Hydrogels Enable Future Smart Batteries

Peihua Yang, Jin-Lin Yang, Kang Liu, and Hong Jin Fan*

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ABSTRACT: The growing trend of intelligent devices ranging from wearables and soft robots to artificial intelligence has set a high demand for smart batteries. Hydrogels provide opportunities for smart batteries to self-adjust their functions according to the operation conditions. Despite the progress in hydrogel-based smart batteries, a gap remains between the designable functions of diverse hydrogels and the expected performance of batteries. In this Perspective, we first briefly introduce the fundamentals of hydrogels, including formation, structure, and characteristics of the internal water and ions. Batteries that operate under unusual mechanical and temperature conditions enabled by hydrogels are highlighted. Challenges and opportunities for further development of hydrogels are outlined to propose future research in smart batteries toward all-climate power sources and intelligent wearables.
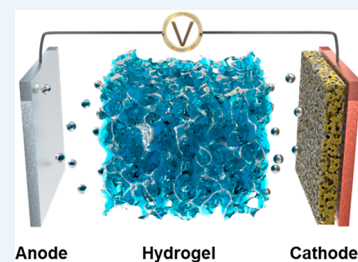
The rapid development of portable and wearable electronics, from smartphones to virtual reality, requires smaller and lighter energy storage devices with higher energy and power density.[1,2] Aqueous rechargeable batteries are promising candidates due to their low cost and environmental friendliness.[3,4] However, aqueous solution electrolytes create technical difficulties for large-scale integration and encapsulation especially for wearable devices. In addition, it is also necessary that these batteries are intelligent and can work under some extreme conditions such as high and low temperatures and repeated mechanical deformations.[5] For this purpose, it is of significant importance to explore advanced materials and battery design to render high chemical stability, excellent temperature adaptability, and strong mechanical properties.

Hydrogels are made from water-saturated and cross-linked polymer networks. Hence, hydrogels are intrinsically compatible with aqueous batteries. The polymer networks make the hydrogel an elastomer, which is beneficial for device flexibility, and the water molecules make the hydrogel an ionic conductor, which guarantees ion transport in the battery during charging and discharging.[6] In addition, more functions could be generated by exploiting gelation physics and chemistry with versatile molecular building blocks and functional additives,[7,8] laying a solid foundation for smart batteries. Here, smart batteries refer to batteries that can adapt spontaneously to external environment variations, such as temperature and mechanical stimuli. Therefore, hydrogels will play an important role in developing aqueous-based smart batteries for future energy management components and systems.

This Perspective aims to discuss the ways in which hydrogels can be used as a key electrolyte component in smart batteries. As comprehensive reviews on hydrogel and their broad applications have been available,[9,10] this Perspective will only briefly introduce the basic properties of gel formation, network structure, and water/ion behaviors and put focus on analyzing the advantages provided by hydrogel electrolytes as alternatives to inorganic and non-aqueous ionic conductors. We highlight the advantages brought by tuning the functions and extending the application of hydrogels as smart electrolytes in aqueous batteries. Our opinions on the present challenges and future opportunities are also provided, which hopefully will convince the reader that hydrogels, when judicially designed, will have great potentials in smart batteries, energies, and beyond.

FUNDAMENTALS OF HYDROGELS

Hydrogels have broad application prospects in flexible electronics due to their superior softness, stretchability, and intrinsic ionotronic properties. Ionic hydrogels contain mobile ions or fixed ionic groups. These charges exhibit specific ionic effects in electric, force, and chemical potential fields, endowing hydrogels with special functions such as ionic
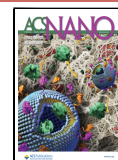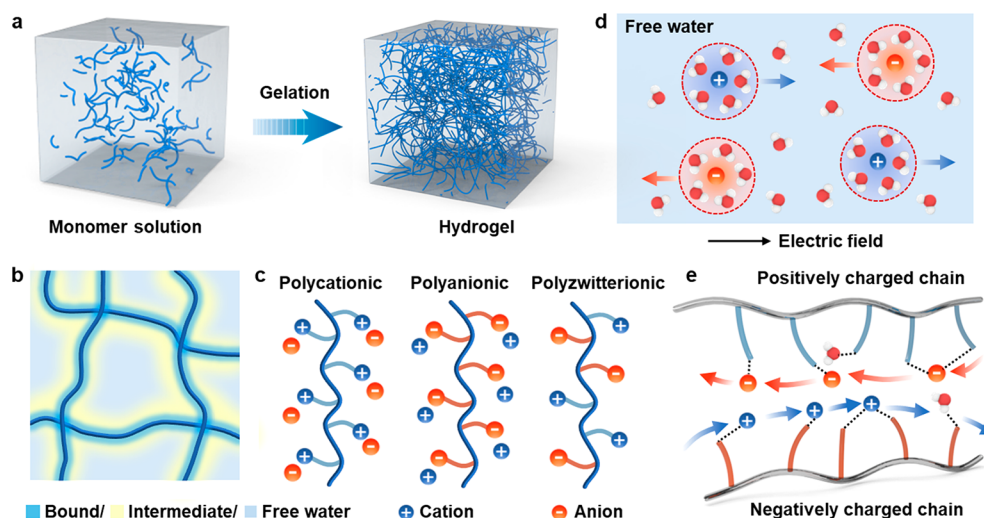
Figure 1. Hydrogel formation and basic properties. (a) Polymer networks cross-linking from monomers. (b) Water states in the hydrogel. (c) Polyionic hydrogel chains. (d) Diffusion of solvated ions in free water. (e) Interaction of ions with polyionic polymer chains.

conductivity, electrostatic adhesion, and controlled swelling degree.

Hydrogel Formation. Hydrogels form by the cross-linking of polymer chains in an aqueous environment. Gelation can be achieved through a variety of mechanisms, including physical entanglement, electrostatic interactions, and covalent chemical cross-linking.[11] With the chemical cross-linking as an example (Figure 1a), a more stable hydrogel matrix can be realized with substantially improved flexibility and spatiotemporal accuracy compared to those with physical methods, as stronger covalent bonds are formed between the chains during polymerization. By introducing a double network structure with two inter-penetrating polymer networks, in which one is stiff and brittle and the other is soft and flexible, one can realize robust and tough hydrogels.[12] To further increase the mechanical strength of hydrogels for soft robotics and wearable applications, hybridization strategies by mixing multiple components such as inorganic nanoparticles and cellulose have been attempted.[13,14]

In addition to conventional hydrogel synthesis in designed molds, 3D printing is amenable to smart polymers with arbitrary configuration,[15] including direct ink writing, stereo-lithography, and fused deposition modeling. Although 3D printing can, in principle, provide on-demand precision fabrication, more efforts are needed to develop advanced inks with desirable mechanical, physical, and chemical properties.

Structure and Water Properties. Macroscopically, hydrogels behave like both solids and liquids and can be considered as a type of quasi-solid material between liquids and solids. High water content makes hydrogels similar to liquid water, including permeability to a wide range of chemicals and transparency to light. On the other hand, due to the constraint of the polymer network, water molecules within the hydrogel cannot flow freely like liquid water. Hence, hydrogels can maintain a certain shape such as a solid, which is the basis for its application in flexible and stretchable devices.

The water in a hydrogel can be divided into bound water, intermediate water, and free water (Figure 1b).[16] Free water has a structure and mobility similar to that of liquid water, whereas bound water is physically bound to polymer chains through strong hydrogen bonds. Between free and bound water, intermediate water interacts weakly with the polymer

chain and surrounding free water molecules. The theory of a water−water interaction and a water−polymer interaction in hydrogels has been largely enriched in recent years.[17−20] The fundamental properties of these water molecules and polymer chains will determine the environmental and electrochemical stability of hydrogels, which is crucial in energy storage devices. For example, when expanding the electrochemical potential window of the batteries containing a hydrogel electrolyte, it is unclear whether the water molecules or the polymer chains decompose first. Water decomposition is closely associated with hydrogen evolution in aqueous batteries, so it is necessary to unveil the stability of water in hydrogels under an electric field.

Conductivity Principles. Introducing ions, including free ions and immobile ionic groups, into the hydrogel can affect the interactions between the components inside the hydrogel, thereby regulating the physicochemical properties of hydrogels to realize their ionotronic applications. According to the source of ions, ionic hydrogels can be divided into two categories: free ionic hydrogels and polyionic hydrogels (Figure 1c). In free ionic hydrogels, the ions are derived from the dissociated salts in the aqueous solution, and they are not bound by the polymer chains and can move freely. In contrast, the ions in polyionic hydrogels originate from ionic groups on the polymer chain, and counterions with opposite charges are close to the ionic groups. The ionic groups bound to the polymer chains cannot move freely, whereas the counterions are mobile, but their movement is affected by the electrostatic interaction of ionic groups. Depending on the charged properties of ionic groups, we may subdivide polyionic hydrogels into polycationic hydrogels, polyanionic hydrogels, and polyzwitterionic hydrogels (Figure 1c). In polyzwitterionic hydrogels, an equal number of anionic groups and cationic groups distribute on the polymer chain, which can retain water and provide ion migration channels. Therefore, the poly-zwitterionic electrolyte is promising in energy storage applications.[21−23]

The charge conduction, contributed by ions and electrons, has different principles at the interface and in bulk. There are two charge conduction mechanisms at the electrode−hydrogel interface: capacitive charge conduction and faradaic charge conduction.[24] The capacitive mechanism is prevalent at the
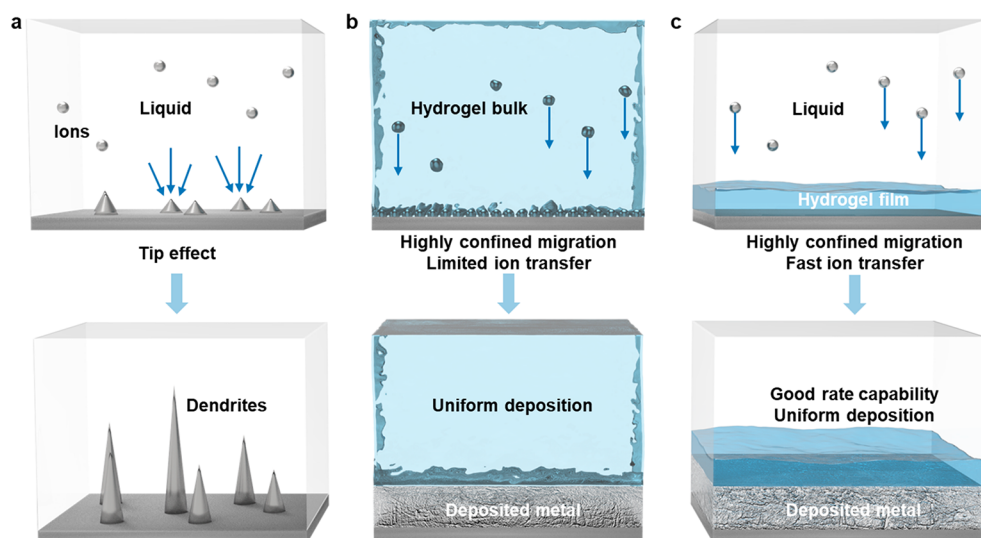
Figure 2. Hydrogel stabilizes the metal anode in aqueous electrolytes. (a) Anode metal plating in aqueous electrolyte and generation of detrimental dendrites. (b) Hydrogel electrolyte regulates ion flux and promotes uniform metal deposition. (c) Hydrogel film protection for the metal anode.

interface of all ionic conductors and electronic conductors. The ions accumulate at the interface and do not carry a continuous current. When an electrochemical reaction happens, for example, during charging and discharging of a battery, a redox reaction with faradaic charge conduction occurs at the electrode—hydrogel interface. Such an ion conduction is accompanied by continuous electron transfer across the electrode.

In contrast to the interface conduction, charge conduction in the bulk of an ionic hydrogel is based on the migration of charge carriers under an electric field. Since free ionic hydrogels contain a large amount of aqueous electrolyte solution, the electrochemical properties of free ionic hydrogels are close to that of aqueous electrolyte solutions. The charge conduction in such a hydrogel is dominated by vehicular diffusion (Figure 1d). However, the presence of the polymer networks usually reduces the diffusion rate of free ions and thus lowers the ionic conductivity of hydrogel. Additionally, charged functional groups on the network in polyionic hydrogels can become hopping sites for ion migration (Figure 1e), which is known as Grotthuss diffusion. In the actual situation of hydrogel electrolytes, these two mechanisms can coexist. By choosing appropriate mobile ions and functional groups, highly conductive hydrogels with an ionic conductivity magnitude of 100 mS cm^{-1} can be obtained,[25] which is roughly the same as aqueous electrolytes with similar ion concentrations. It is important to note that hydrogels can be electronically conductive when the polymer chains contain conjugated units or when conductive nanoparticles are percolated in the hydrogel matrix.[26] These conductive hydrogels are not suitable as electrolytes but may be used for electrode materials in energy storage devices.

PROPERTIES OF SMART BATTERIES

Batteries are becoming indispensable in the daily life of humans. Demand for high energy density batteries keeps increasing in portable electronics, electric vehicles, and household power sources. Aqueous batteries are prospected as a promising next-generation technology owing to their nontoxicity and low-cost metrics. Battery usage scenarios vary

with the electronics it powers and occasionally must be adaptive to extreme mechanical and temperature conditions. In the following, basic requirements for future smart batteries are elaborated with a focus on aqueous batteries.

Chemical Stability. In addition to high capacity, the chemical stability of electrode materials is a formidable issue in its operation. The metal anode in aqueous batteries inevitably forms dendrites due to limited nucleation sites and inhomogeneous plating (Figure 2a), which may finally lead to inner shorting and battery failure. In addition, dendrite formation is also accompanied by hydrogen evolution and electrode surface passivation, resulting in battery bulge and capacity decay, respectively. Numerous strategies have been developed to mitigate this issue, including anode structural design, anode interfacial protection, and electrolyte engineering.[27,28] Their main purpose is to stabilize metal stripping/plating and limit side reactions.

A hydrogel electrolyte with a 3D polymer network is proven to be effective in suppressing dendrite formation during battery operation, resulting in a homogeneous and smooth anode surface (Figure 2b). This is consistent with our results in zinc batteries with polyacrylamide hydrogel electrolytes.[29] Such a phenomenon can be attributed to an electro-chemo-mechanical multifield combination rather than just one factor.[30] First, the polymers with high shear modulus and appropriate stiffness on the anode have been successfully applied to suppress the metal dendrite growth.[31,32] Second, the hydrogel polymer networks can make ion flux in the bulk uniform and induce lateral ion flux near the interface,[33] which can be helpful in regulating the metal ion deposition in a homogeneous way and avoiding dendrite formation. Moreover, by introducing polyanions into the polymer network, such as a carboxylate group ($-COO^-$)[34,35] and sulfonate group ($-SO_3^-$),[36−38] the ion-confinement capability in the hydrogel electrolyte may restrict the movement of cations and further stabilize the metal anode. These hydrogel strategies in aqueous batteries are equally applicable to ionogels in non-aqueous batteries, such as lithium and sodium batteries.[39]

Hydrogel electrolytes in stable batteries require consideration from two aspects. First, the ion conductivity of the
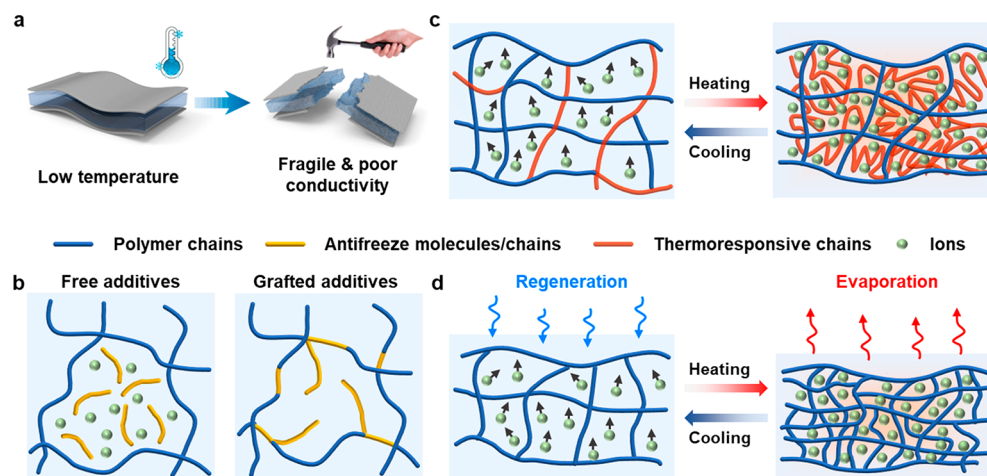
Figure 3. Temperature adaptability of aqueous batteries enabled by hydrogels. (a) Performance deterioration due to freezing of aqueous electrolyte at low temperatures. (b) Antifreezing by introducing additives to hydrogel. (c) Phase transition of hydrogel electrolyte that regulates the migration of ions. (d) Reversible water evaporation and regeneration in hygroscopic hydrogel electrolyte.

hydrogel is still several times lower than that of the liquid electrolyte, so the internal resistance of batteries with bulk hydrogel can be considerable. Therefore, there is an urgent need to develop highly conductive hydrogels or engineer the configuration of hydrogels for batteries that require high-rate capabilities. The other aspect is to create robust adhesion of the hydrogel with a metal anode. This will stabilize the hydrogel/electrode interfaces and subsequently regulate metal deposition and suppress hydrogen evolution.

Combining the interfacial protection concept with hydrogels provides a distinct idea for stabilizing aqueous batteries. We used a polyanionic hydrogel thin film on a zinc metal anode as the protective layer (Figure 2c).[40] The hydrogel layer chemically bonded on the Zn metal surface possesses an anticatalysis effect, which effectively suppresses both the hydrogen evolution reaction and dendrite formation. As a result, stable and reversible Zn stripping/plating over 1000 h can be realized with a rigorous cutoff condition of 10 mA cm^{-2}/5 mAh cm^{-2}. Different from the bulk hydrogel electrolyte, the micron-scale hydrogel-modified electrode does not change the aqueous environment and can retain the capacity advantages and rate capability of aqueous batteries. A similar result may be obtained by employing zwitterionic polymers,[41] in which it is still polyanionic groups that exhibit high bonding energy with cations and ensure uniform metal deposition. Although the hydrogel film protection achieves excellent battery performance, it is more suitable for coin/pouch cells and static energy storage rather than flexible devices because of the liquid electrolytes.

Despite the considerable progress made on metal anode stabilization, high-performance anodes do not always translate to high-performance devices; the stability of cathodes should not be neglected. Luckily, the hydrogel does help improve cathode stability. For example, dissociated sodium ions in alginate hydrogel can alleviate the collapse of the crystal structure of the Na$_{0.65}$Mn$_2$O$_4$ cathode during the charging process,[42] thus offering a superior stable battery. More work is needed to reinforce this conclusion. Different from the dendrites and side reactions on the anode, the main issue for cathodes is structure instability of the materials. Little is known about how the hydrogel structure and polyionic groups affect the cathode material stability.

Temperature Adaptability. The principles of batteries are essentially chemical reactions governed by electrochemical thermodynamics and kinetics, both of which depend on temperature. Therefore, the battery performance is inevitably affected by temperature. Generally, batteries will not operate normally in extremely cold or hot climates. At subzero temperatures, the electrolyte (both aqueous solution and hydrogel) will have freezing problems, leading to reduction in ionic conductivity and subsequently capacity (Figure 3a). It is possible to apply external thermal insulation or heating elements to keep the temperature above 0 °C. Alternatively, an all-climate battery with an internal short-circuit design has also been reported,[43] which can heat itself from temperatures below 0 °C. Despite being an innovative concept, this approach complicates the battery design and increases the fabrication cost and safety risk.

To achieve low-temperature operation of batteries, it is more feasible to engineer electrolytes with a low freezing point and decent ionic conductivity.[44] By adding salt/organic additives or adjusting the structure of cross-linked polymer chains/functional groups (Figure 3b), hydrogel electrolytes can realize a wide range of operating temperatures (−50 to 100 °C).[44,45] The introduced free ions and additives can change the hydrogen bonds in water and reduce the interaction of water molecules under subzero temperatures. Although the addition of antifreeze has been proven to be effective, the solute, especially organic small molecules additives, may escape from the hydrogel network. In contrast, additives grafted on the polymer chains present a more stable freezing tolerance. For example, a high-strength and antifreezing hydrogel can be achieved with ethylene glycol anchored on the polymer network,[46] where the hydrogen bonds between ethylene glycol, water molecules, and the polymer matrix hinder the formation of ice crystals. The combination of intrinsic cold endurance and mechanical robustness means such a hydrogel electrolyte has great potential for flexible batteries and wearable electronics in cold environments.

In contrast to low temperatures, high temperatures will usually increase ion conductivity, which favors the rate capability of a battery. However, concomitant side reactions in batteries at elevated temperatures may occur and cause permanent capacity fading or risk of fire (when organic
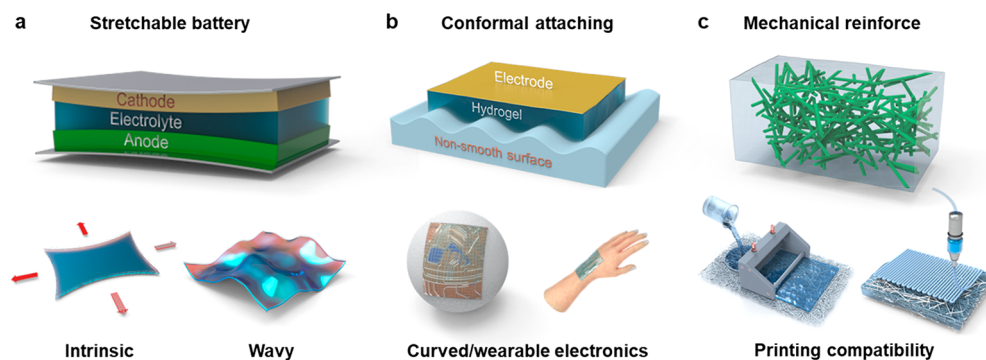
Figure 4. Mechanical regulation of batteries with hydrogel electrolytes. (a) Stretchable battery enabled by wavy structures. (b) Conformal design for structural batteries and wearable electronics. (c) Schematic of framework-reinforced hydrogel electrolyte.

electrolytes are employed). Hydrogels ward off fires due to the intrinsic endothermic effect of water evaporation and the oxygen barrier effect of inner salts,[47,48] but the hydrogels are still limited by the instability of the electrolyte/electrode interface. The external thermal management system cools down the batteries by fans or flowing liquids, which increases the complexity and footprint of the entire system. Therefore, it is of great significance to develop smart batteries that stop working at high temperatures, i.e., a function of thermal self-protection.

Thermoresponsive polymers with ionic and electronic modulation offer viable opportunities.[49,50] For example, poly(N-isopropylacrylamide) hydrogel is a typical thermoresponsive polymer, in which the internal chains present swollen (ion conductive) and shrunken (ion resistive) states below and above the phase transition temperature, respectively. Figure 3c illustrates the principle of smart batteries based on the poly(N-isopropylacrylamide) electrolyte. When the temperature increases, the hydrogel transforms from a hydrophilic to a hydrophobic state, and the transition is reversed after being cooled. Such a hydrogel can also be modified on porous separators to enable thermal self-protection of batteries.[51] However, these thermoresponsive polymers still allow notable ionic mobility in the shrunken state, so the battery is not completely deactivated at high temperatures. This imperfection needs to be addressed by engineering the polymer or the porous electrode structure.

Apart from the use of phase-change hydrogels, we recently demonstrated an original thermal self-protection approach for flexible batteries (Figure 3d).[29] Hygroscopic hydrogels are employed as smart electrolytes. When the temperature increases, a large amount of water in the hydrogel evaporates quickly like sweating. Consequently, the ion transport in the hydrogel electrolyte is gradually restricted until completely cut off, and the overheated battery thus shuts down automatically. When the battery cools down to room temperature, the dehydrated hydrogel spontaneously absorbs moisture from the surrounding air and regenerates itself, and the battery returns to its original state. The thermal switch is intense and repeatable. A major drawback of this approach is the slow recovery (a few hours). For practical application of such a thermal protection method, it is necessary to combine battery design and polymer engineering to further improve thermal regulation capability and response speed.

Mechanical Regulation. Deformable batteries are needed to power wearable electronics that interface tightly with irregular or nonsmooth surfaces including human skin.[52] In a hydrogel−electrolyte battery (Figure 4a), the hydrogels play dual roles of electrolyte and separator. It may also provide a solution to avoid aqueous electrolyte leakage under tensile strain. Based on the intrinsic mechanical advantages of hydrogel electrolytes, stretchable batteries can be assembled through hydrogel prestretching.[53,54] Specifically, flat electrodes are paved on each side of the prestretched hydrogel, thus the battery demonstrates a wavy structure in a relaxed state. In this way, hydrogel electrolytes with suitable monomers and networks endow excellent stretchable batteries. For example, zinc−air batteries based on a dual-network hydrogel electrolyte presented superstretchable capability up to 800% of their original size.[55] In contrast to the electrolyte prestrain strategy, electrode film shrinkage can also create curved-surface electronics for localized stretchable applications.[56] The negative side of this strategy is that delamination of electrode materials and hydrogel electrolyte under reiterant mechanical deformation will cause capacity degradation. This issue is serious but has received relatively less attention. Efforts can be devoted to not only electrode architecture design but also interfacial adhesion strength, for example, by directly cross-linking the hydrogel electrolyte on electrodes. In addition to the inherent stretchability of hydrogels, batteries may also be made stretchable by macrostructure design. As the hydrogel-based batteries are shape-tailorable into desirable structures (e.g., zigzag, honeycomb), it is possible to design zinc batteries into a honeycomb structure with a maximum tensile strain up to 3500%.[57]

Most wearables do not sustain frequent large tensile strains. One possible solution is that the functional device conforms to the irregular surfaces of the substrate,[58,59] which may guarantee the consistency of deformation (Figure 4b). To achieve this, the entire device must be very thin. Kotov and co-workers designed functionalized poly(vinyl alcohol) film with a thickness of approximately 10 μm and fabricated biomorphic structural zinc batteries to stick on robotics.[60] In general, the volumetric capacity of such types of thin and conformal batteries can be much greater compared to that of a stand-alone Li-ion battery. However, due to the limited active materials, the batteries may present much lower areal capacity. Hence, they are suitable for low power consumption or emergency power supply. Achieving high capacity is urgent for conformal batteries, although it has remained challenging. For this purpose, researchers need to exploit structural configurations and high-capacity electrode materials to accelerate the success of reliable conformal batteries for future skin-attachable devices and wearable electronics.

Table 1. Summary of Advantages and Limitations of Hydrogel Electrolytes in Batteries

|	advantage	limitation
mechanical property	●designable networks	●sluggish ion transport
	●flexibility and stretchability	●interface compatibility
	●shape diversity	●interfacial resistance
temperature adaptation	●freezing resistance	●surface stability
	●nonflammability	●encapsulation technique
	●ion flux homogenization	●rate capability
chemical stability	●dendrite suppression	●water electrolysis
	●active species retention	●pore wettability
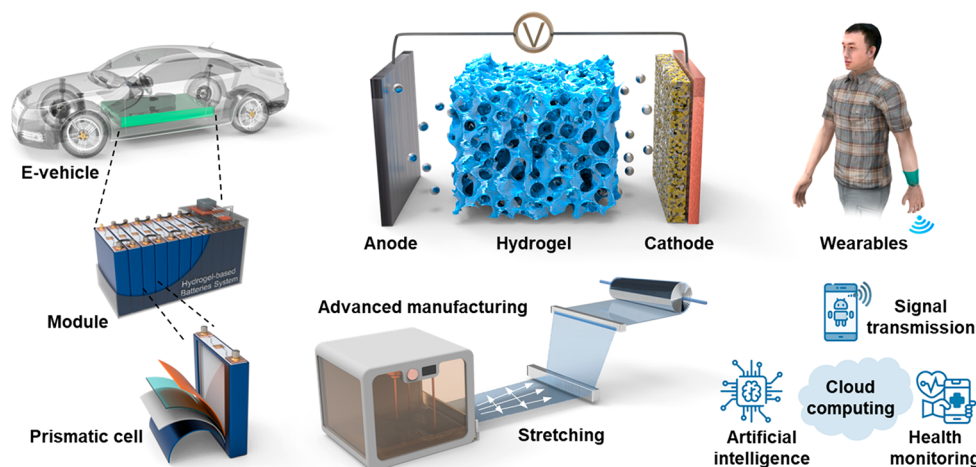
Figure 5. Perspective of hydrogels for future smart batteries.

Another challenge in flexible and wearable batteries is to maintain the operation upon extreme mechanical stimuli, such as pressing, bending, and squeezing. Reinforcing the mechanical properties of hydrogel electrolytes by constructing frameworks helps to improve the overall strength of the device (Figure 4c). These frameworks are generally hydrophilic skeletons, which are compatible with hydrogel formation, such as polyacrylonitrile networks,[61] chitin nanofibers,[62] and cellulose paper.[63] As a typical example, the hydrogel−cellulose paper composite presents higher mechanical strength and maintains the printability of the original paper. The printed batteries on such a hydrogel paper are cuttable and compatible with flexible circuits. These results are encouraging and highlight the feasibility of reinforced hydrogel−cellulose paper for omnipresent flexible and eco-friendly electronics. Given that cellulose fibers can be obtained from various biomass waste materials, there are enormous opportunities for large-scale fabrication of hydrogel−cellulose hybrids.

PERSPECTIVES AND CONCLUSIONS

Hydrogels provide a variety of functions for smart batteries. When the temperature adaptability and mechanical properties of hydrogels are properly tuned, batteries have been initially applied to wearable electronics under different environments (Table 1). It is expected that smart batteries will evolve into powerful energy cornerstones to be part of the Internet of Things (Figure 5). Our perspective to the future is as follows.

Advanced Manufacturing. It is worth noting that the above-mentioned advantages may not coexist if only one type of hydrogel electrolyte is used, neither do the limitations are all on one hydrogel. However, it is likely that the functions of hydrogels can be enriched by composition engineering and advanced manufacturing technologies. Ultrathin hydrogel films are endowed with excellent mechanical properties and rapid stimuli response. Surface-initiated polymerizations including atom transfer radical polymerization and electrochemical deposition have distinct advantages,[64,65] through which precise control of polymer composition, topology, and site-specific functionality is achievable. In contrast, additive manufacturing is a suitable technology for complex geometries and large-scale production, which can be compatible with structural batteries.[66] Recently, 4D-printed hydrogels have spurred burgeoning interests.[67] The so-called 4D-printed hydrogels are 3D-printed jelly objects that can change their properties and functions when triggered by external electrical, mechanical, or thermal stimuli. More investigations into their responsiveness to stimuli could be the future direction of smart batteries. Advanced manufacturing technologies should be ideally compatible with the current battery industry, so that smart hydrogels can be applied first to cells and modules, ultimately serving as a battery pack.

Beyond Room Temperature. Temperature adaptability of rechargeable batteries determines whether they can be operatable in intercontinental regions.[68] As a typical example, hydrogel electrolytes in Zn−MnO$_2$ batteries can be stable over a wide temperature range from −40 to 60 °C.[69] At low temperatures, the electrolyte needs to have prominent conductivity to keep the battery running. In terms of antifreezing thermodynamics and ion diffusion kinetics, double networks, functional groups, and additives that interact with water can be introduced in the hydrogels to restrain the formation of hydrogen bonds between water molecules.[70−72] In contrast, at excessive temperatures, the battery should preferably be in a shutdown state to ensure safety. The thermal

self-protection function is achievable by employing thermo-sensitive groups to control ion mobility. Research may be directed to the engineering of polymer chains by appropriately designing polyanionic, water-interactive, and thermal-responsive groups in one hydrogel electrolyte. Hence, high-performance and stable batteries for all seasons can be realized in the near future.

Wearable Design. Wearables directly on the human body need to consider biocompatibility of materials and mechanical adaptability of devices. Batteries with all hydrogel components present great potential for comfort and implantability.[73] The design principle of each component requires special attention, in which electrolyte and electrode should be ionically and electrically conductive, respectively. Energy autonomy is another concern for the next generation of portable and wearable devices. In this context, a sweat-activated battery offers a promising choice.[74] These batteries can be assembled with salt-free hydrogels for storage and activated by sweat for operation.[75] The sweat can further act as a health monitoring parameter according to the battery performance, eventually to realize smart wearables. Multifunctionality rendered by various hydrogels should not result in significant sacrifice in energy density, power density, and life span.

In conclusion, a functional hydrogel is a wonderful gift to emergent batteries. Despite fundamental progress made in research laboratories, hydrogel-based smart batteries are still in their infancy and far from industrial production. A clear understanding of water molecules and ion transport in hydrogels is still lacking, and more study is required to elucidate the electrochemical behavior and interfacial chemistry. It is likely that hydrogels will be a key material for fabricating energy storage devices with a market share in widely adaptable wearable electronics. With ongoing progress in materials, electronics, and manufacturing technologies, the potential of smart batteries will continue to grow, ranging from human health, e-vehicles, and power regulation. Finally, smart communities will be constructed by integrating cloud computing and the Internet of Things (Figure 5), so that human beings can live in a more refined and intelligent way.

AUTHOR INFORMATION

Corresponding Author
Hong Jin Fan — *School of Physical and Mathematical Science, Nanyang Technological University, Singapore 637371;* orcid.org/0000-0003-1237-4555; Email: fanhj@ntu.edu.sg

Authors
Peihua Yang — *The Institute of Technological Sciences, Wuhan University, Wuhan 430072, China;* orcid.org/0000-0003-0178-6896

Jin-Lin Yang — *School of Physical and Mathematical Science, Nanyang Technological University, Singapore 637371;* orcid.org/0000-0002-5722-3948

Kang Liu — *MOE Key Laboratory of Hydrodynamic Transients, School of Power and Mechanical Engineering, Wuhan University, Wuhan 430072, China;* orcid.org/0000-0002-2781-2581

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsnano.2c07468

Author Contributions
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Notes
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REFERENCES
(1) Sumboja, A.; Liu, J.; Zheng, W. G.; Zong, Y.; Zhang, H.; Liu, Z. Electrochemical Energy Storage Devices for Wearable Technology: A Rationale for Materials Selection and Cell Design. *Chem. Soc. Rev.* **2018**, *47*, 5919−5945.

(2) Zhao, Q.; Stalin, S.; Zhao, C.-Z.; Archer, L. A. Designing Solid-State Electrolytes for Safe, Energy-Dense Batteries. *Nat. Rev. Mater.* **2020**, *5*, 229−252.

(3) Chao, D.; Zhou, W.; Xie, F.; Ye, C.; Li, H.; Jaroniec, M.; Qiao, S.-Z. Roadmap for Advanced Aqueous Batteries: From Design of Materials to Applications. *Sci. Adv.* **2020**, *6*, eaba4098.

(4) Ruan, P.; Liang, S.; Lu, B.; Fan, H. J.; Zhou, J. Design Strategies for High-Energy-Density Aqueous Zinc Batteries. *Angew. Chem., Int. Ed.* **2022**, *61*, e202200598.

(5) Chen, M.; Zhang, Y.; Xing, G.; Chou, S.-L.; Tang, Y. Electrochemical Energy Storage Devices Working in Extreme Conditions. *Energy Environ. Sci.* **2021**, *14*, 3323−3351.

(6) Yang, C.; Suo, Z. Hydrogel Ionotronics. *Nat. Rev. Mater.* **2018**, *3*, 125−142.

(7) Guo, Y.; Bae, J.; Zhao, F.; Yu, G. Functional Hydrogels for Next-Generation Batteries and Supercapacitors. *Trends Chem.* **2019**, *1*, 335−348.

(8) Duan, J.; Xie, W.; Yang, P.; Li, J.; Xue, G.; Chen, Q.; Yu, B.; Liu, R.; Zhou, J. Tough Hydrogel Diodes with Tunable Interfacial Adhesion for Safe and Durable Wearable Batteries. *Nano Energy* **2018**, *48*, 569−574.

(9) Guo, Y.; Bae, J.; Fang, Z.; Li, P.; Zhao, F.; Yu, G. Hydrogels and Hydrogel-Derived Materials for Energy and Water Sustainability. *Chem. Rev.* **2020**, *120*, 7642−7707.

(10) Fu, F.; Wang, J.; Zeng, H.; Yu, J. Functional Conductive Hydrogels for Bioelectronics. *ACS Mater. Lett.* **2020**, *2*, 1287−1301.

(11) Zhang, Y. S.; Khademhosseini, A. Advances in Engineering Hydrogels. *Science* **2017**, *356*, eaaf3627.

(12) Nonoyama, T.; Gong, J. P. Tough Double Network Hydrogel and Its Biomedical Applications. *Annu. Rev. Chem. Biomol. Eng.* **2021**, *12*, 393−410.

(13) Yasui, T.; Kamio, E.; Matsuyama, H. Inorganic/Organic Double-Network Ion Gels with Partially Developed Silica-Particle Network. *Langmuir* **2018**, *34*, 10622−10633.

(14) Guan, Q.-F.; Yang, H.-B.; Han, Z.-M.; Ling, Z.-C.; Yin, C.-H.; Yang, K.-P.; Zhao, Y.-X.; Yu, S.-H. Sustainable Cellulose-Nanofiber-Based Hydrogels. *ACS Nano* **2021**, *15*, 7889−7898.

(15) Li, J.; Wu, C.; Chu, P. K.; Gelinsky, M. 3D Printing of Hydrogels: Rational Design Strategies and Emerging Biomedical Applications. *Mater. Sci. Eng., R* **2020**, *140*, 100543.

(16) Gun'ko, V. M.; Savina, I. N.; Mikhalovsky, S. V. Properties of Water Bound in Hydrogels. *Gels* **2017**, *3*, 37.

(17) Yan, C.; Kramer, P. L.; Yuan, R.; Fayer, M. D. Water Dynamics in Polyacrylamide Hydrogels. *J. Am. Chem. Soc.* **2018**, *140*, 9466−9477.

(18) Liu, X.; Wei, W.; Wu, M.; Liu, K.; Li, S. Understanding the Structure and Dynamical Properties of Stretched Water by Molecular Dynamics Simulation. *Mol. Phys.* **2019**, *117*, 3852−3859.

(19) Liu, Y.; Liu, X.; Duan, B.; Yu, Z.; Cheng, T.; Yu, L.; Liu, L.; Liu, K. Polymer-Water Interaction Enabled Intelligent Moisture Regulation in Hydrogels. *J. Phys. Chem. Lett.* **2021**, *12*, 2587−2592.

(20) Roget, S. A.; Piskulich, Z. A.; Thompson, W. H.; Fayer, M. D. Identical Water Dynamics in Acrylamide Hydrogels, Polymers, and Monomers in Solution: Ultrafast IR Spectroscopy and Molecular Dynamics Simulations. *J. Am. Chem. Soc.* **2021**, *143*, 14855−14868.

(21) Peng, X.; Liu, H.; Yin, Q.; Wu, J.; Chen, P.; Zhang, G.; Liu, G.; Wu, C.; Xie, Y. A Zwitterionic Gel Electrolyte for Efficient Solid-State Supercapacitors. *Nat. Commun.* **2016**, *7*, 11782.

(22) Mo, F.; Chen, Z.; Liang, G.; Wang, D.; Zhao, Y.; Li, H.; Dong, B.; Zhi, C. Zwitterionic Sulfobetaine Hydrogel Electrolyte Building Separated Positive/Negative Ion Migration Channels for Aqueous Zn-MnO₂ Batteries with Superior Rate Capabilities. *Adv. Energy Mater.* **2020**, *10*, 2000035.

(23) Leng, K.; Li, G.; Guo, J.; Zhang, X.; Wang, A.; Liu, X.; Luo, J. A Safe Polyzwitterionic Hydrogel Electrolyte for Long-Life Quasi-Solid State Zinc Metal Batteries. *Adv. Funct. Mater.* **2020**, *30*, 2001317.

(24) Yuk, H.; Lu, B.; Zhao, X. Hydrogel Bioelectronics. *Chem. Soc. Rev.* **2019**, *48*, 1642−1667.

(25) Lee, C.-J.; Wu, H.; Hu, Y.; Young, M.; Wang, H.; Lynch, D.; Xu, F.; Cong, H.; Cheng, G. Ionic Conductivity of Polyelectrolyte Hydrogels. *ACS Appl. Mater. Interfaces* **2018**, *10*, 5845−5852.

(26) Paulsen, B. D.; Fabiano, S.; Rivnay, J. Mixed Ionic-Electronic Transport in Polymers. *Annu. Rev. Mater. Res.* **2021**, *51*, 73−99.

(27) Wang, T.; Li, C.; Xie, X.; Lu, B.; He, Z.; Liang, S.; Zhou, J. Anode Materials for Aqueous Zinc Ion Batteries: Mechanisms, Properties, and Perspectives. *ACS Nano* **2020**, *14*, 16321−16347.

(28) Zuo, Y.; Wang, K.; Pei, P.; Wei, M.; Liu, X.; Xiao, Y.; Zhang, P. Zinc Dendrite Growth and Inhibition Strategies. *Mater. Today Energy* **2021**, *20*, 100692.

(29) Yang, P.; Feng, C.; Liu, Y.; Cheng, T.; Yang, X.; Liu, H.; Liu, K.; Fan, H. J. Thermal Self-Protection of Zinc-Ion Batteries Enabled by Smart Hygroscopic Hydrogel Electrolytes. *Adv. Energy Mater.* **2020**, *10*, 2002898.

(30) Kwon, D.-S.; Kim, H. J.; Shim, J. Dendrite-Suppressing Polymer Materials for Safe Rechargeable Metal Battery Applications: From the Electro-Chemo-Mechanical Viewpoint of Macromolecular Design. *Macromol. Rapid Commun.* **2021**, *42*, 2100279.

(31) Monroe, C.; Newman, J. The Impact of Elastic Deformation on Deposition Kinetics at Lithium/Polymer Interfaces. *J. Electrochem. Soc.* **2005**, *152*, A396.

(32) Kong, X.; Rudnicki, P. E.; Choudhury, S.; Bao, Z.; Qin, J. Dendrite Suppression by a Polymer Coating: A Coarse-Grained Molecular Study. *Adv. Funct. Mater.* **2020**, *30*, 1910138.

(33) Jin, S.; Yin, J.; Gao, X.; Sharma, A.; Chen, P.; Hong, S.; Zhao, Q.; Zheng, J.; Deng, Y.; Joo, Y. L.; Archer, L. A. Production of Fast-Charge Zn-Based Aqueous Batteries via Interfacial Adsorption of Ion-Oligomer Complexes. *Nat. Commun.* **2022**, *13*, 2283.

(34) Tang, Y.; Liu, C.; Zhu, H.; Xie, X.; Gao, J.; Deng, C.; Han, M.; Liang, S.; Zhou, J. Ion-Confinement Effect Enabled by Gel Electrolyte for Highly Reversible Dendrite-Free Zinc Metal Anode. *Energy Storage Mater.* **2020**, *27*, 109−116.

(35) Zhang, B.; Qin, L.; Fang, Y.; Chai, Y.; Xie, X.; Lu, B.; Liang, S.; Zhou, J. Tuning Zn²⁺ Coordination Tunnel by Hierarchical Gel Electrolyte for Dendrite-Free Zinc Anode. *Sci. Bull.* **2022**, *67*, 955−962.

(36) Cui, Y.; Zhao, Q.; Wu, X.; Chen, X.; Yang, J.; Wang, Y.; Qin, R.; Ding, S.; Song, Y.; Wu, J.; Yang, K.; Wang, Z.; Mei, Z.; Song, Z.; Wu, H.; Jiang, Z.; Qian, G.; Yang, L.; Pan, F. An Interface-Bridged Organic-Inorganic Layer that Suppresses Dendrite Formation and Side Reactions for Ultra-Long-Life Aqueous Zinc Metal Anodes. *Angew. Chem., Int. Ed.* **2020**, *59*, 16594−16601.

(37) Cong, J.; Shen, X.; Wen, Z.; Wang, X.; Peng, L.; Zeng, J.; Zhao, J. Ultra-Stable and Highly Reversible Aqueous Zinc Metal Anodes with High Preferred Orientation Deposition Achieved by a Polyanionic Hydrogel Electrolyte. *Energy Storage Mater.* **2021**, *35*, 586−594.

(38) Fan, H.; Wang, M.; Yin, Y.; Liu, Q.; Tang, B.; Sun, G.; Wang, E.; Li, X. Tailoring Interfacial Zn²⁺ Coordination via a Robust Cation Conductive Film Enables High Performance Zinc Metal Battery. *Energy Storage Mater.* **2022**, *49*, 380−389.

(39) Wang, S.; Jiang, Y.; Hu, X. Ionogel-Based Membranes for Safe Lithium/Sodium Batteries. *Adv. Mater.* **2022**, *34*, 2200945.

(40) Yang, J.-L.; Li, J.; Zhao, J.-W.; Liu, K.; Yang, P.; Fan, H. J. Stable Zinc Anodes Enabled by a Zincophilic Polyanionic Hydrogel Layer. *Adv. Mater.* **2022**, *34*, 2202382.

(41) Chen, R.; Liu, Q.; Xu, L.; Zuo, X.; Liu, F.; Zhang, J.; Zhou, X.; Mai, L. Zwitterionic Bifunctional Layer for Reversible Zn Anode. *ACS Energy Lett.* **2022**, *7*, 1719−1727.

(42) Dong, H.; Li, J.; Zhao, S.; Jiao, Y.; Chen, J.; Tan, Y.; Brett, D. J. L.; He, G.; Parkin, I. P. Investigation of a Biomass Hydrogel Electrolyte Naturally Stabilizing Cathodes for Zinc-Ion Batteries. *ACS Appl. Mater. Interfaces* **2021**, *13*, 745−754.

(43) Wang, C.-Y.; Zhang, G.; Ge, S.; Xu, T.; Ji, Y.; Yang, X.-G.; Leng, Y. Lithium-Ion Battery Structure That Self-Heats at Low Temperatures. *Nature* **2016**, *529*, 515−518.

(44) Liu, S.; Zhang, R.; Mao, J.; Zhao, Y.; Cai, Q.; Guo, Z. From Room Temperature to Harsh Temperature Applications: Fundamentals and Perspectives on Electrolytes in Zinc Metal Batteries. *Sci. Adv.* **2022**, *8*, eabn5097.

(45) Jian, Y.; Handschuh-Wang, S.; Zhang, J.; Lu, W.; Zhou, X.; Chen, T. Biomimetic Anti-Freezing Polymeric Hydrogels: Keeping Soft-Wet Materials Active in Cold Environments. *Mater. Horiz.* **2021**, *8*, 351−369.

(46) Mo, F.; Liang, G.; Meng, Q.; Liu, Z.; Li, H.; Fan, J.; Zhi, C. A Flexible Rechargeable Aqueous Zinc Manganese-Dioxide Battery Working at − 20 °C. *Energy Environ. Sci.* **2019**, *12*, 706−715.

(47) Shang, K.; Liao, W.; Wang, J.; Wang, Y.-T.; Wang, Y.-Z.; Schiraldi, D. A. Nonflammable Alginate Nanocomposite Aerogels Prepared by a Simple Freeze-Drying and Post-Cross-Linking Method. *ACS Appl. Mater. Interfaces* **2016**, *8*, 643−650.

(48) Zhang, H.; Liu, Z.; Mai, J.; Wang, N.; Liu, H.; Zhong, J.; Mai, X. A Smart Design Strategy for Super-Elastic Hydrogel with Long-Term Moisture, Extreme Temperature Resistance, and Non-Flammability. *Adv. Sci.* **2021**, *8*, 2100320.

(49) Chen, Z.; Hsu, P.-C.; Lopez, J.; Li, Y.; To, J. W. F.; Liu, N.; Wang, C.; Andrews, S. C.; Liu, J.; Cui, Y.; Bao, Z. Fast and Reversible Thermoresponsive Polymer Switching Materials for Safer Batteries. *Nat. Energy* **2016**, *1*, 15009.

(50) Mo, F.; Li, H.; Pei, Z.; Liang, G.; Ma, L.; Yang, Q.; Wang, D.; Huang, Y.; Zhi, C. A Smart Safe Rechargeable Zinc Ion Battery Based on Sol-Gel Transition Electrolytes. *Sci. Bull.* **2018**, *63*, 1077−1086.

(51) Zhu, J.; Yao, M.; Huang, S.; Tian, J.; Niu, Z. Thermal-Gated Polymer Electrolytes for Smart Zinc-Ion Batteries. *Angew. Chem., Int. Ed.* **2020**, *59*, 16480−16484.

(52) Pan, Z.; Yang, J.; Jiang, J.; Qiu, Y.; Wang, J. Flexible Quasi-Solid-State Aqueous Zn-Based Batteries: Rational Electrode Designs for High-Performance and Mechanical Flexibility. *Mater. Today Energy* **2020**, *18*, 100523.

(53) Mackanic, D. G.; Kao, M.; Bao, Z. Enabling Deformable and Stretchable Batteries. *Adv. Energy Mater.* **2020**, *10*, 2001424.

(54) Song, W.-J.; Lee, S.; Song, G.; Park, S. Stretchable Aqueous Batteries: Progress and Prospects. *ACS Energy Lett.* **2019**, *4*, 177−186.

(55) Ma, L.; Chen, S.; Wang, D.; Yang, Q.; Mo, F.; Liang, G.; Li, N.; Zhang, H.; Zapien, J. A.; Zhi, C. Super-Stretchable Zinc-Air Batteries Based on an Alkaline-Tolerant Dual-Network Hydrogel Electrolyte. *Adv. Energy Mater.* **2019**, *9*, 1803046.

(56) Rich, S. I.; Lee, S.; Fukuda, K.; Someya, T. Developing the Nondevelopable: Creating Curved-Surface Electronics from Non-stretchable Devices. *Adv. Mater.* **2022**, *34*, 2106683.

(57) Yao, M.; Yuan, Z.; Li, S.; He, T.; Wang, R.; Yuan, M.; Niu, Z. Scalable Assembly of Flexible Ultrathin All-in-One Zinc-Ion Batteries with Highly Stretchable, Editable, and Customizable Functions. *Adv. Mater.* **2021**, *33*, 2008140.

(58) Wang, C.; He, K.; Li, J.; Chen, X. Conformal Electrodes for On-Skin Digitalization. *SmartMat* **2021**, *2*, 252−262.

(59) Hu, M.; Zhang, J.; Liu, Y.; Zheng, X.; Li, X.; Li, X.; Yang, H. Highly Conformal Polymers for Ambulatory Electrophysiological Sensing. *Macromol. Rapid Commun.* **2022**, *43*, 2200047.

(60) Wang, M.; Vecchio, D.; Wang, C.; Emre, A.; Xiao, X.; Jiang, Z.; Bogdan, P.; Huang, Y.; Kotov, N. A. Biomorphic Structural Batteries for Robotics. *Sci. Robot.* **2020**, *5*, eaba1912.

(61) Li, H.; Han, C.; Huang, Y.; Huang, Y.; Zhu, M.; Pei, Z.; Xue, Q.; Wang, Z.; Liu, Z.; Tang, Z.; Wang, Y.; Kang, F.; Li, B.; Zhi, C. An Extremely Safe and Wearable Solid-State Zinc Ion Battery Based on a Hierarchical Structured Polymer Electrolyte. *Energy Environ. Sci.* **2018**, *11*, 941−951.

(62) Liu, C.; Xu, W.; Mei, C.; Li, M.; Chen, W.; Hong, S.; Kim, W.-Y.; Lee, S.-y.; Wu, Q. A Chemically Self-Charging Flexible Solid-State Zinc-Ion Battery Based on VO_2 Cathode and Polyacrylamide−Chitin Nanofiber Hydrogel Electrolyte. *Adv. Energy Mater.* **2021**, *11*, 2003902.

(63) Yang, P.; Li, J.; Lee, S. W.; Fan, H. J. Printed Zinc Paper Batteries. *Adv. Sci.* **2022**, *9*, 2103894.

(64) Matyjaszewski, K. Advanced Materials by Atom Transfer Radical Polymerization. *Adv. Mater.* **2018**, *30*, 1706441.

(65) Cross, E. R. The Electrochemical Fabrication of Hydrogels: A Short Review. *SN Appl. Sci.* **2020**, *2*, 397.

(66) Zhu, Z.; Ng, D. W. H.; Park, H. S.; McAlpine, M. C. 3D-Printed Multifunctional Materials Enabled by Artificial-Intelligence-Assisted Fabrication Technologies. *Nat. Rev. Mater.* **2021**, *6*, 27−47.

(67) Dong, Y.; Wang, S.; Ke, Y.; Ding, L.; Zeng, X.; Magdassi, S.; Long, Y. 4D Printed Hydrogels: Fabrication, Materials, and Applications. *Adv. Mater. Technol.* **2020**, *5*, 2000034.

(68) Wang, H.; Chen, Z.; Ji, Z.; Wang, P.; Wang, J.; Ling, W.; Huang, Y. Temperature Adaptability Issue of Aqueous Rechargeable Batteries. *Mater. Today Energy* **2021**, *19*, 100577.

(69) Chen, M.; Chen, J.; Zhou, W.; Han, X.; Yao, Y.; Wong, C.-P. Realizing an All-Round Hydrogel Electrolyte toward Environmentally Adaptive Dendrite-Free Aqueous $Zn-MnO_2$ Batteries. *Adv. Mater.* **2021**, *33*, 2007559.

(70) Zhang, D.; Liu, Y.; Liu, Y.; Peng, Y.; Tang, Y.; Xiong, L.; Gong, X.; Zheng, J. A General Crosslinker Strategy to Realize Intrinsic Frozen Resistance of Hydrogels. *Adv. Mater.* **2021**, *33*, 2104006.

(71) He, S.; Cheng, Q.; Liu, Y.; Rong, Q.; Liu, M. Intrinsically Anti-Freezing and Anti-Dehydration Hydrogel for Multifunctional Wearable Sensors. *Sci. China: Mater.* **2022**, *65*, 1980−1986.

(72) Jiang, L.; Dong, D.; Lu, Y.-C. Design Strategies for Low Temperature Aqueous Electrolytes. *Nano Research Energy* **2022**, *1*, e9120003.

(73) Ye, T.; Wang, J.; Jiao, Y.; Li, L.; He, E.; Wang, L.; Li, Y.; Yun, Y.; Li, D.; Lu, J.; Chen, H.; Li, Q.; Li, F.; Gao, R.; Peng, H.; Zhang, Y. A Tissue-Like Soft All-Hydrogel Battery. *Adv. Mater.* **2022**, *34*, 2105120.

(74) Manjakkal, L.; Yin, L.; Nathan, A.; Wang, J.; Dahiya, R. Energy Autonomous Sweat-Based Wearable Systems. *Adv. Mater.* **2021**, *33*, 2100899.

(75) Lv, J.; Thangavel, G.; Li, Y.; Xiong, J.; Gao, D.; Ciou, J.; Tan, M. W. M.; Aziz, I.; Chen, S.; Chen, J.; Zhou, X.; Poh, W. C.; Lee, P. S. Printable Elastomeric Electrodes with Sweat-Enhanced Conductivity for Wearables. *Sci. Adv.* **2021**, *7*, eabg8433.