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An anti-freezing and anti-drying multifunctional gel electrolyte for flexible aqueous zinc-ion batteries

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ABSTRACT Aqueous zinc-ion batteries (ZIBs) have attracted immense attention for flexible energy storage devices due to their high safety and low cost. However, conventional flexible aqueous ZIBs will undergo severe capacity loss at subzero temperature due to the inevitably freeze of electrolytes. In addition, under large bending or stretching strains, the encapsulation of devices would be damaged, which causes the evaporation of water in electrolytes and results in device failure. Herein, an anti-freezing and anti-drying gel electrolyte based on polyacrylamide (PAM) and glycerol (Gly) is developed. The strong hydrogen-bonding interactions between PAM or Gly and water molecules not only avoid the crystallization of the gel electrolyte at low temperatures, but also constrain the free water and restrict its evaporation. Therefore, such gel electrolyte displays a high ionic conductivity of $9.65 \times 10^{-5} \text{ S cm}^{-1}$ at -40°C . Furthermore, it can restrict the dehydration process when the electrolyte is exposed to ambient environment. The flexible ZIBs based on such gel electrolyte exhibit excellent electrochemical performance at -40°C and the devices without encapsulation retain 98% of their initial capacity in ambient condition after 30 days. This work provides a route to design anti-freezing and anti-drying gel electrolytes for aqueous energy storage devices.

Keywords: gel electrolytes, anti-freezing, anti-drying, glycerol, aqueous zinc-ion batteries

INTRODUCTION

Aqueous zinc-ion batteries (ZIBs) are regarded as a promising candidate for flexible energy storage devices due to their intrinsically high safety and low cost [1–15]. However, conventional flexible aqueous ZIBs are not capable of working at low temperatures, where electrolytes will inevitably freeze and further restrict the ionic transportation, resulting in the degradation of their electrochemical performance [16–20]. In addition, under large bending or stretching strains, the packages of flexible aqueous ZIBs would be damaged, which causes the evaporation of water in electrolytes [21–23]. The loss of water can seriously affect the migration of ions in electrolytes and result in the failure of devices [24–26]. Consequently, it is highly desired to develop anti-freezing and anti-drying electrolytes to

meet the demands of flexible aqueous ZIBs.

Gel electrolytes combine the advantages of high ionic conductivity of liquid components and excellent mechanical properties of polymer matrices, which have been the most commonly used electrolytes of flexible energy storage devices [27–30]. Generally, the anti-freezing property of gel electrolytes could be realized by the addition of organic solvents (e.g., ethylene glycol (EG), glycerol (Gly) and dimethyl sulfoxide) or soluble ions (e.g., sulfuric acid, potassium hydroxide and zinc chloride) with high concentrations [31–38]. These solutes with high concentrations could inhibit the crystallization of water and depress the freezing points of electrolytes. However, these gel electrolytes often exhibit limited abilities to restrict free water when they are exposed to ambient environments. The key of designing gel electrolytes with both anti-freezing and anti-drying properties is to weaken the original hydrogen bonds between their water molecules. Polyacrylamide (PAM), which is usually utilized as the polymer matrix of gel electrolytes, often forms strong hydrogen bonds with water molecules due to its abundant amide groups [39–42]. In addition, as a common cryoprotectant and humectant, Gly can provide a large number of hydroxyl groups for constructing strong hydrogen bonds with water molecules [43–46]. Consequently, the combination of the PAM matrix and Gly additive would weaken the hydrogen bonds between water molecules in gel electrolytes, which not only avoids the crystallization of gel electrolytes at low temperatures, but also retards the dehydration of gel electrolytes when they are exposed to ambient conditions. Inspired by this, we developed an anti-freezing and anti-drying gel electrolyte based on PAM and Gly. Owing to the strong hydrogen-bonding interactions between PAM or Gly and water molecules, the gel electrolyte displays a low freezing point and excellent drying tolerance. As a result, the gel electrolyte possesses high ionic conductivity at low temperatures and long-term electrochemical stability at ambient environment. Furthermore, the excellent mechanical properties of such hydrogel endow it with ability to serve as the electrolyte of flexible ZIBs. As a proof of concept, flexible aqueous ZIBs were fabricated based on this gel electrolyte. Impressively, they exhibited excellent electrochemical stability under different bending states even at low temperatures. And the devices also displayed high capacity retention rate when they were exposed to external environment.

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EXPERIMENTAL SECTION

Preparation of anti-freezing and anti-drying gel electrolytes

Acrylamide (2 g), ammonium persulphate (0.25 g), methylene-bis-acrylamide (1.5 mg) and zinc trifluoromethanesulfonate ($\text{Zn}(\text{CF}_3\text{SO}_3)_2$, 2.8 g) were dispersed in 10 mL deionized water to obtain a homogeneous solution. Then Gly with various volume percentages to water was added into the mixed solution. The mixtures were deoxygenized and then heated at 90°C for 2 h for polymerization. After being cooled to room temperature, the anti-freezing and anti-drying gel electrolytes were obtained.

Preparation of flexible aqueous ZIBs

Polyaniline (PANI) nanorods were prepared according to the previous literature [47]. PANI, single-walled carbon nanotubes (SWCNTs) and polyvinylidene fluoride were mixed with a weight ratio of 7:2:1 in *N*-methyl-2-pyrrolidone, forming a slurry, which was then coated on steel meshes. After vacuum drying at 60°C for 24 h, the SWCNTs/PANI cathodes were obtained. The SWCNTs/PANI cathodes, filter paper, and Zn foil anodes were stacked together and then immersed into the solution that contains the precursor of gel electrolytes. All the components were deoxygenized and then heated at 90°C for 2 h for polymerization. After being cooled to room temperature, the flexible aqueous ZIBs were obtained.

Characterizations and electrochemical measurements

The morphologies of materials, electrodes and freeze-dried gel electrolytes were characterized *via* a scanning electron microscope (SEM, JEOL JSM7500F and Phenom XL) and transmission electron microscope (TEM, Talos F200X G2). The Fourier transform infrared (FTIR) spectra of gel electrolytes were collected through Bruker Tensor II. The tensile tests of gel electrolytes were measured on a dynamic mechanical analyzer (TA DMA Q800). The thermal properties of gel electrolytes were characterized using a differential scanning calorimeter (DSC, NETZSCH). The samples were first equilibrated at 25°C and then cooled at a rate of 5°C min⁻¹ to -70°C. After an isothermal period of at least 90 min, the samples were heated up at 2°C min⁻¹ to the initial equilibration temperature (25°C). The ionic conductivity of gel electrolytes was calculated by bulk resistance, which was measured on an electrochemical workstation (Zahner, IM6ex) with an amplitude of 5 mV in the frequency ranging from 100 kHz to 1 Hz. The ionic conductivity σ was calculated by:

$$\sigma = \frac{l}{RA}, \quad (1)$$

where l , R , and A represent the thickness, the bulk resistance, and the test area of the gel electrolyte, respectively. Cyclic voltammetry (CV) curves of ZIBs were tested on an electrochemical workstation (CHI Instruments, CHI660E). Galvanostatic charge/discharge (GCD) curves were recorded on a battery test system (LAND CT2001A). Electrochemical impedance spectroscopy curves were measured in the frequency range from 100 kHz to 100 mHz on an electrochemical workstation (Zahner, IM6ex). The specific capacity of ZIBs was calculated based on the mass of the PANI.

Computational methods

The binding energy calculations were performed using the density functional theory (DFT) program DMol³ in Material

Studio. The physical wave functions were expanded in terms of numerical basis sets, Dmol³/GGA-PBE/DNP (3.5) basis set. The core electrons were treated with DFT semi-core pseudo potentials. The exchange-correlation energy was calculated with Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA). A Fermi smearing of 0.005 Ha (1 Ha = 27.211 eV) and a global orbital cutoff of 5.2 Å were employed. The convergence criteria for the geometric optimization and energy calculation were set as follows: (a) a self-consistent field tolerance of 1.0×10^{-6} Ha atom⁻¹; (b) an energy tolerance of 1.0×10^{-5} Ha atom⁻¹; (c) a maximum force tolerance of 0.002 Ha Å⁻¹; and (d) a maximum displacement tolerance of 0.005 Å.

RESULTS AND DISCUSSION

The gel electrolyte was synthesized *via* the free radical polymerization by an acrylamide solution of Gly and zinc trifluoromethanesulfonate ($\text{Zn}(\text{CF}_3\text{SO}_3)_2$). Since such polymerization is a process of converting polymer monomer solution into hydrogel, the shapes of resultant electrolytes could be readily designed by injecting the precursor solution into customized molds (Fig. S1), certifying their outstanding processability. During the polymerization process, acrylamide molecules cross-linked with each other through covalent bonds to construct PAM matrix with three-dimensional (3D) porous structure (Fig. 1a). The size of the pores is in a range of 1–3 μm, as suggested by the SEM image of the freeze-dried gel electrolyte (Fig. 2a). The 3D porous architecture ensures the gel electrolyte with excellent mechanical properties and fast ionic transportation. Furthermore, since Gly and PAM chains possess abundant hydroxyl groups and amide groups, respectively, the original hydrogen bonds between water molecules are destructed, and the stronger hydrogen-bonding interactions are formed between PAM or Gly and water molecules, as suggested by DFT calculations (Fig. 1b and Fig. S2). During the DFT calculation, the binding energy (E_{binding}) represents the intensity of the interaction between the components in the system and it can be calculated according to this equation:

$$E_{\text{binding}} = E_{\text{total}} - \sum E_{\text{component}}, \quad (2)$$

where E_{total} is the total energy of the system and $E_{\text{component}}$ is the energy of each component. The higher absolute value of the negative E_{binding} represents a stronger interaction [48]. The binding energy of PAM-H₂O (-37.76 Kcal mol⁻¹) and Gly-H₂O (-40.66 Kcal mol⁻¹) is much lower than the case of H₂O-H₂O (-5.08 Kcal mol⁻¹). This result proves that PAM-H₂O and Gly-H₂O systems are more stable than the H₂O-H₂O system, suggesting that water molecules prefer to bond with PAM and Gly molecules rather than other water molecules. Furthermore, the binding energy of PAM-H₂O-Gly (-64.8 Kcal mol⁻¹) is also much lower than the case of H₂O-H₂O, indicating that the PAM-H₂O-Gly system possesses higher stability and stronger hydrogen-bonding interactions. Meanwhile, the PAM-H₂O-Gly system is more stable than the common gel electrolyte systems such as PAM-H₂O-EG (-53.1 Kcal mol⁻¹), poly(vinyl alcohol) (PVA)-H₂O-Gly (-52.6 Kcal mol⁻¹), and poly(acrylic acid) (PAA)-H₂O-Gly (-60.4 Kcal mol⁻¹) (Fig. 1c). This result reveals that sufficient hydroxyl groups and amide groups are beneficial to constructing strong hydrogen-bonding interactions with water molecules. Additionally, the strong hydrogen-bonding interactions of these systems can be observed more intuitively through the average hydrogen bond length [49–51]. As shown in

Figure 1 (a) Configuration and bonding mechanism of the anti-freezing and anti-drying gel electrolyte. (b) DFT optimized structures, (c) calculated interaction energies and average lengths of hydrogen bonds of PAM-H₂O-Gly, PAM-H₂O-EG, PVA-H₂O-Gly, and PAA-H₂O-Gly.

Figure 2 (a) SEM image of PAM-H₂O-Gly. (b) FTIR spectra, (c) tensile strain, (d) DSC curves, (e) phase diagram and (f) contents of free water and bound water of PAM-H₂O-Gly with different contents of Gly.

Fig. 1c, the average hydrogen bond length of PAM-H₂O-Gly is shorter in comparison with the cases of common gel electrolyte systems, suggesting a higher stability of the PAM-H₂O-Gly system, which is consistent with the results of binding energy. Furthermore, the hydrogen bonds were further identified by their characteristic peaks in the FTIR spectra. As shown in Fig. 2b, the characteristic peak at 3270 cm⁻¹ is ascribed to the hydroxyl [52,53]. With the increase of the Gly volume content from 0% to 40%, this characteristic peak gradually shifts to the lower wavenumber in the PAM-H₂O-Gly system, indicating an enhancement of intermolecular hydrogen-bonding interactions due to the formation of more hydrogen bonds between Gly and H₂O molecules.

The hydrogen bonds also play an important role in the mechanical properties of gel electrolytes [54]. After introducing Gly into the PAM matrix, more hydrogen bonds will form between Gly molecules and PAM polymer chains, which can dissipate the energy between PAM chains under deformation and homogenize the polymer network [55]. As a result, the combination of covalent cross-linking bonding and physical hydrogen bonding endows gel electrolytes with excellent flexibility and enhanced strain tolerance [56–58]. As shown in Fig. S3, the strain tolerance of the PAM-H₂O-Gly electrolyte will be remarkably improved with addition of Gly. When the Gly volume content reaches 40%, the electrolyte displays a high strain tolerance of 2760% (Fig. 2c and Fig. S4), which is much larger than the case of the electrolyte without Gly. Apart from the enhanced strain tolerance of the gel electrolyte, the freezing point of the gel electrolyte will be significantly reduced by the addition of Gly since the strong hydrogen-bonding interactions between Gly and water can disrupt the formation of ice crystal in electrolytes at low temperatures. The decreased freezing points of gel electrolytes were detected by DSC measurement. As shown in Fig. 2d, the exothermic peak in DSC curves represents the crystallization of the gel electrolyte, where the liquid phase in the gel electrolyte will transform into solid phase [59]. When the Gly volume content increases from 0% to 40%, the exothermic peak of gel electrolytes gradually shifts towards left, indicating the decrease of their freezing points [60–62]. When the Gly volume content reaches 40%, the gel electrolyte exhibits an ultralow freezing point of -51°C, which is much lower than the case (-9°C) of the gel electrolyte without addition of Gly (Fig. 2e). Furthermore, the low freezing point of gel electrolytes can be deeply understood by the content of free water in gel electrolytes. Free water has almost no interaction with the polymer network. Therefore, free water displays similar physical properties with pure water and it will unavoidably freeze at low temperatures, which causes the crystallization of gel electrolytes [51]. The content of free water (W_{free}) can be calculated through the enthalpy change (ΔH) during the heating process in the DSC curve by this equation:

$$W_{\text{free}} = \frac{\Delta H}{\Delta H_0} \times 100\%, \quad (3)$$

where ΔH_0 is the enthalpy value of pure water (334 J g⁻¹). As shown in Fig. 2f, with the increase of the Gly content, the content of free water in gel electrolytes is gradually decreased, leading to the low freezing point of gel electrolytes. To demonstrate their freezing tolerance more intuitively, the states of gel electrolytes with different Gly contents under different environmental temperatures were further monitored. It can be seen that when the addition of Gly is up to 20 vol%, the PAM-

H₂O-Gly electrolyte would not freeze even at -40°C (Fig. 3a and Fig. S5), displaying an outstanding anti-freezing behavior. The ionic conductivity at low temperatures is a key feature to evaluate anti-freezing electrolytes. At -40°C, PAM-H₂O-Gly-20% still retains an excellent ionic conductivity of 9.65×10^{-5} S cm⁻¹ due to its low freezing point (Fig. 3b and Fig. S6), though the ionic conductivity of the PAM-H₂O-Gly electrolyte is gradually reduced with the increase of Gly content at room temperature, which is ascribed to the decreased content of free water in the electrolyte [63].

The excellent mechanical properties and ionic conductivity endow PAM-H₂O-Gly hydrogel with the ability to serve as the electrolyte of flexible ZIBs. As a proof of concept, flexible aqueous ZIBs were fabricated based on the PAM-H₂O-Gly electrolyte, where SWCNTs/PANI served as cathodes and Zn foil acted as anodes (Fig. 3c and Fig. S7). The ZIBs based on the PAM-H₂O-Gly-20% electrolyte deliver a discharge capacity of 67.8 mA h g⁻¹ under room temperature at 1 A g⁻¹ (Fig. 3d, Figs S8 and S9a), which is comparable to those of previously reported PANI-based ZIBs. Impressively, owing to the excellent anti-freezing behavior and high ionic conductivity of the PAM-H₂O-Gly-20% electrolyte, the ZIBs still exhibit a specific capacity of 52 mA h g⁻¹ at -40°C. In contrast, the capacity of ZIBs based on the PAM-H₂O-Gly-0 electrolyte deteriorates seriously with the decrease of temperature, which ultimately causes device failure at -40°C. The severe performance degradation possibly results from the faded ionic conductivity of the gel electrolyte at low temperatures. Furthermore, even at different current densities, the ZIBs based on the PAM-H₂O-Gly-20% electrolyte also display outstanding discharge capacity at -40°C (Fig. S9b). Moreover, even after charge/discharge for 500 cycles, the ZIBs based on PAM-H₂O-Gly-20% still maintain 76.8% of its initial capacity at -40°C, exhibiting a superior cycling performance at low temperatures (Fig. S9c). To demonstrate the excellent electrochemical performance of anti-freezing ZIBs at low temperatures more visually, two ZIBs based on PAM-H₂O-Gly-20% were integrated in series to power a thermometer at -40°C (Fig. 3e). It is noted that the thermometer works well under low temperatures. More impressively, at cold condition, the flexible anti-freezing ZIBs also exhibit stable electrochemical performance under different bending states due to their all-in-one configurations and excellent freezing tolerance of electrolytes. As shown in Fig. 3f, when the ZIBs were bent into cylinders and then returned to flat state during the cycling process at -40°C, their capacities were almost unchanged in comparison with the case at the initial state, indicating that the flexible anti-freezing ZIBs possess great promise for the practical application in cold conditions.

In addition to anti-freezing behavior, the PAM-H₂O-Gly electrolyte also exhibits a remarkable anti-drying performance in ambient environment since the evaporation of water in electrolytes is inhibited. As shown in Fig. 4a, b, dehydration tests of PAM-H₂O-Gly electrolytes with different contents of Gly were carried out at 25°C and 70% humidity for 30 days, where the volume change and weight retention of electrolytes were recorded. The results reveal that the electrolyte with higher content of Gly exhibits superior anti-dehydration performance. When the addition of Gly reaches 40 vol%, there is only 6% weight loss of the gel electrolyte after 30 days, whereas the gel electrolyte without addition of Gly loses 41% of its weight after 10 days and finally converts into hard scaffolds without water. The out-

Figure 3 (a) Optical images and (b) ionic conductivities of PAM-H₂O-Gly with different contents of Gly from 20 to -40°C. (c) The configuration of flexible anti-freezing ZIBs. (d) Capacities of flexible anti-freezing ZIBs at different temperatures. (e) Optical image of a thermometer powered by two flexible anti-freezing ZIBs in series at -40°C. (f) Cycling performance of flexible anti-freezing ZIBs at different bending states under -40°C at 1 A g⁻¹. The insets are the optical images of flexible anti-freezing ZIBs at different bending states.

standing anti-drying performance of gel electrolytes is attributed to the strong hydrogen-bonding interactions between Gly and water molecules, which effectively suppress the evaporation of free water in electrolytes [64–66]. Furthermore, such excellent anti-dehydration behavior endows gel electrolytes with high ionic conductivity even after long-term exposure to ambient environment. As shown in Fig. 4c, the PAM-H₂O-Gly-20% electrolyte retains a superior ionic conductivity of $2.03 \times 10^{-4} \text{ S cm}^{-1}$ after 30 days. However, when the Gly volume content of gel electrolytes is further increased, the ionic conductivities of electrolytes gradually decrease, probably because excessive Gly restricts most of the free water and hinders the migration of ions in electrolytes [47,67–69]. The excellent anti-dehydration performance of the PAM-H₂O-Gly electrolyte makes it promising to serve as the electrolyte of flexible anti-drying ZIBs. The flexible ZIBs based on the PAM-H₂O-Gly electrolyte were assembled without encapsulation. The charge/discharge performance of such devices was tested at 25°C and 70% humidity. After 30 days, the capacity of ZIBs based on the PAM-H₂O-Gly-20% electrolyte still retains 66.4 mA h g⁻¹, exhibiting a remarkable capacity retention of 98% (Fig. 4d and

Fig. S10). In contrast, the capacity of ZIBs based on the PAM-H₂O-Gly-0 electrolyte fades rapidly, resulting in device failure only after 2 days. Consequently, the outstanding anti-dehydration behavior of electrolytes greatly enhances the durability of devices.

CONCLUSIONS

In summary, the PAM-H₂O-Gly gel electrolytes with anti-freezing and anti-drying behaviors were developed through constructing a strong hydrogen-bonding system. Since the hydrogen-bonding interactions between PAM or Gly and water molecules were stronger than the cases of water, the formation of crystal lattices in electrolytes at low temperatures was disrupted and the evaporation of free water was also suppressed. Therefore, such gel electrolytes displayed high ionic conductivity at -40°C and restricted their dehydration process in ambient environment. Based on this anti-freezing and anti-drying gel electrolyte, the flexible ZIBs were fabricated. They exhibited excellent electrochemical performance at -40°C and retained 98% of their initial capacity without encapsulation after 30 days. This work broadens the horizons of designing anti-freezing and

Figure 4 (a) Optical images, (b) weight retentions and (c) ionic conductivities of PAM-H₂O-Gly with different Gly contents after 30 days in ambient environment. (d) Cycling performance of flexible anti-drying ZIBs with different contents of Gly. The insets are GCD curves of flexible anti-drying ZIBs after 1, 15, and 30 days, respectively.

anti-drying gel electrolytes for flexible energy storage devices.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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基于耐低温、保湿多功能凝胶电解质的柔性水系锌离子电池

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摘要 水系锌离子电池由于具有安全性高、成本低的特点, 在柔性储能领域得到广泛关注。然而, 传统柔性水系锌离子电池处于零下温度时, 由于其电解质的凝固, 电池容量会发生严重衰减。此外, 当电池承受大幅度的形变后, 其外包装易发生破损, 造成电解质中水分的挥发, 最终导致器件失效。在本文中, 我们开发了一种基于聚丙烯酰胺(PAM)和甘油(Gly)的耐低温、保湿凝胶电解质。PAM和Gly与水分子之间的强氢键作用不仅抑制了凝胶电解质在低温时的凝固, 而且限制了电解质中自由水的挥发。基于该电解质的柔性水系锌离子电池在 -40°C 时仍具有优良的电化学性能, 并且无封装的电池在30天后仍保持了初始容量的98%。该工作提供了一种设计水系储能器件用耐低温、保湿凝胶电解质的新思路。