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Application of hydrogel for energy storage and conversion

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ABSTRACT

Hydrogels have increasingly become a focus of interest within academic and industrial research spheres, particularly for their potential application in energy storage and conversion systems. This is largely due to their exceptional mechanical properties, inherent multifunctionality, and noteworthy biocompatibility. The goal of this review is to provide an in-depth analysis of the recent advancements made in the field of multifunctional hydrogels as applied to energy storage and conversion. The work reviews key factors that are critical to the functionality of hydrogels in energy storage and conversion processes, including mechanical strength, resistance to swelling, and conductivity. We explore contemporary methodologies for enhancing these essential properties. It provides insights into the existing and prospective uses of hydrogels in the realm of energy storage and conversion, specifically highlighting their role in supercapacitors, batteries, and ion thermoelectric systems. The present work anticipates potential future research trajectories, with an emphasis on the further development and application of hydrogels within energy conversion and storage systems.

1. Introduction

Novel approaches to energy utilization are critical in mitigating greenhouse gas emissions and addressing global climate change [1–5]. Low-grade thermal energy, which refers to energy with a temperature below 100 °C derived from sources such as industrial waste heat or the human body, represents a promising and sustainable energy source [6, 7]. The increasing demand for self-powered energy sources driven by wearable electrical devices has led to the concept of harvesting energy from the environment or the human body [8–14]. Hydrogels, which are three-dimensional hydrophilic polymer networks crosslinked by polymer chains, exhibit excellent mechanical properties [15]. With the doping of different redox couples, inorganic salts, or secondary polymers, hydrogels not only can provide pathways for charge carriers, demonstrating excellent conductivity but also provide large surface areas for active sites and abundant pendant groups for versatile function, as illustrated in Fig. 1. Under the induction of a temperature gradient, the relative movement of charge carriers causes redox couples to react on the hot and cold electrode plates, forming thermoelectric couples, or causes the charge carriers to accumulate on the hot and cold electrode plates, forming thermoelectric capacitors, which provide multiple possibilities for the development of hydrogel thermoelectric systems [16]. Furthermore, hydrogels exhibit excellent biocompatibility, making

them ideal for energy self-supply in flexible electrical devices [17]. In this paper, we review the latest advances in multifunctional hydrogels for energy storage and conversion. The discussion commences with an exploration of the mechanisms, adjustment methods, and research examples concerning the mechanical properties, resistance to swelling, and conductivity of hydrogels. Subsequently, the applications of hydrogels in self-powered energy sources for flexible wearable electrical devices are introduced. These applications encompass supercapacitors, batteries, and ion thermoelectric systems, as illustrated in Fig. 2. Lastly, an overview of the prospects and challenges associated with hydrogels in the realm of energy storage and conversion is provided. Hydrogels are expected to find extensive applications in self-powered wearable electrical devices as well as waste heat harvesting and storage.

2. Properties of hydrogels

2.1. Mechanical characteristics

Excellent mechanical properties are of paramount importance in broadening the application scope of hydrogels. Hydrogel-based supercapacitors or batteries serve as self-powered energy sources for wearable devices. Throughout the usage of these self-powered wearable devices, inevitable mechanical stresses, including tension, compression, and

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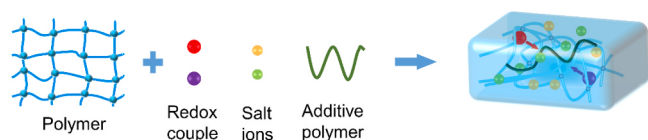


Fig. 1. Hydrogel network and functional additives including redox couples, salt ions, and additive polymers.

repetitive bending, come into play, thereby imposing stringent requirements on their mechanical characteristics [69,70]. A tough hydrogel is generally defined as having a tensile stress between 0.1 and 1.0 MPa and a fracture energy between $10^2\text{--}10^3\text{ J/m}^2$, as reported in previous studies [17]. High-toughness hydrogels with favourable mechanical properties play a critical role in diverse fields, such as flexible electrical devices, soft robotics, tissue engineering, and various engineering applications [18]. The enhancement of fracture energy in most traditional hydrogels is mainly due to the energy dissipation around the crack under external forces. However, their mechanical strength and extensibility are often limited by the lack of effective energy dissipation mechanisms [19]. To address this issue, different toughening mechanisms can be added while maintaining the original configuration after deformation to effectively design and synthesize tough hydrogels. These tough hydrogels can dissipate significant amounts of mechanical energy in the bridging zone during crack propagation, thereby enhancing their mechanical properties [20]. The basic principle for designing tough hydrogels is to dissipate mechanical energy after undergoing large deformation while maintaining the original configuration. Currently, common design methods for tough hydrogels include establishing a dual network, a topological network, a sliding-ring structure, physical reinforcement, and ion addition [21,22].

The concept of sacrificial bonds is currently the widely accepted

mechanism for toughening hydrogels. In this mechanism, the first layer of the brittle network undergoes internal fracture during deformation, which reduces local stress concentration and dissipates energy in the crack. The second network, which is plastic, then fills the fracture space, enhancing ductility to maintain large deformation [23,24]. Highly entangled hydrogels with a fabric-like topology have been proposed by Suo et al. [25]. Common hydrogels have a crosslinked network as the main structure, resulting in a mesh topology. However, highly entangled hydrogels possess a fabric-like topology, which allows them to transmit tensile stress along the length direction of the polymer chains, dissipate elastic potential energy, and improve their tensile strength and toughness [26–28]. Elastomers are typically composed of long polymer chains that are interconnected through chemical crosslinking and physical entanglements to form a three-dimensional network. However, chemical crosslinking can make the polymer brittle, as suggested by the theory proposed by Lake and Thomas in 1967 [29], where toughness is inversely proportional to the square of the crosslink density. Physical entanglement, on the other hand, can maintain the good toughness of elastomers. When a highly entangled polymer network is stretched, entanglement points act as slip tracks, tension is transmitted along the chains, and it is transferred to other chains via entanglements. When a covalent bond breaks, the stored elastic energy is dissipated by the longer chains surrounding it, leading to relaxation of the network and preventing fracture of the elastomer, as shown in Fig. 3 [30]. Gong et al. proposed the introduction of force-sensitive moieties into double network polymers to trigger force-coupled reactions when the polymer is stretched near its breaking point, which enhances the overall length of the polymer chain and therefore greatly improves the toughness of the hydrogel. They added bicyclo[6.2.0]decene (BCD) to the double network gel, which caused substantial changes in its energy dissipation mechanism. With the addition of BCD, the breaking of the

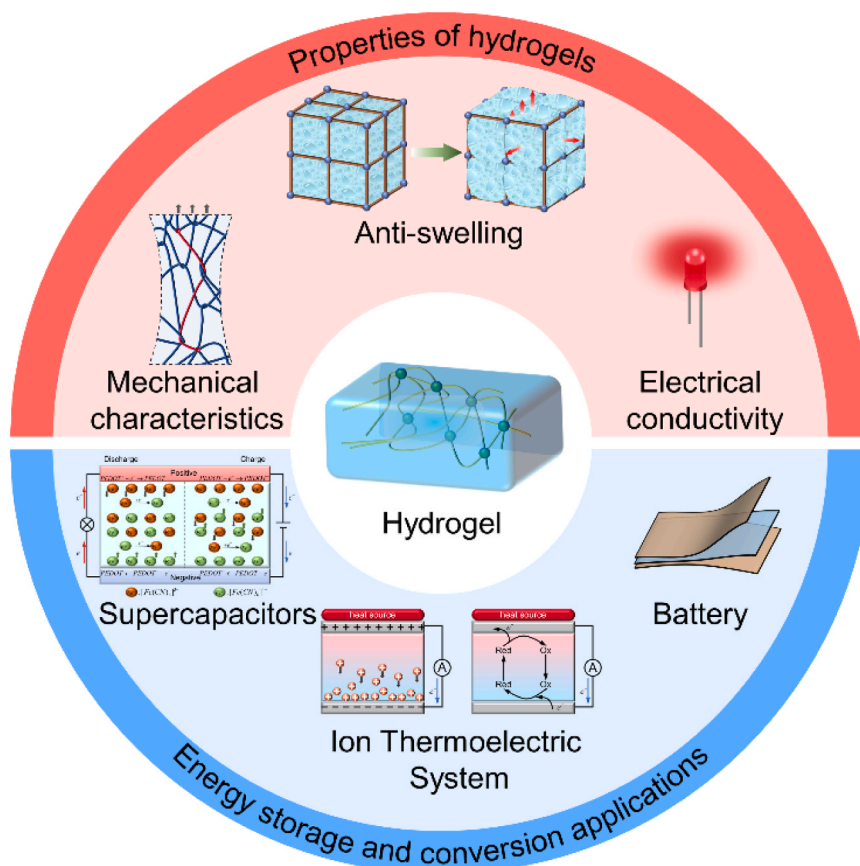


Fig. 2. A graphical illustration of application of Hydrogel for energy storage and conversion.

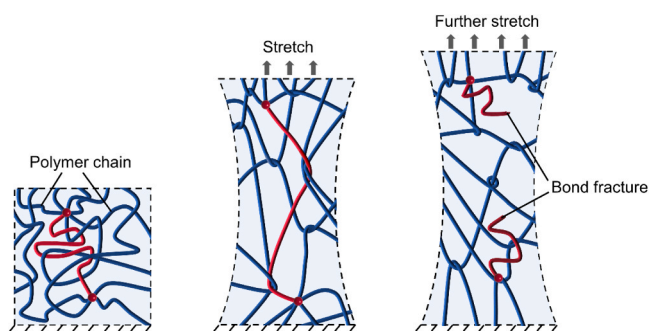


Fig. 3. A schematic diagram showing the states of a highly crosslinked hydrogel with abundant entanglements, including the unstrained state, the strained state, and the energy-releasing state due to bond fracture.

four-membered ring does not propagate to the entire polymer chain during the stretching of the hydrogel, but releases the "pre-stored" length, increasing the total chain length by about 40%. Consequently, the hydrogel can be stretched by 40–50% more, exhibiting twice the tear energy and significantly improved toughness [31]. Zhu et al. proposed the reversible manipulation of the mechanical properties of hydrogels through ion-induced regulation of polymer chain aggregation. The ionically regulated hydrogels manufactured in their study showed an increase in tensile strength from 50 ± 9 kPa to 15 ± 1 MPa and an increase in elongation from $300 \pm 100\%$ to $2100 \pm 300\%$ [32].

The widely accepted mechanical testing methods for hydrogels include tensile testing, compression testing, pure shear testing, peel testing, single-sided notched testing, and tear testing. Among these methods, the axial tensile-unloading cyclic test is often employed to assess the fatigue resistance of hydrogel materials. A notable hysteresis in the stress-strain curve of hydrogels can be observed, which is indicative of the presence of numerous non-covalent interactions in the material that can be ruptured after tensile deformation, thereby consuming energy [33]. Additionally, the compression-unloading cyclic test is frequently used to investigate the fatigue resistance of hydrogels. When a material is elastic, loading and unloading occur along the same stress-strain curve and do not dissipate energy. However, hydrogels, being non-elastic, follow different stress-strain curves during loading and unloading, and the area enclosed by these curves represents the amount of dissipated energy per unit volume of the material [34]. Due to the uneven distribution of networks and crosslinks, conventional hydrogels often display minor cracks and defects, leading to brittle failure. Nevertheless, this energy dissipation mechanism can improve the strength, toughness, fatigue resistance, and notch insensitivity of hydrogels.

2.2. Anti-swelling properties

Most hydrogels are synthesized through hydrophilic polymerization. However, under high-humidity conditions, small molecule solvents can permeate and diffuse between the large polymer molecules, thereby weakening the intermolecular forces, leading to volume expansion and degradation of mechanical performance [35–37]. Hydrogels, characterized by high water content, permeability, and adaptability, exhibit excellent potential in diverse areas such as drug delivery, wound dressings, tissue engineering, and wearable flexible electrical devices [38–40]. Nevertheless, traditional hydrogels often display poor mechanical properties and anti-swelling characteristics, which impede their practical applications. The swelling degree of hydrogels relies on the competition between the force of solvent permeation and diffusion and the force of polymer cross-linking network [41,42]. To control the expansion behavior of hydrogels, researchers have employed strategies such as increasing cross-linking density and adjusting the interaction between polymers and water. The use of nanomaterials and nanoparticle

gel agents has been explored to increase the cross-linking density and control the swelling of hydrogels. Additionally, introducing hydrophobic polymer chains into hydrogel networks can help modulate the interaction between polymers and water [43–45].

Liu et al. presented a supramolecular poly(N-acryloylglycylglycine) (PNAGA) hydrogel, in which the hydrogen bonding between the side chain amide groups was reinforced and reorganized, leading to an increased crosslinking density of the gel's polymer network. The supramolecular interactions of the hydrogen bonding reached an equilibrium, resulting in a slight increase in water content after swelling but negligible overall volume change, indicating excellent anti-swelling ability properties [46]. Cui et al. developed a highly swell-resistant and mechanically robust poly(acrylic acid) (PAAc)/gelatin composite hydrogel via a synergistic effect induced by MXene activation and zirconium ions (Zr^{4+}) induction. MXene, mixed with the thermal initiator APS, generated a large number of free radicals at room temperature, which quickly initiated the polymerization of acrylic acid. Meanwhile, the Zr^{4+} in the precursor solution rapidly crosslinked the polymer chains to achieve fast gelation. To achieve anti-swelling ability, gelatin was simultaneously introduced into the system, and the dynamic hydrogen bonding between the gelatin and PAAc raised the upper critical solution temperature (UCST) of the hydrogel above room temperature, thereby realizing its anti-swelling ability at room temperature [47]. Inspired by the natural extracellular matrix (ECM), Wu et al. infiltrated a flexible long-chain polymer network into a rigid macromolecular framework (chitosan) and performed in situ polymerization, resulting in a controllable swelling water gel. The pre-made macromolecular framework acted as a skeleton to "lock" the water gel and limit its expansion, as shown in Fig. 4 [48].

2.3. Electrical conductivity

The conductivity of hydrogels has become increasingly important in the context of the continuous development of flexible wearable electrical devices. Currently, the conductivity mechanism of hydrogels can be categorized into two types: electrical conductivity and ionic conductivity. Electrical conductive materials include conductive polymers, conductive nanomaterials, MXenes, and metal-based materials, while ion conductive materials include polyelectrolytes and electrolytes [49].

Electrical conductive hydrogels are formed by crosslinking conductive polymers or conductive nanofillers into the hydrogel matrix, as shown in Table 1. The conductivity of the hydrogel is relatively low when the electron concentration is below the percolation threshold. To address this, a second network can be established in the hydrogel to enhance the electron concentration and establish a relatively low-resistance electrical transport pathway [59].

Conductive polymers possess notable characteristics such as good electrical conductivity, high water content, and low modulus, and are extensively employed in hydrogel manufacturing due to their adjustable conductivity and ease of synthesis. Zheng et al. have successfully created a SF/TA@PPy conductive hydrogel with stretch ability, skin

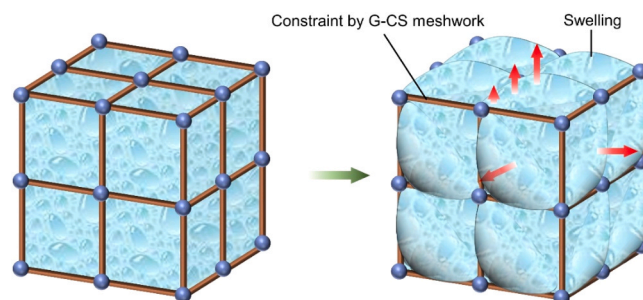


Fig. 4. schematic diagram of the working mechanism of the anti-swelling Hydrogel constraint by G-CS meshwork.

Table 1
Comparison of conduction range of hydrogels with different dopants.

| Materials | Conductivity (S/m) | Ref. |
|--|--------------------|------|
| PEDOT:PSS/ionic liquid | 1×10^4 | [50] |
| PEDOT:PSS | 4×10^4 | [51] |
| PAA/BaFe ₁₂ O ₁₉ | 12.2 | [52] |
| PEDOT:PSS/alginate | 87 | [53] |
| PPy/agarose | 350 | [54] |
| PEDOT:PSS/PVA | 1×10^4 | [55] |
| MXene-cellulose nanocrystals-tamarind gum-PAAm | 2.93 | [56] |
| HSAH/PHEAA | 0.194 | [57] |
| PAA/PANI | 5.12 | [58] |

conformability, antibacterial properties, and biocompatibility by in-situ polymerization of conductive polymer polypyrrole (PPy) with silk fibroin (SF) and tannic acid (TA) in the same gel network. SF/TA@PPy exhibits excellent wet adhesion to different materials and possesses a broad operating range, high strain sensitivity, and fast resistance response [60]. Li et al. have proposed a "deswelling-in-situ assembly" approach to devise a double-network hydrogel, with a rigid and brittle PEDOT:PSS network serving as the first network, and a soft and stretchable PVA network acting as the second network, creating a hydrogel with a high conductivity (10 S/cm) and high stretch ability (150% fracture elongation). This hydrogel exhibits remarkable flexibility, biocompatibility, matching with tissue, and resolves the long-standing challenge of the electrical conductivity and mechanical properties of conductive hydrogels being imbalanced. This development has offered novel materials and ideas for the advancement of flexible bioelectronics [61].

MXenes, a type of two-dimensional transition metal carbides or nitrides, possess excellent electrical conductivity, unique hydrophilicity, and abundant surface functional groups, which render them highly dispersible in the aqueous phase of hydrogels and capable of forming robust interactions with the polymer network, thus establishing stable pathways for electron transport [62]. Guan et al. proposed the incorporation of MXenes and hydrolyzed keratin (HK) into hydrogel polymers, leading to the development of a hydrophobic cross-linked hydrogel with multiple desirable features. The resulting hydrogel exhibited outstanding conductivity, ultra-stretch ability (>2000%), and good self-adhesion, opening up new possibilities for the advancement of soft intelligent sensors [63].

Ionic conductive hydrogels are a type of hydrogel where ion salts are typically dissolved, resulting in a high concentration of free ions within the polymer network. The three-dimensional framework structure of the hydrogel enables the movement of these ions [64]. Yao et al. developed a semi-interpenetrating network (ICH) platform by incorporating carbon nanofibers (CNFs) into a phenylboronic acid ionic liquid (PBA-IL)/acrylamide cross-linked network. The dynamic boronic ester bonds and physical interactions, such as hydrogen bonds and electrostatic interactions, within the cross-linked network enhanced the mechanical and electrical properties of the hydrogel [65].

Conductivity serves as a fundamental attribute of hydrogels as advanced intelligent materials, playing a crucial role in the storage and conversion of energy.

3. Energy storage and conversion applications

3.1. Supercapacitors

Supercapacitors, which consist of a sandwich-like structure composed of two electrodes and an electrolyte, have attracted significant attention as an electrochemical sensor due to their fast charging and discharging, long lifespan, and excellent safety features [66], making them a promising technology for wearable electrical devices and

energy storage and conversion equipment [67]. A high-strength and safe electrolyte is a crucial component in energy storage system design, and solid electrolytes have been widely investigated for this purpose [68]. Hydrogel electrolytes, as solid electrolytes with their diverse chemical composition, can be tailored to achieve different functions such as excellent pliability, high conductivity, leak-free behavior, high-temperature resistance, and tunable mechanical properties, providing more possibilities for energy storage device design and development. The high-water content of hydrogels enables the network to maintain solid stability while providing free ions with molecular dynamics similar to liquids, which favors the further development of flexible energy storage devices [69].

Zeng et al. have reported on the development of a hydrogel supercapacitor with arbitrary deformability and stable energy output, based on a double-network structure of polyacrylamide (PAM) and sodium alginate (SA) [70]. Carbon nanotubes and PEDOT:PSS were incorporated to enhance the electrical conductivity and electrochemical properties, while Na₂SO₄ inorganic salt and potassium ferricyanide/ferrocyanide [K₃Fe(CN)₆/K₄Fe(CN)₆] redox pairs were introduced to improve the ion conductivity and redox activity. The long-chain polymer SA was included to form a three-dimensional mechanical support network through molecular chain entanglement and intermolecular interactions. The charge storage mechanism of the hydrogel supercapacitor is illustrated in Fig. 5, where K₃Fe(CN)₆/K₄Fe(CN)₆ facilitates the redox transformation to create ion channels for charge transfer and storage. The unique 3D crosslinked double-network structure provides excellent mechanical flexibility, enabling arbitrary deformation of the supercapacitor. The issues of poor mechanical performance and deformation capability in traditional hydrogels, which hinder their support for repetitive bending and twisting, have been addressed. The high ion conductivity of the hydrogel electrolyte and the charge storage mechanism induced by the redox pairs endow the supercapacitor with outstanding specific capacitance (232 mF/cm² at 5 mV/s and 128 mF/cm² at 1 mA/cm²), energy density (3.6 μWh/cm²), and long cycle life (over 5000 cycles), providing inspiration for the development of self-powered wearable electrical devices. Furthermore, Wu et al. have utilized a multiscale structural engineering technique to fabricate MXene hydrogel capacitors, where the unidirectional freezing resulted in a vertically aligned layer-by-layer structure of MXene flakes. In comparison to MXene aerogels obtained by direct freeze-drying and MXene films formed by layer stacking, the ordered MXene hydrogel exhibited a high capacitance (393 F/g at 5 mV/s) and excellent rate capability (198 F/g at 1000 mV/s). The increased layer distance between the vertically arranged MXene structures and MXene films led to improved diffusion and transportation of conducting ions, as well as an enlarged accessible surface area for ions. The MXene supercapacitors produced using this method had a honeycomb-like compartment

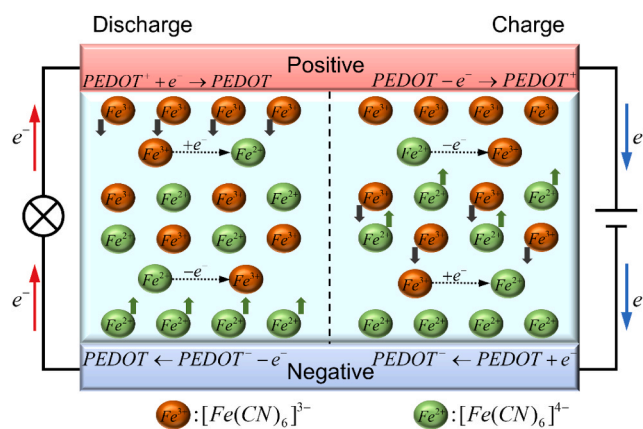


Fig. 5. Diagram of charge storage mechanism for all-hydrogel supercapacitors [70].

structure, with a remarkably high areal capacitance of 2.0 F/cm^2 and a high energy density of 0.1 mWh/cm^2 . In contrast to the layer-by-layer stacking manufacturing process of traditional capacitors, the high energy density advantage of the ordered MXene hydrogel supercapacitor will provide more possibilities for energy storage applications [71].

Additionally, Silki Sardana et al. successfully fabricated a three-dimensional ternary nanocomposite hydrogel on carbon cloth using a two-step synthesis approach. This hydrogel serves as a binder-free supercapacitor electrode, achieving a high specific capacitance of 1124 F/g at a current density of 0.25 A/g and a maximum specific capacitance of 1134.28 F/g at 1 A/g . It also exhibits excellent capacitance retention, maintaining 82.2% at a current density of 7.5 A/g and 76.46% at 10 A/g [72,73]. The maximum specific power and specific energy values for the hierarchical three-dimensional polyaniline/doped graphene nanocomposite hydrogel supercapacitor cell prepared by Anil Ohlan et al. are 0.44 kW/kg and 13.63 Wh/kg , respectively. Consequently, the composite hydrogel offers the advantage of being utilized directly as a binder-free supercapacitor electrode and is a viable choice for high-performance and cost-effective energy storage devices in scientific terms [74,75].

3.2. Battery

In addition to supercapacitors, hydrogel-based batteries, which offer long-term, high-capacity energy storage, have also found extensive applications. Batteries are common energy storage devices in daily life and scientific experiments, typically composed of conductive electrolytes and two active electrochemical electrodes. Liquid electrolytes are used to ensure ion conduction during battery reactions. However, organic liquid electrolytes often lead to safety issues, making it necessary to explore safe and stable solid-state electrolytes. Hydrogel electrolytes as solid-state electrolytes have gained considerable attention. Compared to conventional electrochemical batteries, flexible batteries using hydrogels as the electrolyte matrix exhibit excellent energy storage performance and greater flexibility, which is crucial for the development of self-powered wearable electronic devices [76]. With the increasing demand for wearable electronic devices, researchers are widely interested in flexible energy storage devices with low cost, high safety, and high energy density.

Zinc-air batteries, which offer ultra-high energy density, are considered to be a breakthrough in the development of new-generation long-lasting energy storage systems [77]. Among various hydrogel electrolytes, CNFs-based hydrogel electrolytes have been widely used in zinc-air batteries as the main conductive doping. The zinc-air batteries made using these hydrogel electrolytes exhibit better mechanical properties and energy density compared to other hydrogel electrolytes, making them safer and longer-lasting [78]. Wei et al. proposed a PAM-CNF/KOH/KI hydrogel electrolyte [79]. The micro-porous structure and ion concentration of each electrolyte affect their ion conductivity. Specifically, the ion conductivity of PAM-CNF hydrogel is 216 mS/cm , that of PAM/KOH hydrogel is 195 mS/cm , and that of PAM-CNF/KOH/KI hydrogel is 223 mS/cm . The PAM-CNF/KOH/KI electrolyte shows excellent performance at both $20 \text{ }^\circ\text{C}$ and $-40 \text{ }^\circ\text{C}$, achieving a high electrolyte retention of 86% due to its ultra-high ion concentration and complex 3D network [80]. The wide temperature range of hydrogel electrolytes is of great significance for expanding the application of high-performance zinc batteries. Wu et al. proposed a polymer acidic hydrogel electrolyte, PAGE, rich in $-\text{SO}_3^-\text{H}^+$ groups, for high-performance Zn/PANI batteries at room temperature and $-35 \text{ }^\circ\text{C}$ subzero temperatures [81]. PAGE guides the deposition of Zn^{2+} to the electrode surface, enabling the battery to exhibit excellent anti-freezing performance. Therefore, PAGE provides high ionic conductivity at both $25 \text{ }^\circ\text{C}$ and $-35 \text{ }^\circ\text{C}$. Zn/PANI batteries with PAGE can deliver a high specific capacity of 174.3 mAh/g at $25 \text{ }^\circ\text{C}$ and 152.4 mAh/g at $-35 \text{ }^\circ\text{C}$ under the condition of 0.5 A/g . They also exhibit high stability, achieving over 30,000 cycles at $25 \text{ }^\circ\text{C}$ and 70,000 cycles at $-35 \text{ }^\circ\text{C}$ under

the condition of 15 A/g . Researchers have also investigated the performance of hydrogel electrolytes at ultra-low temperatures. Yan et al. developed a hydroxyl-functionalized poly(ionic liquid) (PIL-OH) hydrogel electrolyte for aqueous lithium-ion batteries (ALIBs) [82]. The ultra-low-temperature tolerance of the hydrogel electrolyte arises from the synergistic effect of ion hydration and hydrogen bonding interactions between PIL-OH and water molecules, which damages the hydrogen bonding network of water and greatly reduces its freezing point. The electrolyte exhibits a high ionic conductivity of 0.08 mS/cm at $-80 \text{ }^\circ\text{C}$ and a capacity retention rate of 93% after 200 cycles.

3.3. Ion thermoelectric system

Given the limited energy utilization efficiency, the enormous amount of waste heat generated from industrial manufacturing not only leads to energy loss but also exacerbates climate change problems [83]. Hydrogel thermoelectric materials show great potential for converting low-grade thermal energy into electrical energy. Based on different charge carriers, thermoelectric materials can be classified into electrical thermoelectric materials and ion thermoelectric materials [84]. Electrical thermoelectric materials utilize the Seebeck effect to achieve good conductivity, and their Seebeck coefficients are usually less than 1 mV/K , making it difficult to achieve volt-level application voltage levels [85–87]. Depending on the different conduction mechanisms, ion thermoelectric materials can be categorized as thermocouples based on redox reactions [88,89] and thermocapacitors based on ion thermal diffusion effects [90].

Ion thermoelectric systems based on hydrogels are increasingly prevalent, and the working mechanism of these systems relies mainly on the interactions among ions, electrodes, and solvent-rich electrolytes, encompassing Faraday, non-Faraday, and synergistic effects [16]. Depending on specific practical requirements, hydrogels exhibit strong tunability and exceptional adaptability, making them highly compatible with ion thermoelectric systems [15,91]. Firstly, leveraging the chemistry of gels, hydrogels effectively integrate electrodes, redox couples, ions, and ion channels. Secondly, the solvent-rich environment with high water content facilitates ion dissociation and ion transport. Thirdly, the polymer matrix reduces convective heat transfer within the hydrogel, thereby sustaining the temperature difference and enhancing thermoelectric conversion efficiency. Additionally, connecting independent thermoelectric units in series can amplify the voltage and current output, bringing the system closer to volt-scale application scenarios [13].

The typical configuration of thermogalvanic cells (TGCs) comprises of an electrolyte that contains redox couples, placed between a hot electrode and a cold electrode. Under a thermal gradient, the thermocouples undergo redox reactions on the cold and hot electrode plates, resulting in a loop current through an external circuit, as shown in Fig. 6 (a). The TGCs' performance is significantly influenced by the different redox couples employed [16]. Recently, Zhao et al. reported a super-elastic TGC based on a hydrogel. They introduced $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ redox couples into a double-network hydrogel of

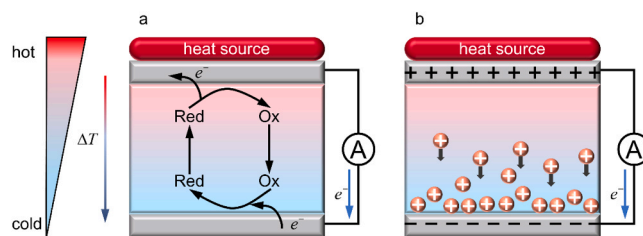


Fig. 6. (a) Schematic diagram of the working mechanism of thermogalvanic cell, (b) schematic diagram of the working mechanism of thermal-diffusion capacitor [16].

polyacrylamide/chitosan (PAM/CS), to enhance ion coordination and interchain interactions, thereby improving the hydrogel's mechanical properties. The equivalent Seebeck coefficient of the P-type thermocouple hydrogel was as high as 1.29 mV/K, much higher than that of microvolt-level semiconductor thermocouples [92]. However, TGCs based on redox couples containing toxic metals are not in line with the green and sustainable development concept. Therefore, it is crucial to develop non-toxic TGC electrolytes with excellent mechanical and thermoelectric properties. Tian et al. developed a stretchable and flexible TGC device by cross-linking a novel non-toxic redox couple of $\text{SO}_4^{2-}/\text{SO}_3^{2-}$ with PEDOT:PSS. The introduction of redox couples significantly improved the ion conductivity and thermoelectric properties. At an optimal concentration of 0.1 M, the Seebeck coefficient was as high as 1.63 mV/K [93].

Currently, the Soret effect is considered as the theoretical foundation for ion thermoelectric systems based on hydrogels, which can enhance the thermoelectric efficiency by regulating the ion migration rate in hydrogel materials. However, in practical applications, there is no precise estimation method yet established for liquid mixtures or hydrogels. Among them, the mechanisms of solvent transport, ion interactions, solute concentration, and pressure in the system still require further exploration [16].

Hydrogel thermocapacitors are devices that operate based on the Seebeck effect, where ions of opposite charges diffuse at different velocities under a temperature gradient, as shown in Fig. 6(b). The power of thermocapacitance can be improved by effectively controlling ion movement in the hydrogel electrolyte. Chen et al. proposed incorporating LiCl into a polyacrylamide (PAAm) polymer network and evenly dispersing Li^+ and Cl^- in the hydrogel electrolyte. Under a temperature difference ΔT between two electrodes, Li^+ migrates to the cold side by thermal diffusion, as it has a smaller volume and higher relative mobility than Cl^- . As a result, high concentrations of Li^+ accumulate on the cold side and Cl^- accumulates on the hot side, generating a thermoelectric voltage. At a temperature difference of 20 K, the ion Seebeck coefficient was as high as 11.3 mV/K. The demonstration of lighting up a light-emitting diode (LED) showed the potential for self-powering in flexible wearable electrical devices [94]. In general, at a certain ion concentration, the lower the polymer crystallinity, the better the ion conductivity, while polymers with higher crystallinity will limit ion movement in the polymer network. Chen et al. proposed a polyvinyl alcohol (PVA) hydrogel, in which H^+ has different ion conductivity under different crystallinities. By adjusting the crystallinity of the hydrogel and changing the hydrogen bonding distance between PVA chains, followed by introducing hydrochloric acid solution to introduce H^+ , a thermoelectric hydrogel based on H^+ as the charge carrier was obtained. The strong hydrogen bonding system enhanced the diffusion of H^+ while limiting the movement of Cl^- , ultimately resulting in a Seebeck coefficient as high as 38.20 mV/K. This high-performance ion thermoelectric hydrogel offers more possibilities for energy harvesting and storage in flexible materials [95]. In the context of mitigating carbon emissions and addressing the growing global electricity demand, the utilization of low-grade thermal energy for direct power generation through ion thermoelectric systems holds great promise.

4. Summary and outlook

In the context of reducing carbon emissions, novel methods for energy storage and conversion have garnered significant attention. This review article primarily focuses on the latest advancements in the research of hydrogels for energy storage and conversion. The mechanical properties, anti-swelling and conductivity mechanisms, tuning methods, and specific research examples of hydrogels are discussed. Furthermore, the applications of hydrogels in self-powered flexible wearable electrical devices are introduced. The three-dimensional network structure of hydrogels, their molecular-level customizable properties, and the interaction with functional additives, make them an

ideal platform for collecting low-grade energy from both theoretical and practical viewpoints. However, there are still many unknown mechanisms that need to be further explored. As a successful application in ion thermoelectric systems, multifunctional hydrogels act as poly-electrolytes, transport media, ion channels, and surface functional layers, enabling significant progress in converting thermal energy gradients into electrical energy. Through the serial connection of independent ion thermoelectric systems, it becomes feasible to realize a volt-scale energy recovery system for everyday portable use. However, there are still many unknown working mechanisms that need to be further addressed. Overall, to better understand the thermal gradient conversion system of hydrogels, more advanced characterization tools and in-situ techniques are required to observe the microscale interactions among water, polymers, and ions. Furthermore, it is essential to explore an effective and predictive unified power density assessment model, especially for different operational modes or mechanisms of various systems, particularly for supercapacitors, batteries, and thermoelectric systems. In addition, hydrogel toughness, size stability, water retention, frost resistance, and anti-swelling performance should be considered to meet practical application requirements. Ion hydrogels are expected to play a crucial role in self-powering flexible wearable electrical devices as they provide excellent power output stability and are easy to manufacture. Moreover, exploiting the phase-change characteristics of hydrogel electrolytes to store and convert industrial waste heat is a promising future research direction.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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