Modulated bonding interaction in propanediol electrolytes toward stable aqueous zinc-ion batteries

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ABSTRACT Aqueous Zn-based batteries are promising energy storage technology due to their low cost and high safety. However, the solvation structure of electrolyte leads to dendrite growth, parasitic reactions, and poor low-temperature properties, limiting their practical application. Here, we report 1,2-propanediol (PG) electrolyte with a modulated solvation structure, which can suppress Zn dendrite growth and parasitic reactions. PG can break the interaction between H₂O molecules and the interaction between H₂O and Zn²⁺ due to the higher electron density of O and higher Gutmann donor number of PG than those of H₂O, which increase the H–O covalent bond strength, decrease the water activity and freezing point, and change the solvation structure of Zn²⁺. As a result, the battery exhibits high cycling stability (Zn//Zn battery cycle over 1000 h), high reversibility (Coulombic efficiency of 98.9%), high capacity properties (specific capacity of 225 mA h g^{−1} at 5 A g^{−1}, and capacity retention of 92.6% for 5000 cycles), and excellent anti-freezing properties (specific capacity of 190 mA h g^{−1} at −20°C over 500 cycles). This work provides a promising strategy for the development of high-performance aqueous zinc-ion batteries.

Keywords: electrolyte, Gutmann donor number, low-temperature, aqueous zinc-ion battery

INTRODUCTION

Lithium-ion batteries have recently dominated most of the market, but their widespread application is hindered by their rare natural sources, safety issues, and environmental unfriendliness [1–6]. However, zinc is relatively abundant, cheap and stable on the Earth and possesses high compatibility with air and water, which is beneficial to its practical operation [7–11]. Because of the multiple electron transfer, zinc-ion batteries have a higher storage capacity than lithium-ion batteries [12]. The zinc-ion battery has emerged as a promising energy storage technology in recent years due to its high safety, low cost, abundant reserves, and good compatibility with cathode materials and aqueous electrolytes, as well as the low redox potential (−0.76 V vs. standard hydrogen electrode) and high theoretical capacity (820 mA h g^{−1}) of Zn metal anode [13–17]. However, several issues remain in the development of aqueous zinc-ion

battery, such as dendrite, irreversible plating/stripping, and poor low-temperature properties. Serious corrosion, pierced separator, and battery failure can all result from these issues. A coating layer [18,19], a three-dimensional (3D) porous anode [20,21], a separator [22], and electrolyte [23,24] have all been proposed as solutions to the problems. Generally, designing electrolytes is a simple and effective method, including high concentration [25], organic [26], polymer [27], and additive-assisted electrolyte [28]. Among them, the use of an additive-electrolyte is a cost-effective and safe strategy.

The parasitic water reaction caused by abundant water in the electrolyte is the primary reason for dendrite and failure [29]. The unshared electron pair in water acts as a strong Lewis base to interact with cations, which occupies the solvation shell of cations, resulting in the water around cations [30]. Six water molecules surround a zinc ion in an aqueous zinc-ion battery. Water can be split into H₂ during the plating/stripping of Zn metal; the local pH environment change leads to the formation of by-products Zn(OH)₂, Zn₄SO₄(OH)₆·xH₂O, and so on [31]. Therefore, reducing the activity and amount of water can alleviate these problems. Moreover, aqueous electrolytes contain a large amount of water, which has a high freezing point, restricting the operation at low temperatures. Alcohols, such as methanol [32] and ethylene glycol [33–35], have recently been shown to be effective additives, significantly improving battery performance and decreasing the freezing point. Inspired by these discoveries, we hypothesize that 1,2-propanediol (PG) would be a superior additive with a higher Gutmann donor number than water. The electron donor ability of molecules is represented by Gutmann donor numbers [36], which can reflect the bonding tendency between the molecules and Zn²⁺ (the Zn²⁺ is regarded as an electron acceptor).

As shown in Table S1, most alcohols have a higher Gutmann donor number than H₂O (18) due to the higher electron density of OH in alcohols, e.g., methanol (20.4), ethylene glycol (21.8), 1-butanol (22.1), and so on [37]. Similarly, PG as a kind of alcohol with OH should possess a higher donor number than water and preferentially interact with cations. Here, we show that adding PG into the ZnSO₄ electrolyte of the aqueous reversible zinc-ion battery can improve battery performance by expanding the electrochemical stability window, lowering the freezing point, and suppressing the dendrite formation and side-

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reactions on the Zn anode. Owing to the higher donor number of PG than H_2O , PG can preferentially conscript the cosolvents in the structure of solvation sheath of Zn^{2+} , change the Zn^{2+} solvation structure, and suppress the parasitic reaction, leading to improved zinc-ion storage performance. Therefore, this strategy is scalable and promising for high-performance rechargeable aqueous zinc-ion batteries.

EXPERIMENTAL SECTION

Material preparation

Electrolyte synthesis: All chemicals and reagents were used directly without further purification. The 3 mol L^{-1} ZnSO_4 solution was prepared firstly through the constant volume method by adding 0.03 mol of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (Sinopharm Group, analytical reagent (AR)) into 0.313 mol of H_2O (self-made by Milli-Q). The ZnSO_4/PG hybrid electrolytes were prepared by mixing PG (Sinopharm Group, AR) with 3 mol L^{-1} ZnSO_4 solution at a series of volume ratios (5%, 10%, 20%, 30%, and 50%).

Cathode material synthesis: A hydrothermal method was used to synthesize the V_2O_5 powder. Commercial V_2O_5 (10 mmol, Alfa Aesar) was dissolved in a mixture solution containing 30 mL of deionized water and 20 g of ethylene glycol (Sinopharm Group) under vigorous stirring to obtain a homogeneous solution. The mixture was transferred to a 100-mL autoclave and heated at 200°C for 24 h. The collected products were centrifuged, washed, and dried for 12 h at 80°C after cooling to room temperature. The collected V_2O_5 powder was prepared by annealing the as-obtained products at 330°C for 30 min with a heating rate of 2°C min^{-1} .

Material characterization

A field emission scanning electron microscope (FESEM, AURIGA) with an accelerating voltage of 10.0 kV was used to obtain the morphologies and energy dispersive spectroscopy (EDS) mapping images of V_2O_5 powder and the electrode. The Rigaku SmartLab 9KW X-ray diffractometer was used to obtain X-ray diffraction (XRD) patterns using Cu-K α radiation ($\lambda = 1.540593\text{ nm}$). The nuclear magnetic resonance (NMR) spectra were acquired on a Bruker AVANCE AV III 400 spectrometer using D_2O as the field frequency lock. The electrolyte structure was investigated using a Fourier transform infrared (FTIR) spectrometer (iS50R). The freezing point was tested by differential scanning calorimetry (DSC) through a TA-Q2000 Instrument from -60 to 20°C at a heating rate of 2°C min^{-1} . A conductivity meter (FE28, Mettler Toledo) was used to determine the ionic conductivity of electrolytes. A phone's camera was used to take digital photos of the battery and separator. The low-temperature properties were tested in the refrigerator with a temperature ranging from -18.6 to -21.2°C and all samples were rested in the refrigerator over 24 h before being tested.

Electrochemical measurements

The synthetic V_2O_5 powder ($\text{S-V}_2\text{O}_5$) was mixed with active carbon (conductive additive) and polyvinylidene fluoride (binder) with a weight ratio of 7:2:1 to make the V_2O_5 cathode. The slurry was stirred vigorously and then spread onto 14-mm stainless steel mesh (500 mesh) and dried in an oven at 80°C for 5 h. The batteries were assembled with the cathode, anode and separator using the CR2030-type coin cells in the air atmo-

sphere. The electrochemical windows of an electrolyte were tested using a CHI660E electrochemical workstation with stainless steel as the cathode and Zn as the anode from -0.2 to 2.6 V at a scan rate of 1 mV s^{-1} to determine the linear sweep voltammetry (LSV) curves. The ohmic-corrected cyclic voltammogram (CV) curves were measured to test the Zn^{2+} deposition potential of electrolytes by the CHI660E electrochemical workstation with stainless steel as the cathode and Zn as the anode from -0.2 to 0.6 V with a scan rate of 1 mV s^{-1} . The CHI660E electrochemical workstation was used to perform the CV of full battery from 0.3 to 1.6 V . The BTS 3000 Network Battery Testing System generated the galvanostatic charge/discharge (GCD) profiles.

RESULTS AND DISCUSSION

Properties of $\text{ZnSO}_4/\text{H}_2\text{O}/\text{PG}$ electrolyte

FTIR, NMR, and theoretical calculations were used to investigate the influence of PG on hybrid electrolytes at the molecular level. Compared with the pure H_2O (Fig. 1a), the FTIR spectra of $\text{H}_2\text{O}/\text{PG}$ show a slight blue shift at $3000\text{--}3500\text{ cm}^{-1}$ of OH stretching vibration and H_2O bending vibration at $1600\text{--}1700\text{ cm}^{-1}$, implying the disturbed hydrogen bonding interaction between H_2O molecules by PG [38,39]. Due to the higher electron density of O in PG than that in H_2O [33], the tendency of the oxygen atom (in PG) to attract electrons is lower than that in water, leading to a weakened hydrogen bonding between PG and H_2O than between H_2O and H_2O , resulting in the enhanced H–O covalent bond in the water molecules and the shift of the corresponding FTIR spectra. The higher absorbed wavenumber of the H–O bond indicates the increased H–O covalent bond strength of H_2O in PG electrolyte, which can increase the stability of electrolyte [40]. NMR analysis can be used to further characterize the interaction between PG and H_2O . As shown in Fig. 1b, the ^1H of H_2O shifts to higher field with increasing PG content, indicating there is higher electron density around the H atoms with increasing PG content, which means more electron shielding. The hydrogen-bonding interaction between the O atom in PG and the H atom in H_2O can be attributed to this result [41]. Fig. 1c shows the FTIR spectra of $\text{H}_2\text{O}/\text{PG}/\text{ZnSO}_4$ electrolyte. Compared with pure ZnSO_4 electrolyte, the $\nu(\text{SO}_4^{2-})$ vibration shifts to a higher wavenumber with the addition of PG, which is similar to the vibration wavenumber of ZnSO_4 powder at $\sim 1092.4\text{ cm}^{-1}$ [42], implying that PG can break the solvation sheath structure of Zn^{2+} [43]. Density functional theory (DFT) calculation was used to compare the relative binding energies between different molecules to further validate the connection tendency of molecules. As shown in Fig. 1d, the relative binding energies between different molecules are ranked in the order of $\text{PG-H}_2\text{O} > \text{H}_2\text{O-H}_2\text{O}$ and $\text{Zn}^{2+}\text{-PG} > \text{Zn}^{2+}\text{-H}_2\text{O}$, implying that the connection between PG and H_2O is easier to form and the Zn^{2+} tends to connect with PG. Therefore, the addition of PG can break the interaction of $\text{H}_2\text{O-H}_2\text{O}$ and $\text{Zn}^{2+}\text{-H}_2\text{O}$. The main influence mechanism of PG on electrolytes is shown in Fig. 1e. A hydrogen-bonding interaction is formed between PG and H_2O due to the higher electron density of O in PG than in H_2O . Besides, because PG has a higher donor number than H_2O , it is easier for it to interact with Zn^{2+} , which weakens the interaction between H_2O and Zn^{2+} and enhances the interaction between PG and Zn^{2+} . The addition of PG can decrease the hydrogen bonding between water mole-

Figure 1 (a) FTIR spectra of H_2O -xPG ($x = 0\%, 5\%, 10\%, 20\%, 30\%, 50\%$) solvent without ZnSO_4 , (b) ^1H -NMR spectra of ZnSO_4 - H_2O -xPG electrolyte, (c) FTIR spectra of the ZnSO_4 - H_2O -xPG electrolyte, (d) Relative binding energies between different molecules obtained from DFT calculation, (e) Schematic illustration on a possible mechanism of changes in the chemistry of hybrid electrolyte with PG, (f) LSV profiles of the electrolytes, (g) CV profiles of Zn//stainless steel cells, (h) DSC curves of the electrolytes.

cules, strengthen the H–O covalent bond, and change the solvation structure of Zn^{2+} , which inhibits water activity, improves the stability of electrolytes, and adjusts the Zn deposition.

The LSV and the ohmic-corrected CV were used to further investigate the effects of PG on electrolyte stability. As shown in Fig. 1f, the voltage stability window is expanded in $\text{ZnSO}_4/\text{H}_2\text{O}/\text{PG}$ electrolyte with an increased oxygen evolution voltage, lower initial voltage of hydrogen evolution, and lower Zn deposition voltage than that without PG, resulting from the decreased water activity [44]. The CV curves of batteries with various electrolytes are shown in Fig. 1g. In the ZnSO_4 electrolyte, the nucleation overpotential is 76.9 mV, but after adding PG, an increased nucleation overpotential is achieved (147.9 mV, 50 vol% PG). The high nucleation overpotential corresponds to a doughy driving force for nucleating and will be likely to yield fine-grained deposits, whereas the low nucleation overpotential has an opposite effect, that is, the deposits rapidly grow into dendrites due to the “tip effect” [45]. The morphology of Zn deposition in PG electrolytes can be greatly optimized due to the high nucleation overpotential [34]. Moreover, the peak intensity of CV profiles can reflect the reaction kinetics of electrolytes. The larger radii of complexes of $[\text{Zn}(\text{H}_2\text{O})_m(\text{PG})_n]^{2+}$ than that of $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$, which leads to a more sluggish diffusion of PG electrolyte, result in lower peak intensity in the $\text{ZnSO}_4/\text{H}_2\text{O}/\text{PG}$

electrolyte, implying slower reaction kinetics. [35]. This is further confirmed by the decreased ionic conductivity of the electrolytes (i.e., the conductivity of Zn^{2+}) with the addition of PG (Fig. S1), which reduces the mass transfer process and prevents the rapid growth of Zn dendrites, benefiting a uniform deposition of Zn on the electrode surface and an improved performance in PG electrolyte. SEM images of the Zn electrode after deposition in hybrid electrolytes with a current density of 0.5 mA g^{-1} confirm the influence of PG on nucleation and growth of Zn. Fig. S2a shows the morphology of the Zn electrode deposited for 10 min with and without PG (30 vol%), showing that the surface of the electrode in $\text{ZnSO}_4/\text{H}_2\text{O}$ electrolyte is uneven with some big Zn dendrites in the size of 2–10 μm . The surface of the Zn electrode becomes smoother and denser and the deposited grains are finer and more uniform after adding PG, indicating the Zn deposition process is greatly adjusted by PG. The dendrites in the $\text{ZnSO}_4/\text{H}_2\text{O}$ electrolyte become more severe when the deposition time is increased to 30 min (Fig. S2b). Furthermore, because of the alcohol’s excellent anti-freezing performance, the electrolytes’ low-temperature properties were measured by freezing experiments and DSC analysis. Fig. S3 shows the photos of hybrid electrolytes at -20°C for 24 h, showing that the electrolyte without PG is frozen. When the amount of PG is beyond 10 vol%, the electrolytes remain in a

liquid state. The corresponding DSC analysis implies that the freezing points of 5%, 10%, 20%, and 30% PG decrease to -12°C , -20°C , -29°C , and -35°C , respectively, resulting from the broken hydrogen-bonding interaction between H_2O molecules by PG (Fig. 1b). The excellent anti-freezing performance with PG is beneficial to service in some special conditions. The ionic conductivity decreased as the amount of PG increased, lowering the battery's overall performance. In the remaining experiments, 20 vol% PG was used based on the ionic conductivity and freezing points, taking into account the battery's practical performance and low-temperature properties.

Electrochemical properties of various electrolytes

Zn//Zn symmetrical batteries were built under galvanostatic conditions at room temperature (25°C) to investigate the effects of PG on long-term cycling stability. As illustrated in Fig. 2a and Fig. S4a, after cycling for 110 h at an areal capacity of 0.2 mA h cm^{-2} and 100 h at 1.0 mA h cm^{-2} , the sudden short circuit appears in $\text{ZnSO}_4/\text{H}_2\text{O}$ electrolyte with an irreversible decrease of the polarization voltage (0 V, insets of Fig. 2a). It is worth noting that the competitive gas evolution occurs during the cycling process in the $\text{ZnSO}_4/\text{H}_2\text{O}$ electrolyte, as verified by the obvious volume expansion of the cell (Fig. S5), which is caused by the narrow electrochemical stabilization window. Batteries treated with PG, on the contrary, exhibit stable polarization voltages with an extended cycling life (over 1000 h at 0.2 mA h cm^{-2} and over 300 h at 1.0 mA h cm^{-2} without any potential fluctuation or short circuit), which is expected to give the improved stability of electrolyte and suppresses the formation of Zn dendrites. In the enlarger profiles of certain cycles in Zn//Zn symmetrical batteries, the battery with PG exhibits a higher overpotential (85 mV) than the battery in ZnSO_4 , which is associated with the ionic conductivity and can reflect the Zn deposition. The larger the overpotential is, the smoother Zn deposition is, thus resulting in the battery's stability [35]. Therefore, the battery with PG exhibits a smoother Zn deposition and more stable long-term cycling properties. The Zn//Zn symmetrical batteries were tested at high current densities of 1 and 2 mA cm^{-2} to further investigate the actual applicability of the electrolytes. Fig. 2b and Fig. S4b show that the cycling life of Zn//Zn batteries is vastly longer with a steady cycle after adding PG, while the voltage polarization occurs within 60 h cycles in ZnSO_4 electrolyte. After 40 h of cycling (0.2 mA cm^{-2} , 0.2 mA h cm^{-2}), the batteries were disassembled and the separator in PG electrolyte was cleaner than in the non-PG electrolyte (Fig. 2c and d). FESEM was used to characterize the surface morphology of cycled Zn electrode, illustrating that the surface of Zn electrode in the $\text{ZnSO}_4/\text{H}_2\text{O}$ electrolyte is rough and irregular and there are many large particles with sizes of $2\text{--}30\text{ }\mu\text{m}$, which can pierce the separator. Inversely, the surface of the electrode in 20 vol% PG electrolyte is uniform, without large particle products.

We used electrochemical impedance spectroscopy (EIS) of Zn//Zn coin cells before and after cycling to assess the effect of PG on by-products (Fig. 2e and f). There is only one semi-circle in each of these EIS profiles, indicating a simple charge transfer at the electrode-electrolyte interphase [46]. The initial impedance values are similar, but after 40-h cycling, the impedance value in the $\text{ZnSO}_4/\text{H}_2\text{O}$ electrolyte increases significantly. The lower cycled impedance value in the PG electrolyte results from the inhibition effect of PG on by-products during cycling. Owing

to the decreased water activity and the increased stable voltage window, fewer water molecules decompose, resulting in less OH^- generation, which ultimately inhibits the generation of by-products $\text{Zn}_4\text{SO}_4(\text{OH})_6\cdot x\text{H}_2\text{O}$, as confirmed by XRD patterns of the cycled Zn electrode, in Fig. S6. The peak positions located at 12.1° , 26.2° , and 24.5° , 51.5° are consistent with the standard PDF card of $\text{Zn}_4\text{SO}_4(\text{OH})_6\cdot 6\text{H}_2\text{O}$ and $\text{Zn}_4\text{SO}_4(\text{OH})_6\cdot 3\text{H}_2\text{O}$, respectively. After adding PG electrolyte, the peaks nearly vanish, indicating the inhibition of by-products in the PG electrolyte. As a result of the use of PG, the growth of by-products and dendrites can be inhibited, resulting in improved long-term cycling stability.

We fabricated Cu//Zn half-batteries to test the Coulombic efficiency (CE), using Cu as the working electrode and Zn as the counter and reference electrodes at a current density of 0.5 mA cm^{-2} and a cut-off voltage of 0.5 V to see how PG affected the Zn plating/stripping process. As illustrated in Fig. 3a, an average CE of 95% was obtained in the first 50 cycles with the ZnSO_4 electrolyte and the CE fluctuated at the 52nd cycle. Fig. 3b shows the specific cycling voltage profiles in the ZnSO_4 electrolyte, showing that the voltage is very unstable during cycling, which can lead to battery failure [47]. In contrast, Cu//Zn cells with the addition of PG display a significantly boosted CE and stable profiles (Fig. 3c), along with an average CE of 98.9% from the 21st to 150th cycles. Besides, the XRD pattern of the cycled Cu electrode in the PG electrolyte shows a relatively weak peak of $\text{Zn}_4\text{SO}_4(\text{OH})_6\cdot 5\text{H}_2\text{O}$, indicating that PG can inhibit the production of by-products (Fig. 3d). The deposited morphologies of Zn on Cu electrode after 20 h plating/stripping cycles were characterized by FESEM to further investigate the influence of PG (Fig. 3e and 3f). After 20 h cycles, the surface of the Cu electrode is smooth and uniform without big aggregates in the PG electrolyte, while the surface of the Cu electrode in the $\text{ZnSO}_4/\text{H}_2\text{O}$ electrolyte is fluffy and uneven with many bulk aggregates in sizes of $1\text{--}5\text{ }\mu\text{m}$, which can pierce the separator. EDS analysis was used to determine the exact elemental content, as shown in Fig. S7. In the $\text{ZnSO}_4/\text{H}_2\text{O}$ electrolyte, distinct S element can be found on the electrode surface, indicating the formation of by-products. In contrast, deposited Zn surface in the $\text{ZnSO}_4/\text{H}_2\text{O}/\text{PG}$ electrolyte owns no S element and less O content, implying the inhibited formation of by-products in the PG electrolyte, which is consistent with the XRD results. These results show that PG can improve the stability of the battery and adjust the formation of by-products and Zn dendrites.

Characterization of Zn// V_2O_5 battery

We built a zinc-ion battery using V_2O_5 powder as the cathode and Zn foil as the anode to demonstrate the versatility of PG/ H_2O hybrid electrolytes in an aqueous zinc-based energy storage system. The XRD pattern of S- V_2O_5 powder shows that the phase is pure and all peak positions correspond well with the standard crystalline phase of V_2O_5 (PDF # 44-0674) (Fig. S8). Fig. S9 is the SEM image of the S- V_2O_5 powder. To further evaluate the long-term cycling properties, S- V_2O_5 powder was used as the cathode in the assembly of Zn// V_2O_5 full batteries.

Fig. 4a shows the cyclic stability and CE profiles of the Zn// V_2O_5 battery at a current density of 5 A g^{-1} . The activation process of the V_2O_5 cathode causes the specific capacity to rapidly increase during the first 90 cycles. The battery with PG presents a high capacity of 225 mA h g^{-1} and capacity retention

Figure 2 Characterizations of Zn//Zn symmetrical batteries with and without PG (20 vol%): (a) Galvanostatic Zn plating/stripping in Zn//Zn symmetrical batteries with and without PG at a current density of 0.2 mA cm^{-2} and a capacity of 0.2 mA h cm^{-2} , (b) Zn plating/stripping in Zn//Zn symmetrical batteries at a high current density of 1 mA cm^{-2} and capacity of 1 mA h cm^{-2} , (c, d) SEM images of Zn electrode after 40 h cycles without and with PG, (e, f) EIS curves of Zn//Zn symmetric cells before and after 40 h cycles without and with PG.

of 92.6% after 5000 cycles, while the battery without PG only retains 29% of its initial capacity (the highest capacity after activation), which implies that better cycling performance is achieved with PG due to the inhibited water activity and dendrite growth. We tested the cyclic stability and efficiency at a low current density of 500 mA g^{-1} to further verify the effects of PG on the properties of a full battery (Fig. S10). After 300 cycles, the battery with PG delivered a discharge specific capacity of 348 mA h g^{-1} , which is 96.9% retention of the initial capacity

(the highest capacity after activation). The battery without PG, on the contrary, only retains 80% of its capacity, indicating that PG can improve the full battery's cycling stability. Long-term cycling performance at -20°C was obtained to evaluate the battery's low-temperature properties. Fig. 4b shows the long-term cycling profiles of the Zn// V_2O_5 battery at -20°C , showing that the battery with PG exhibits a stable specific capacity of 190 mA h g^{-1} , while the capacity of the battery without PG drastically decreases to 0 mA h g^{-1} . The excellent anti-freezing

Figure 3 Characterizations of Cu//Zn batteries: (a) CE of Zn plating/stripping in different electrolytes, (b, c) voltage profiles of Zn plating/stripping processes at different cycles in electrolytes with and without PG, (d) XRD profiles of the Cu electrode after 20 h plating/stripping, (e, f) SEM images of the deposited Zn on Cu electrode after 20 h plating/stripping deposition without and with PG.

properties of PG electrolytes are caused by the broken hydrogen bonding between H₂O molecules by PG. The GCD profiles with and without PG at the 2nd cycle were carried out at a current density of 500 mA g⁻¹ to see if PG affects the battery's oxidation/reduction process. As shown in Fig. 4c, both profiles have the same charging/discharging plat voltages, suggesting that PG does not influence the oxidation/reduction process. CV profiles of Zn//V₂O₅ batteries with and without PG further confirm this result (Fig. 4d). Both profiles have two pairs of redox peaks, which means PG has no effects on the redox reaction. However, the gap between redox peak positions becomes bigger, implying the slower reaction kinetics of PG electrolyte, which is consistent with the results of ionic conductivity. Moreover, to explore whether PG influences cathode materials, the SEM and XRD analyses of the cycled cathode plates at 500 mA g⁻¹ were applied. The morphologies of the cycled cathode in 20% PG electrolyte are identical to the pristine plate, while the pure ZnSO₄ cathode shows slight dissolution and side products, according to SEM images (Fig. S11). The PG does not affect cathode materials, according to the XRD pattern (Fig. S12). We used Zn//V₂O₅ batteries with the ZnSO₄/PG electrolyte to light several LED

bulbs to test the battery's practical usability. As shown in Fig. 4e, the batteries can light several bulbs, suggesting the practical usability of PG in the battery. Those results indicate that PG has no effects on the redox reaction and can improve cycle stability and capacity, suggesting that PG is a superior additive.

CONCLUSIONS

In this study, the PG electrolyte was found to be able to regulate aqueous Zn²⁺ electrochemical reversibility on a molecular level, resulting in decreased water activity, inhibited Zn dendrite and side-reactions, and improved properties. The experiments and DFT calculations imply the PG has a stronger interaction with Zn²⁺ and H₂O than water. Following the addition of PG, water molecules interact with PG, lowering water activity and the freezing point and inhibiting the decomposition of solvated H₂O, resulting in a wider electrochemical stability window and less parasitic reactions. In addition, PG replaces solvated H₂O in the Zn²⁺ solvation cells, weakening the Zn²⁺ solvation in the electrolyte and improving the cycling stability. When 20 vol% PG was added into 3 mol L⁻¹ ZnSO₄ aqueous electrolyte, high cycling stability over 1000 h in the Zn//Zn symmetric battery

Figure 4 Cycling stability and performance of the Zn//V₂O₅ battery: (a) long-term cycling performance of the Zn//V₂O₅ battery at 5 A g⁻¹, (b) the low-temperature properties of the Zn//V₂O₅ battery at -20°C, (c) GCD curves of the Zn//V₂O₅ battery at 2nd cycling with a current density of 500 mA g⁻¹, (d) CV profiles of the Zn//V₂O₅ battery at 2nd cycling with a scan rate of 0.1 mV s⁻¹, (e) working picture of lights with the Zn//V₂O₅ battery.

and significant average CE of 98.9% in the Cu//Zn cell were achieved. The effectiveness of PG electrolyte is valid in the Zn//V₂O₅ battery. The battery exhibited a stable specific capacity of 348 mA h g⁻¹ at 500 mA g⁻¹ and superior long-term cycling stability with 92.6% capacity retention over 5000 cycles at 5 A g⁻¹, which are prominently higher than that without PG. Over 500 cycles at -20°C, the battery with PG maintained a stable specific capacity of 190 mA h g⁻¹ at 0.5 A g⁻¹, demonstrating an excellent low-temperature performance.

Received 1 September 2021; accepted 21 October 2021;
published online 8 December 2021

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Acknowledgements This work was supported by the National Key R&D Program of China (2017YFE0133800), the CASHIPS Director’s Fund (YZJJ201902 and YZJJZX202018), and Anhui Provincial Natural Science Foundation (1908085QB52 and 2008085ME135).

Author contributions Wei T conceived and designed the experiments. Wei T, Peng Y, Li Z, and Hu L contributed to the experiment and data analysis. Mo L and Chen S contributed to the photographing. Ghadari R contributed to the DFT calculation. Wei T and Li Z contributed to the writing. All the authors contributed to the general discussion.

Conflict of interest The authors declare no competing financial interest.

Supplementary information The DFT calculation details and supporting data are available in the online version of the paper.

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丙二醇电解液键结构调控及其水系锌离子电池稳定性研究

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摘要 水系锌基电池具有低成本和高安全性的优点, 是很有潜力的储能技术. 然而, 枝晶、副反应和较差的低温性能限制了其实际应用, 这与电解液的溶液组成密切相关. 在本工作中, 我们通过调控丙二醇电解液的溶剂结构及键相互作用, 有效抑制了锌枝晶和副反应. 丙二醇具有较高的电子云密度和DN (Donor number) 值, 可以破坏水分子间和水分子与 Zn^{2+} 间的相互作用, 从而提高H-O共价键的强度, 降低水活性和冰点, 改变 Zn^{2+} 的溶剂化结构. 制备的电池器件表现出高的循环稳定性 (Zn//Zn电池循环超过1000 h), 高可逆性(库伦效率达到98.9%), 高储锌性能(在 5 A g^{-1} 下比容量为 225 mA h g^{-1} , 循环5000圈容量保持率为92.6%)和优异的防冻性能(在 -20°C 下循环500圈比容量为 190 mA h g^{-1}). 本工作为高性能水系锌离子电池的发展提供了一种有前景的策略.