Biomimetic organohydrogel electrolytes for high-environmental adaptive energy storage devices

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Abstract
Conventional hydrogel electrolytes suffer from the following notable defects: (a) water molecules inevitably evaporate from hydrogels under ambient conditions, and high temperature accelerates the dehydration process, leading to deterioration of electrochemical performance; (b) at subzero temperatures, the water existed in gel matrix would freeze and inhibit the ion transportation of hydrogel electrolyte; (c) while operating under water, the gel electrolyte absorbs water and swells, resulting in the loss of adhesion between electrodes and electrolyte. The exchange of solutes causes the decrease of ion concentration and depresses the device performance. These environmental effects fundamentally limit the long-term stability and utilization of aqueous flexible energy storage devices under severe conditions. Hence, inspired by epidermal tissue of mammalian skin, we propose a biomimetic organohydrogel (BM-gel) electrolyte with extreme temperature tolerance and long-term moisture lock-in property, which is synthesized in an ethylene glycol/water solvent system with a chemically elastomeric coating on the surface. The BM-gel electrolyte exhibits high ionic conductivity when containing different ions, such as Zn²⁺, Li⁺, H⁺, and Na⁺ ions. A rechargeable Zn-MnO₂ battery is constructed with the BM-gel electrolyte, which exhibits excellent electrochemical performance over the temperature range from −20°C to 80°C. The specific capacity retains over 70% and coulombic efficiencies approach ~100% in full temperature scale. Even after a prolonged storage of 30 days without package, 84.6% capacity is retained benefiting from the superior antidehydration property bestowed by the thin elastomer coating. Furthermore, another two types of energy storage devices were also fabricated with the novel hydrogel, demonstrating the universal feature of our strategy.

KEYWORDS
biomimetic organohydrogel, energy storage, environmental adaptive, flexible

Funian Mo and Guojin Liang contributed equally to this work.

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**INTRODUCTION**

Owing to their intrinsic safety, flexibility, and cost-effectiveness, hydrogel electrolytes are attracting immense attention in the field of flexible aqueous energy storage devices.\(^1\)-\(^6\) Up to now, numerous attempts have been made to investigate hydrogel materials with distinctive properties, and high-performance solid-state batteries equipped with these electrolytes have been realized.\(^7\)-\(^10\) In fact, these reported flexible batteries normally feature the sandwich architecture, which comprises an indispensable hydrogel electrolyte (serving as a separator simultaneously) sandwiched between two soft electrodes, and no extra layer of package is wrapped outside. However, even under the ambient conditions, water inevitably evaporates from hydrogels, and the loss of water seriously affects the migration of electrolytic ions and the rubbery mechanical elasticity of the polymer framework. Conventional sealed package requires stringent and complicated fabrication processes, along with volume/mass economy due to the use of an additional component, thus little emphasis has been placed on the focus of water retention of hydrogel electrolyte. In addition, the foremost performance metrics, such as reliability, flexibility, and electrochemical properties for flexible aqueous batteries, are all influenced by temperature. Unfortunately, high temperatures would accelerate the drying out process of hydrogels, while subzero temperatures result in freezing of the hydrogels.\(^11\),\(^12\) Almost all the hydrogel electrolytes cannot resist high and cold temperatures, and the fabricated batteries are limited in short-term usage at room temperature. Significant advances with respect to low temperature available and waterproof-coated supercapacitors have been made in recent years, but little emphasis has been placed on batteries.\(^13\),\(^14\) Therefore, it is highly desirable to develop novel hydrogel electrolytes with the synergy properties of antiheating, antifreezing, and long-term stability in a wide temperature window.

In the epidermal tissue of mammalian skin, the elastomer-like epidermis effectively prevents the hydrogel-like muscle tissue it covers from dehydration (Scheme 1), that is, the epidermis can effectively separate muscle tissue from external environments and keep the muscle stable. Inspired by the function of epidermis, grafting elastomer onto the activated surface of hydrogel may provide a feasible solution to stabilize the hydrogel from any variation of external environments. The internal hydrogels function as flexible ionic conductors, while the coated elastomers are expected to not only serve as stretchable dielectrics but also act as seals to retard dehydration and the exchange of solutes from the external environment.\(^15\)-\(^18\) Moreover, the hydrophobic thin elastomer layer with low solubility of water bestows the inner hydrogel with waterproof capabilities when the devices are placed under water.\(^19\) In addition, ethylene glycol (EG), as a kind of nontoxic antifreezing agent, has been widely used to improve the freezing resistance of hydrogel electrolyte at subzero temperature. One effective strategy is to modify the hydrogel by a solvent-displacement process, where EG was introduced by soaking prefabricated hydrogels into EG.\(^20\) Another promising strategy is to synthesize the organohydrogels by using an EG-water binary solvent as the dispersion medium. The EG can form stable molecular clusters with H\(_2\)O molecules that compete with hydrogen bonds in water, and thus inhibits the crystallization and depress the freezing point of hydrogel.\(^21\)

With the use of aforementioned design principles, we fabricated an elastomer-coated EG-based Zn-alginate/polyacrylamide (PAM) organohydrogel electrolyte, which possesses antidehydration and antifreezing properties, and successfully applied it to diverse energy storage devices. In order to form strong adhesion between the gel matrix and superficial elastomer layer, silane-coupling agents were previously added into both the precursors of organohydrogel and elastomer. During the manufacturing process of polymer matrix, the reactive silane-coupling agents condensate and
generate tough bonding across the interface. The elastomer layers not only function as seals to prevent water evaporation but also retard the exchange of solutes between inside organohydrogel and external environment, guaranteeing the long-term usability. We first chose a rechargeable aqueous Zn-MnO₂ battery system, which has attracted extensive attention recently in virtue of its intrinsic safety, high capacity, and cycling stability as a model system to combine with this biomimetic organohydrogel (BM-gel) electrolyte for detailed studies. As a proof of universality, we also formulated diverse energy storage devices equipped with this elaborately designed organohydrogel electrolyte afterwards. These results indicated that the assembled devices had realized ultrastable electrochemical performance in a wide range of temperature (from −20 °C to 80 °C), superior water retention in air, and waterproof properties under water. These capabilities make up for the defects in the research of classical environmental adaptive flexible energy storage devices, which involve an ordinary hydrogel electrolyte.

2 | RESULTS AND DISCUSSION

2.1 | Design principles of high-environmental adaptive organohydrogel electrolyte

The synthesis process of designed BM-gel electrolyte can be divided into three sequential steps, as illustrated in Figure 1A and Figure S1. Firstly, an organohydrogel of alginate/PAM was obtained via free radical polymerization by an acrylamide monomer solution (containing 30 wt% EG) in the presence of dissolved alginate (see the “Experimental Section” section for details, Supporting Information). Note that before polymerization, 3-(trimethoxysilyl) propylmethacrylate (TMSPMA) was added into the hydrogel precursors as the coupling agent. Secondly, the prepared organohydrogel was immersed in a water solution containing 2 mol L⁻¹ ZnSO₄ and 0.2 mol L⁻¹ MnSO₄, together with 0.1 M sodium dodecyl sulfate (SDS) as the surfactant for 1 hour so that the electrolyte solution could fully infiltrate into hydrogel matrix. (Figure 1A-i). In this step, we took advantage of these synergistic effects: (a) strong ionic crosslinks were formed between the dissociated Zn²⁺ ions and the surrounding alginate units, which can effectively dissipate mechanical energy when the gel was under stress loading (Figure 1A-ii). In the organohydrogel matrix, there are two kinds of crosslinking points between the PAM chains. One is the physical hydrogen bonds formed between the carbonyl and amino side groups on different molecular chains. The other one is the chemical crosslinking formed by crosslinking the agent of N,N⁹-methylenebisacrylamide (MBAA) (Figure S1b). The establishment of crosslinked structure can limit the shape expansion caused by the swelling behavior under water. (b) The prehydrolysis coupling agent, TMSPMA, is hydrophobic and would be difficult to stick into the hydrophilic organohydrogel. The surfactant in the mixture solution can be absorbed into the interface layer between organohydrogel and elastomer, and helps the TMSPMA on the interface get solvated and hydrolyzed. As illustrated in Figure 1A-iii, strong hydrogen-bonding interactions formed among water, EG, and PAM chains, which prevent the crystallization of water molecules at subzero temperatures. In addition, the carboxyl and hydroxyl side groups in alginate could also form the hydrogen bonding interactions with the molecules of EG and water, which potentially had a great effect on the antifreezing and mechanical properties (Figure S1c). In the third step, we mixed the curing agent of a Sylgard 184 and another bonding agent, triethoxy(vinyl)silane (TEOV), into the precursor of the elastomer-polydimethylsiloxan (PDMS). Then we dipped the aforementioned organohydrogel into the PDMS precursors for five times and hung at room temperature to drain the excess PDMS (Figure 1A-iv). At this time, the surfactant of SDS contributed to promote internetwork condensation. Actually, the prehydrolysis coupling agent on the PDMS elastomer chains was hydrophobic, and it would be difficult to stick into the organohydrogel. In this case, the surfactant adsorbed at the organohydrogel-elastomer interface could effectively reduce the surface tension and surface free energy, thus helping the coupling agent of TEOV on the PDMS elastomer chains to get solvated and hydrolyzed (Figure S2). After being stored in a 65°C oven for 2 hours sealed in a Petri dish to prevent dehydration, a thin PDMS layer was formed and coated on the surface of organohydrogel through siloxane bonding interaction (Figure 1A-v).

The bonding mechanism of the elastomeric coating process is schematically illustrated in Figure 1B and Figure S1. As mentioned earlier, the silane-coupling agents are previously added into both the precursors of the organohydrogel and the elastomer. When the precursors form separate polymer networks, the added coupling agents with suitable functional groups can copolymerize into the polymer chains, but do not condensate at this stage. After the surface-activation process, the coupling agents in the interfacial layer condensate and form bonds across the contacted interface of the organohydrogel and the elastomer. With regard to the chemical reaction of the trialkoxysilane-coupling agent, the alkoxyl groups first hydrolyze to silanol groups in the presence of water. Subsequently, with the help of surfactant, these silanol groups formed tough siloxane bonds through condensation between the interface of the organohydrogel and elastomeric coating.
2.2 Characterization of the designed high-environmental adaptive organohydrogel electrolyte

With the use of the design principles, a family of BM-gel electrolyte with elastomeric coating was synthesized according to the proposed fabrication method (Figure 2A). The scanning electron microscope (SEM) image reveals that the resulting coating had a thickness of approximately 100 μm. Cross-sectional SEM mapping intuitively depicts the conformal and continuous interface between organohydrogel matrix and superficial coating with close contact.26 Energy dispersive spectrometer (EDS) mappings demonstrate the homogeneous distribution of C, Zn, and
Mn elements in organohydrogel matrix and the signals of Si are well dispersed across the elastomeric-coated layer. Fourier-transform infrared spectroscopy (FTIR) was executed to identify the components of the BM-gel electrolyte (Figure S3). Notably, the spectrum of cross-sectional part exhibited several absorption bands at 1120 cm\(^{-1}\) (NH\(_2\) in-plane rocking), 1654 and 1616 cm\(^{-1}\) (N-H stretching vibration of amide I and II bands), which were the typical absorption bands of the PAM gel matrix.\(^{27,28}\) For the spectrum of the surface part, the characteristic peaks at 790 and 1060 cm\(^{-1}\) were assigned to the Si-O stretching vibration of PDMS silane, which validate the existence of elastomeric coating onto the surface of organohydrogel matrix.\(^{29}\) We further characterized the adhesion energy using the peeling test (Figure S4). Without the coupling agents, the hydrogel peeled on the interface and the adhesion energy is low (~15.0 N m\(^{-1}\)). When the coupling agents were added to both precursors of organohydrogel and elastomer, the adhesion energy was relatively high (~90.0 N m\(^{-1}\)), accompanied with fracture occurred in the organohydrogel. These results firmly demonstrate the formation of covalent bonds in the interfaces between organohydrogel and elastomeric...
coating. In addition, the synthesized BM-gel electrolyte exhibited a transparent state; thus we doped the colorful ink into precursor before polymerization to dye it color for easy observation (Figure S5). The freezing point of the BM gels could be controlled by tuning the EG weight contents as shown in Figure S6. Moreover, differential scanning calorimetry (DSC) was performed on the BM gel with 30% EG content, and the result indicated that the crystallization peak started from about −23°C and terminated at around −30°C as the decreasing temperature. Therefore, the freezing point of the organohydrogel was in the range of −23°C to −30°C (Figure S7a). The thermogravimetric (TG) test indicated that the elastomer coating can effectively prevent the water evaporation over 120°C, while the normal PAM hydrogel lost its weight approaching to its original water contents (~80 wt%) (Figure S7b).

After 1 day of storage at −20°C or 80°C, the mechanical properties of the BM-gel electrolyte were well persevered, exhibiting impressive flexibility to endure large deformations including twisting and compressing (Figure S8). Once the external force withdrew, the BM-gel electrolyte quickly recovered from deformed shapes, showing a high resilience. By comparison, the PAM-hydrogel electrolyte was frozen into solid at −20°C and dried out at 80°C (Figure 2C). Correspondingly, the quantified tensile strength and compression strength of the BM-gel electrolyte display a similar value with subtle changes after cooling or heating, sharply contrasting with the appreciable deterioration in the mechanical properties of the PAM-hydrogel electrolyte (Figure 2D). The excellent temperature tolerance of the BM-gel electrolyte can be attributed to the synergistic effects elucidated as follows: (a) the nonvolatile EG molecules existed in the gel network formed strong hydrogen bonds with water that disrupted the crystallization of ice at subzero temperatures, thus depressing the freezing point of organohydrogel. (b) The antidehydration elastomeric coating layer can prevent the evaporation of water molecules from the inner gel matrix, endowing the organohydrogel with good consistency and durability at high temperatures.

In terms of the long-term stability, the dehydration test was carried out on the BM-gel and PAM-hydrogel electrolyte with the same dimensions under the specific conditions. The test was performed at 25°C and 50% humidity, and we recorded the weight retention at different time intervals. As illustrated in Figure 2E, the results revealed that the weight of BM-gel electrolyte had very minor drift (< 2%) even after 30 days of storage, whereas the uncoated PAM-hydrogel electrolyte lost most its weight after the initial 5 days and finally changed to dry and hard scaffolds. To further verify the antidehydration properties of the BM-gel electrolyte, the BM-gel and PAM-hydrogel electrolytes were placed in a −20°C freeze-dryer or an 80°C oven for 24 hours (Figure 2F). The PAM hydrogel was freeze-dried in cold or transformed a dried bulk polymer in hot, while the BM-gel electrolyte remained soft and elastic under various harsh conditions, caused by the synergies of EG and elastomer coating. In addition, we immersed a piece of BM-gel electrolyte with arbitrary shape in a dye bath for 1 hour. After that, the color was readily washed away by clean water (Figure 2G). This revealed that elastomer coating effectively retarded the mass exchange between the inner organohydrogel and the outer environment. More importantly, no previously existing commercial packing can perfectly seal the hydrogels of arbitrary shape. In order to measure the ionic conductivity of the BM-gel electrolyte, two plates of stainless steel were wrapped into the BM-gel electrolyte before the elastomer coating process. As shown in Figure 2H and Figure S9, the ionic conductivity of BM-gel electrolyte containing 2 mol L⁻¹ ZnSO₄ and 0.1 mol L⁻¹ MnSO₄ was calculated to be 16.3 mS cm⁻¹, which was comparable to other ionic conducting polyelectrolytes with zinc ion in the literature studies (Table S1). No appreciable deterioration in the ionic conductivity can be observed even at −20°C (14.1 mS cm⁻¹), and it possessed a higher value of 18.2 mS cm⁻¹ at 80°C due to the increase of diffusion velocity of zinc ions at high temperature. Only upon cooling down below −25°C, the resistance of the BM-gel electrolyte largely increased in the low frequency of the AC impedance spectra, which was resulted from the freezing of the BM-gel electrolyte (Figure S9c). Furthermore, the BM-gel electrolyte only exhibited a slight decrease in the ionic conductivity even after 30-day storage in air. A possible explanation is that the interfacial contact between the organohydrogel and stainless steel electrodes deteriorated and the dissolved salts in the gel matrix made an adverse effect on the contact part of the electrodes during the long-term storage, leading to a slightly increased interfacial resistance. These results firmly verify the extremely temperature tolerance and antidehydration function of BM-gel electrolyte for long-term applications. In addition, the thickness of elastomer on hydrogel surfaces can be regulated by repeating the coating process, and the thickness of elastomer was not obviously affected by the excellent ionic conductivity of the organohydrogel electrolyte (Figure S10).

### 2.3 | Rechargeable Zn-MnO₂ battery

**based on the high-environmental adaptive organohydrogel electrolyte**

Rechargeable Zn-MnO₂ battery system was first chosen as a model system to integrate with the elaborately
designed BM-gel electrolyte. The binder-free electrodes were prepared by the in situ electrodeposition method, which could provide an intimate direct contact of Zn or MnO₂ with the current collectors of stainless-steel mesh (SS mesh) (Figures S11 and S12). Figure S13A exhibits the XRD pattern of deposited MnO₂@SS mesh electrode, in which all characteristic peaks are well-indexed to Akhtenskite MnO₂ (JCPDS 30-0820). The XPS results reveal that the spin-energy separation of the Mn 3s doublet is 4.84 eV, indicating that the Mn element in the electrodeposited MnO₂ has a charge state of approximately 4.0 (Figure S13B). The SEM images intuitively show that the MnO₂ comprise a highly porous structure of interconnected nanoflakes (Figure S14A). As depicted in the TEM images (Figure S14B), the porous MnO₂ nanoflakes are polycrystalline consisting of nanograins with a size of approximately 10 nm. The SEM image of Zn anode, as given in Figure S14C, showed that the electroplated zinc on the SS mesh exists as uniform porous nanosheet structure, which could possibly facilitate the interfacial compatibility of electrode-electrolyte and enabled a fast charge transport.

In general, for conventional flexible energy storage devices with the sandwich structure, water molecules evaporate from the externally exposed part of hydrogel electrolyte. Our approach of chemical elastomeric coating technology prevents the water evaporation of the naked part of hydrogel electrolyte and can be applicable to diverse flexible energy storage devices. The manufacturing process of environmental adaptive Zn-MnO₂ battery-based BM-gel electrolyte (EA battery) is schematically illustrated in Figure 3A. The prepared electrodes were first fixed nominally in the middle of two glass plates by utilizing a 2-mm-thick silicone spacer that also serves as a reaction mold for the polyelectrolyte. Next, a solution containing precursor was injected into the reaction mold and the organohydrogel electrolyte was achieved after the photoinduced free radical polymerization. After that, an elastomeric coating process was performed onto the surface of the as-prepared battery as described earlier to obtain the biomimetic moisture-lock-in coating of the whole device. In addition, pure PAM-hydrogel electrolyte-based Zn-MnO₂ battery (PAM battery) was also fabricated as the control group. At first, we investigated the electrochemical performance of the fabricated EA battery under the normal conditions (25°C), as shown in Figure S15. The results indicated that the EA battery can deliver a high capacity of 272 mA h g⁻¹ at the current density of 0.1 A g⁻¹ with coulombic efficiencies approaching 100% and had a high volumetric energy density of 26.88 mW h cm⁻³. Next, the real-time influence of temperature was investigated by simulating the actual harsh conditions. The electrochemical properties of the fabricated batteries were examined while the devices were operating inside a thermostat over the temperature ranged from −20°C to 80°C. Figure 3B shows the CV curves of the EA battery recorded for several minutes at −20°C, 25°C, 60°C, and 80°C. At the scan rate of 1 mV s⁻¹, all the CV curves exhibit distinguished reduction/oxidation peaks with negligible voltage polarization, indicating ideal reaction reversibility. The intensity of peaks after cooling or heating appears to increase slightly due to the faster ion transport at high temperature. Electrochemical impedance spectroscopy (EIS) plots of EA battery were also recorded at various temperatures (Figure 3C). In the EIS plots, the semicircle at medium frequencies represents the faradiac charge-transfer resistance, which corresponds to the ionic conductivity. Upon cooling from 25°C to −20°C, the semicircle diameter of the environmental adaptive battery increased from approximately 170 to 366 Ω, which is due to the ion diffusion of Zn²⁺ alleviating at low temperature, leading to a slight decline in ionic conductivity. Similarly, when the battery worked at 80°C, the semicircle contracted owing to the higher ionic conductivity at high temperature. Overall, the impedance of EA battery increased within the reasonable range, revealing the stable ionic transport. These results validate the excellent temperature durability and high compatibility between electrodes and BM-gel electrolyte. Regarding the charge/discharge stability of EA battery, the batteries showed stable rechargeability without evident voltage changes upon cooling and heating (Figure 3D). Even at −20°C, the EA battery still delivered a high specific capacity of 165 mA h g⁻¹ (~70% of the one at 25°C) at 0.2 A g⁻¹, manifesting the superior freeze-resistant properties. At high temperature, the discharge profiles appeared to almost overlap with that at 25°C. These results indicate that the EA battery can withstand low temperature down to −20°C and high temperature up to 80°C.

For the cycling performance, at 25°C and −20°C, the EA battery exhibited 81% (124 mA h g⁻¹) and 66% (76 mA h g⁻¹) capacity retentions of its initial capacity over 500 cycles at 1.6 A g⁻¹ (capacity decay rates of 0.038% and 0.068% per cycle), respectively. The coulombic efficiencies of the EA battery remained as high as approximately 99.5-100.0% even at −25°C (Figure 3E). Moreover, the EA battery presented a stable rechargeability without any obvious fluctuation, whereas the comparison of PAM batteries showed a large augment of voltage hysteresis upon cooling to −20°C (Figure S16). In addition, the variation of specific capacity with temperature (Figure 3F) indicated that the discharge capacity retentions of the EA battery at −20°C and 80°C compared with that at 25°C were 70% and 110%, respectively. The energy densities of the EA battery
at −20°C and 80°C were 65% and 108% retention of that at 25°C. The enhanced battery performance at 80°C was mainly ascribed to the increase of ion transport kinetics in the electrolyte at high temperatures. To verify the thermal stability, cycling tests were executed on the EA battery and PAM battery in a thermostat, as shown in Figure 3G. After the first five cycles, the temperature increased to 80°C, the specific capacity of PAM battery deteriorated significantly with large voltage polarization. The performance degradation possibly resulted from the dehydration of hydrogel electrolyte at a higher temperature (Figure S17). For the EA battery, the energy-storage ability was almost the same as that prior to heating and maintained at a stable capacity of 105 mA h g⁻¹ at
2.0 A g\(^{-1}\) after 150 cycles (over 20 hours) without any performance decay derived from dehydration. Experimental results of the EA battery and PAM battery cycled sequentially at 25°C, −20°C, and 60°C are shown in Figure S18. As the temperature fluctuates, the specific capacity of the EA battery almost restored to the pristine one. After multiple cycles of the cooling-heating-cooling process, no significant capacity attenuation could be identified, guaranteeing its practical application. The long-term stability of the EA battery was certified by the fact that 84.6% capacity retention after a prolonged storage of 30 days under the normal conditions (25°C), outperforming the comparison of PAM batteries (Figure 3H).

### 2.4 High-environmental adaptative Zn-MnO\(_2\) battery

Benefitting from its flexible components as used, our EA battery possessed high flexibility and architectural durability. As a demonstration of this superiority, a series of battery-safety evaluations under extreme conditions including bending tests, soaking tests, antifreezing evaluations, and antiheating of boiling water experiment were performed on the solid-state EA battery. As shown in Figure 4A, the battery could easily withstand various extreme deformations of being twisted, bent, folded, and rolled, and continually powered an electronic watch. At various bending states (60°, 90°, and 180°), the corresponding galvanostatic charge/discharge (GCD) characteristics could be well preserved with subtle changes capacity change (Figure 4B). Moreover, no appreciable deterioration in specificity capacity of the EA battery (quantized by a length of 7.5 cm and a curvature radius of 1.0 cm) was detected even after 500 bending cycles at a bending angle (θ) of approximately 180°, which firmly validates the superior stability against deformations of the EA battery (Figure 4C).^31^ Freeze-resistant performance and thermal durability are of gear importance for practical applications of solid-

![Figure 4](https://example.com/figure4.png)

**Figure 4** Electrochemical performance of the EA battery in different destructive tests. A, Mechanical tests of the EA battery under various deformation conditions; B, bending test at different bending angles; C, capacity retention of after 500 bending cycles at an angle of 180°; D, schematic illustration of the EA battery in ice package under freeze-resistant tests; E, digital images of the EA battery when sealed into an ice solid, powering the electronic watch; F, capacity retention of the EA battery working at −20°C, inset is the corresponding discharge curves at different storage time intervals; G, schematic illustration of the EA battery in boiling water; H, anti-heating test of the EA battery when powering an electronic watch in boiling water.
state batteries working in a harsh environment. To intuitively verify the antifreezing properties, an EA battery was immersed in water in a glass vessel and stored at −20°C to form an ice solid (Figure 4D). As shown in Figure 4E, the ice-solid battery was still capable to power the electronic watch (Movie S1), and its specific capacity well-retained over 90.22% after 72 hours storage at −20°C (Figure 4F). Benefiting from the outer elastomeric coating, the fabricated EA battery was endowed with excellent waterproof and antiheating properties. When immersed in water at room temperature for 120 minutes, the EA battery retained approximately 90.8% retention of its initial specific capacity.
with no appreciable deterioration and continuously powered an electronic watch, remarkably outperforming our previous flexible Zn-MnO$_2$ batteries without encapsulation (Figure S19A,B). Moreover, a piece of EA battery was immersed in boiling water, which bubbled furiously in the pot, and it was impressive that the battery could continuously power an electric watch even for 64 minutes (Figure 4G,H, Movie S2), demonstrating the remarkable antiheating properties.

### 2.5 | Energy storage devices with enhanced environmental adaptability

To demonstrate device scalability, two EA batteries (size $2 \times 3$ cm) could be connected in a series to achieve a higher operation voltage than that of single cells. The tandem units with a high voltage of 3.0 V were able to continuously power a high power watch ($\sim$2.4 V) for over 3 hours with a delivered current of 8 to 12 mA (Figure 5A and Figure S20) and a 29 cm$^2$ electroluminescent panel (size $3 \times 9$ cm) (Figure 5B). Furthermore, we mounted the flexible tandem units as an energy wristband on the demonstrator’s wrist to test their wearable applications. Our wristband-type batteries were capable to maintain high-energy output for powering a digital watch and a yellow LED, which show the great promise for wearable applications.

In addition, the AC impedance spectra given in Figure 5C and Figure S21 indicated that the BM-gel electrolyte exhibited high ionic conductivity when consisting of different ions (such as Zn$^{2+}$, Li$^+$, H$^+$, and Na$^+$ ions) in neutral, acidic, or alkaline environment, implying the promising compatibility of the BM-gel electrolyte to other energy storage devices. Benefiting from wide ion adaptability, the BM-gel electrolyte was also integrated into another battery system of the Zn-LiMn$_2$O$_4$ battery (Zn-LMO battery). As shown in Figures 5D and S22, the Zn-LMO battery exhibited evident reversible redox peaks with a higher potential than those of the Zn-MnO$_2$ battery system. For cycling performance at different temperatures, the Zn-LMO battery delivered a capacity of 90 mA h g$^{-1}$ at 0.3 A g$^{-1}$ with a retention of 97.56% of its initial capacity after 100 cycles at 25°C. A high cycling stability to temperature is also manifested for the Zn-LMO battery with 89.52% (80°C) and 91.17% (−20°C) capacity retentions after 100 cycles at 0.3 A g$^{-1}$, respectively (Figure 5E,F). Furthermore, we fabricated a symmetrical supercapacitor comprising the BM-gel electrolyte and carbon nanotube paper/polypyrrole (CNT@PPy) electrodes as described in the “Experimental Section” in supplementary information (Figure 5G and Figure S23). Capacitive behaviors were researched over the temperature range from −20°C to 80°C through CV and GCD profiles (Figure 5H,I). It can be observed in CVs that the close-rectangular shape of voltammograms is in all temperature scale, verifying the good ionic conductivity of our BM-gel electrolyte at extreme temperatures. The capacitance of the fabricated supercapacitors after heating and cooling cycles between −20°C, 25°C, and 80°C appeared to be almost the same as the one at 25°C (Figure 5J). These results demonstrate the promising applications of BM-gel electrolyte in diverse energy storage devices to enhance their environmental adaptability.

### 3 | CONCLUSION

In summary, inspired by epidermal tissue of mammalian skin, we have successfully fabricated a novel elastomer-coated organohydrogel electrolyte through alginate/AM monomers in EG/water binary solution. The elastomer coating with a thickness of 100 μm on the surface can effectively prevent water evaporation and isolate hydrogel from outer environment, endowing the organohydrogel electrolyte superior antidehydration and antifreezing properties over the temperature range from −20°C to 80°C. The fabricated rechargeable Zn-MnO$_2$ battery with the designed BM-gel electrolyte remained fully functional at extreme temperatures (−20°C to 80°C). At room temperature, the EA battery delivered a high specific capacity of 272 mA h g$^{-1}$ at 0.1 A g$^{-1}$ and a high volumetric energy density of 26.88 mW h cm$^{-3}$. Although operating at an extremely high temperature of 80°C, the charge/discharge characteristics of the EA battery maintained a stable capacity of 105 mA h g$^{-1}$ at 2.0 A g$^{-1}$ after 150 cycles (over 20 hours) without any performance decay derived from dehydration. Even working at −20°C, the EA battery still exhibited a high specific capacity of 165 mA h g$^{-1}$ at 0.2 A g$^{-1}$, and an excellent capacity retention approaching as high as 66% of the initial value after 500 cycles at 1.6 A g$^{-1}$. Furthermore, the EA battery exhibited exceptional durability under adverse harsh conditions, such as being sealed in ice package and immersed in boiling water. Furthermore, we successfully integrated the elaborately designed BM-gel electrolyte with diverse energy storage devices including Zn-LMO battery and supercapacitor, showing great promise for developing environmental adaptive energy storage devices.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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