122]   |
| Bending angle ( $^{\circ}$ )            | $90^{\circ}$ - $180^{\circ}$        | $120^{\circ}$ - $180^{\circ}$                  | [3,123]     |
| Flexibility                             | Good                                | Excellent                                      | [124,125]   |

3D: Three-dimensional.

technologies, 3D printing can precisely construct electrode structures with customized geometric shapes, optimized pore distributions, and high specific surface areas. This precise control of microstructures plays a decisive role in enhancing ion transport kinetics and electronic conductivity networks. The synergistic effects between hydrogel materials and 3D printing technology are particularly notable: on one hand, hydrogels' inherent high ionic conductivity, excellent mechanical flexibility, and biocompatibility provide a material foundation for improving electrochemical performance; on the other hand, 3D printing's spatial precision control capability (with a resolution as high as  $10\text{-}50\text{ }\mu\text{m}$ ) enables the precise construction of complex porous networks and functional gradients.

### Mass transfer kinetics optimization

Three-dimensional printing hydrogels significantly shortens ion diffusion paths and reduces tortuosity by controlling microstructures, thereby improving electrochemical reaction kinetics. Meng *et al.*<sup>[102]</sup> prepared Zn-poly(3,4-ethylenedioxythiophene): polystyrene sulfonate/MXene (Zn-PM) gel electrodes via 3D printing, featuring ultra-high mass loading ( $32.2\text{ mg cm}^{-1}$ ) and high shape fidelity. Even at ultra-high mass loading, the electrodes maintained efficient charge transfer efficiency and ion diffusion kinetics. The electrochemical characterization of the Zn-PM gel electrode demonstrated its exceptional rate performance (capacitance retention of 84% at  $10\text{ A g}^{-1}$ ), high specific capacitance ( $261\text{ F g}^{-1}$  at  $0.5\text{ A g}^{-1}$ ), and outstanding cycling stability (capacity retention near 100%). Using a straightforward PSS chain engineering technique that included the addition of thermally cross-linkable N-(hydroxymethyl)acrylamide segments, Yu *et al.*<sup>[126]</sup> created a PEDOT: PSS-based hydrogel that is highly conductive, naturally soft, durable, and stretchable. The hydrogel satisfies several performance requirements for realistic bioelectronic applications with its high conductivity ( $1,850\text{ S m}^{-1}$ ), high stretchability (> 50%), low Young's modulus (4 MPa), and exceptional toughness ( $400\text{ kJ m}^{-3}$ ).



### Customized geometric configuration

Three-dimensional printing hydrogels have broken through the structural limitations of traditional manufacturing, enabling the precise design of complex geometric configurations such as biomimetic hierarchical channels and periodic lattices, thereby optimizing the specific surface area of electrodes and charge transport pathways. Baur *et al.*<sup>[12]</sup> reported a method to controllably introduce open pores with diameters of tens of nanometers into hydrogels while maintaining substantial mechanical properties, with a compressive modulus greater than 100 kPa. Notably, these hydrogels are 3D printable, allowing for the adjustment of pore sizes within the hydrogel from tens of nanometers to the centimeter scale. This work leverages the 3D printability of the material to locally modify porosity while preserving mechanical performance, making the overall sample easy to handle.

### Future prospects and roadmap for 3D-printed hydrogels in flexible electrochemical energy storage devices

#### *Mechanical and functional synergy of composite hydrogels*

Future 3D-printed hydrogels will break through the performance limits of single materials by achieving synergistic improvements in mechanical strength and electrochemical performance through nanocomposite and multilevel structure design. For example, incorporating ceramic nanoparticles (such as silica or barium titanate) into hydrogel matrices can simultaneously enhance mechanical strength (tensile strength exceeding 10 MPa) and ionic conductivity (maintained above 20 mS cm<sup>-1</sup>). Concurrently, the development of smart hydrogels with photoresponsive or magneto-responsive properties will enable flexible electrochemical energy storage devices to possess dynamic functions such as self-healing and shape memory, thereby adapting to complex environmental demands.

#### *From two-dimensional planes to three-dimensional functionalization*

The introduction of 4D printing technology will enable hydrogel energy storage structures to adapt to their environment. By programming temperature/pH-responsive hydrogels, battery modules can autonomously dissipate heat at high temperatures or contract in shape at low temperatures, thereby enhancing device safety and efficiency. Bionic microstructure design (such as 15–35 μm porous structures regulated by liquid-liquid phase separation) can optimize ion transport pathways, boosting the specific capacitance of SCs to over 500 F g<sup>-1</sup> while maintaining over 90% cycle stability.

#### *Extreme environment stability and energy density enhancement*

To address the performance degradation of hydrogels under extreme temperatures, future efforts will focus on modifying them with antifreeze agents or hydrophobic groups to achieve an ion migration rate degradation of less than 20% at -20 °C. Additionally, the application of phase-change hydrogels will reduce the operating temperature of battery packs by over 8 °C, control cell temperature differences within 5 °C during fast-charging cycles, and extend device lifespan. In terms of energy density, hydrogels directly used as electrode materials can achieve a 95% capacity retention rate at a current density of 1 A g<sup>-1</sup>, driving the practical application of flexible batteries.

## CONCLUSION AND OUTLOOK

In summary, 3D printing has become a revolutionary approach for constructing advanced electrochemical energy storage systems, offering advantages over traditional methods by streamlining production processes, enhancing reproducibility, and providing portability with integrated functionality. This review summarizes the fundamental properties of hydrogels, discusses key 3D printing strategies, and highlights their applications in SCs and batteries. Additionally, the impact of 3D printing hydrogel on electrochemistry has been discussed, highlighting its potential to revolutionize the field. However, the widespread adoption of 3D printing in future electrochemical energy storage systems remains hindered by several critical challenges,



including the rational selection and optimization of electrode materials, achieving optimal electrode packing density, maintaining interface stability, and improving printing precision, speed, repeatability, and long-term stability. To fully harness the potential of 3D printing for electrochemical energy storage applications, further dedicated research is necessary to address these constraints and overcome existing limitations, ultimately enabling the commercial success of these advanced devices.

Currently, the limited availability of 3D printable materials for electrochemical energy storage devices highlights the need to develop novel electrode materials, especially functional nanocomposites, in order to optimize material combinations and synthesis strategies. Establishing a comprehensive material property database and standardizing materials are essential for advancing high-performance 3D-printed energy storage devices. Additionally, 3D printing can create hierarchical pore structures that enhance ion and electron transport, but these structures reduce electrode density, limiting volumetric energy density. Therefore, new densification strategies such as interface chemistry, plasma etching, and strain engineering are necessary to optimize both volumetric and areal energy densities.

To advance the performance of 3D-printed electrochemical energy storage devices, efforts should focus on improving interfacial stability between components, optimizing printing accuracy, and increasing printing speed. Advances in interface engineering, coupled with the optimization of printing parameters and the adoption of multi-head or parallel printing techniques, will improve device efficiency and consistency. Furthermore, addressing issues such as parameter fluctuations and material heterogeneity through standardized protocols, strict quality control, and real-time monitoring will enhance reproducibility and stability. By overcoming these challenges, 3D printing technology can be fully optimized for large-scale, cost-effective production of energy storage devices.

## DECLARATIONS

### Authors' contributions

Contributed equally to this work: Hu, Y.; Zhou, H.; Wang, N.

Data analysis and interpretation: Zhi. L.; Li, N.; Liu. Q.

Topic selection, manuscript review: Chen, Z.; Mo, F.

Editing and supervision: Chen, Z.; Liu, Q.; Mo, F.

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Not applicable.

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### Conflicts of interest

All authors declared that there are no conflicts of interest.

**Ethical approval and consent to participate**

Not applicable.

**Consent for publication**

Not applicable.

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