Fabricating low-temperature-tolerant and durable Zn-ion capacitors *via* modulation of co-solvent molecular interaction and cation solvation

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ABSTRACT Aqueous Zn-based energy-storage devices have aroused much interest in recent years. However, uncontrollable dendrite growth in the Zn anode significantly limits their cycle life. Moreover, the poor low-temperature performance arising from the freezing of aqueous electrolytes at sub-zero temperatures restricts their practical applications in cold regions. Here, we fabricated low-temperature-tolerant and durable Zn-ion hybrid supercapacitors (ZHSCs) *via* modulating a co-solvent water/ethylene glycol electrolyte. The interaction of intermolecular hydrogen bonds between water and ethylene glycol as well as cation solvation was systematically investigated by tuning the co-solvent composition. The results illustrate that the ZnSO₄/water/ethylene glycol (65%) electrolyte possesses high ionic conductivity at low temperatures and effectively prevents the dendrite formation of the Zn anode. The as-fabricated ZHSCs exhibit long-term cyclability and are capable of working at sub-zero temperatures as low as −40°C. The present ZHSCs are anti-freezing and cost-effective, which may find new applications in the fields of next-generation electrochemical energy storage devices.

Keywords: low temperature, co-solvent electrolyte, Zn-ion capacitors, ionic conductivity, rational modulation

INTRODUCTION

Aqueous metal-ion energy-storage devices have recently received considerable attention because of their high safety, excellent rate capability, high energy density, and ultralong cycle life [1]. Among them, aqueous Zn-ion hybrid supercapacitors (ZHSCs) are the most attractive since the metallic zinc has the merits of low cost, natural abundance, high theoretical volumetric capacity

(5855 mA h cm^{−3}) and gravimetric capacity (820 mA h g^{−1}), and suitable electrochemical potential (−0.76 V vs. standard hydrogen electrode) [2–4]. Similar to other Zn-based devices, inhomogeneous Zn plating/stripping at the anode side will induce dendrite growth during charge/discharge processes of ZHSCs, resulting in low Coulombic efficiency and capacity fading [5,6]. Even worse, once the dendrites pierce the separator, short circuit in the devices may occur [7,8]. Therefore, it is a great challenge to develop a dendrite-free Zn anode for long-life ZHSCs [9,10].

Numerous strategies have been proposed in Zn-based devices, including structural engineering of Zn anodes [11–15], surface modification [16–21], and designing new electrolytes [22–34] or separators [35]. Among them, rational modulation of electrolytes is a simple and effective way [25]. Aqueous ZnSO₄ has been considered as a mild electrolyte for Zn-ion batteries/supercapacitors because of the low cost and high compatibility with electrode materials [36]. However, the severe issue of dendrite growth cannot be well addressed in the aqueous ZnSO₄ electrolyte [37]. In recent years, encouraging results based on novel electrolyte design have been reported, such as Zn(CF₃SO₃)₂ [22], “water-in-salt” [23,30], organic [26–27], “deep eutectic solvent” [28,29], ionic liquid [31], and polymer electrolytes [34]. Unlike aqueous electrolytes, these elaborately designed electrolytes alter the solvation sheath of Zn²⁺ by reducing water molecules, thereby suppressing dendrite growth and hydrogen evolution. Nevertheless, the cost of those electrolytes is relatively high. It runs counter to the cost-effective nature of Zn-based devices, which makes them uncompetitive or less competitive in the market [38]. Besides, the tradi-

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tional aqueous electrolytes with a high freezing point will be frozen at sub-zero temperatures, leading to the failure of devices at low temperatures [39]. Such poor low-temperature tolerance of Zn-based devices substantially limits their daily uses in the winter of cold regions, and other special fields, such as aerospace, polar exploration, and astronomical observation [40]. Those well-designed electrolytes in previous reports mainly focused on inhibiting the dendrite growth and improving the cycle life of Zn anodes. There is little concern about the freezing problem of the devices under extremely low temperatures. Therefore, it is urgent to develop cost-effective electrolytes for both dendrite-free and low-temperature-tolerant Zn-based energy-storage devices.

Taking ZHSCs as an example, here we demonstrated the fabrication of aqueous ZHSCs with long-term cyclability by utilizing a low-temperature-tolerant co-solvent electrolyte based on water/ethylene glycol (EG). EG is compatible with the ZnSO_4 salt, forming a homogeneous electrolyte without a delamination phenomenon. The viscosity of EG is relatively high, which plays an important role in zinc deposition processes [41]. Relatively low freezing point of the $\text{H}_2\text{O}/\text{EG}$ hybrid solvent is desirable at low temperatures [42,43]. In this study, we systematically manipulated the interaction of intermolecular hydrogen bonds between water and ethylene glycol at room and sub-zero temperatures and the cation solvation effects were manipulated *via* modulating the composition of the co-solvent. It is demonstrated that the growth of zinc dendrites in the Zn/Zn symmetrical cells is restrained even upon continuous Zn plating/stripping cycles for 5400 h at a current density of 0.5 mA cm^{-2} , and the ZHSCs show long-term cyclability at room temperature. Benefiting from the extremely low freezing point and superior ionic conductivity at low temperatures, the co-solvent-based electrolyte enables reversible cycling of the Zn/Zn symmetrical cells for 1000 h without short circuit or increased overpotential at -20°C . The ZHSCs exhibit remarkable electrochemical performances at low temperatures (even workable at -40°C).

EXPERIMENTAL SECTION

Chemicals

Zinc foils were sanded and then washed by ethanol before used. Activated carbon (YP-50F) was purchased from Kuraray. Before use, it was treated at 700°C for 3 h under Ar atmosphere. EG (analytical grade) and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (analytical grade) were directly used without any further purification.

Preparation of electrolytes

EG was firstly mixed with ultra-pure water in different volume ratios. Then, stoichiometric amount of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ was dissolved in the hybrid solvent by magnetic stirring.

Characterization

The morphologies of the samples were observed by a scanning electron microscope (SEM, Sirion200). The surface topographies of zinc foils were recorded by a three-dimensional (3D) digital microscope (VHX-1000C, Keyence). Fourier transition-infrared (FT-IR) spectra of the electrolytes were obtained from a VERTE 70. The crystal structure of zinc foils was characterized by X-ray diffraction (XRD, PANalytical B.V., Holland). The viscosity of the electrolytes was measured by a rheometer with a shear rate of 100 s^{-1} . The cyclic voltammetry (CV), chronoamperometry (CA) and Tafel curves were tested by an electrochemical workstation (CHI 760E). The low-temperature properties were tested in a high-low temperature test chamber. The wettability was evaluated by a contact angle meter.

The ionic conductivity of the electrolytes was measured by electrochemical impedance spectroscopy (EIS) in a stainless steel/stainless steel cell. The value was calculated according to the following equation:

$$\sigma = L/R_s A, \quad (1)$$

where σ is the ionic conductivity, L (1.35 cm) is the distance between the two stainless steel foils, R_s is the electrolyte resistance that was obtained from the intercept of EIS, and A (0.88 cm^2) is the area of a stainless steel foil.

Electrochemical measurements

The electrochemical performances were tested in 2032 coin-type cells and soft-packed cells. Zn/Zn symmetrical cells were assembled with two Zn foils as the cathode and anode, respectively. A glass fiber saturated with electrolyte was used as separator. Coulombic efficiency was tested by Zn/Ti cells. Zinc was firstly deposited on the Ti foil for 1 h at a current density of 0.5 mA cm^{-2} . Then, the deposited Zn was stripped with a cut-off voltage of 0.5 V. The Coulombic efficiency can be calculated by the ratio of stripping capacity and plating capacity. The cathode slurry for Zn-ion hybrid supercapacitors was prepared by mixing the active material (activated carbon), conductive agent (Super P), and binder (polyvinylidene fluoride (PVDF)) at a weight ratio of 8:1:1 in *N*-methyl pyrrolidone solvent. The as-prepared slurry was then coated on carbon cloth by a doctor blade. Finally, the electrode was fully dried at 80°C for 12 h. Zn foil and glass fiber were

used as the anode and separator, respectively. The electrochemical performances were measured by a LAND testing system.

RESULTS AND DISCUSSION

A series of $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG}-x$ electrolytes that contain 1 mol L^{-1} ZnSO_4 and different contents of EG were prepared, where x represents the volume percentage of EG in the mixed solvent. Fig. 1a, b show the FT-IR spectra of the electrolytes. It is observed that the deformation vibration absorption peaks of H_2O molecules range from 1600 to 1700 cm^{-1} (Fig. 1a and Fig. S1) [44]. They shift toward higher wavenumbers with increasing EG content, indicating the intermolecular hydrogen bonds between H_2O and EG molecules [45]. Two typical absorption peaks between $2840\text{--}2990 \text{ cm}^{-1}$ correspond to the stretching vibration absorption bands of CH_2 [46]. As the EG content increases, the absorption bands shift toward lower wavenumbers, arising from the redistribution of the charge after forming the hydrogen bonding between hydroxyl groups of EG and H_2O molecules [47]. The interaction between EG and H_2O molecules can destroy the hydrogen bonding network inside water molecules, thereby lowering the freezing point [48]. Fig. 1b displays a

comparison of the stretching vibration absorption peaks of CH_2 in $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG}-x$ electrolytes and $\text{H}_2\text{O}/\text{EG}-x$ solvents (take “ $x = 65$ ” as an example). Evidently, the wavenumbers of the CH_2 absorption bands in the $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG}-65$ electrolyte are higher than those in the $\text{H}_2\text{O}/\text{EG}-65$ solvent. This suggests that the interaction between EG molecules and Zn^{2+} ions in the $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG}-x$ electrolytes may occur, and some EG molecules participate in the solvation sheath of Zn^{2+} ions [49]. It is known that ionic conductivity is an important parameter for electrolytes. As shown in Fig. 1c and Fig. S2, the aqueous $\text{ZnSO}_4/\text{H}_2\text{O}$ (0%) electrolyte has a high ionic conductivity (42.2 mS cm^{-1}) at room temperature. If the EG content increases, correspondingly, the ionic conductivity of the $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG}-x$ electrolytes decreases gradually. When the EG content reaches 65%, the ionic conductivity of the electrolyte still remains to be 5.2 mS cm^{-1} . For the ZnSO_4/EG (100%) electrolyte, its ionic conductivity is reduced to 0.9 mS cm^{-1} . Meanwhile, it is found that the viscosity of the electrolyte becomes higher if the EG content is increased (Fig. 1c). Fig. 1d shows the CV profiles for the Zn/stainless steel cells in different electrolytes, where the redox peaks correspond to the stripping/plating processes of zinc [27]. The peak intensity is gradually weakened

Figure 1 Characterizations of $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG}-x$ electrolytes: (a) FT-IR spectra of $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG}-x$ electrolytes with different contents of EG. (b) FT-IR spectra of the $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG}-65$ electrolyte and the $\text{H}_2\text{O}/\text{EG}-65$ solvent. (c) Ionic conductivity and viscosity of the $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG}-x$ electrolytes with different contents of EG. (d) CV profiles for the Zn/stainless steel cells in different $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG}-x$ electrolytes. (e) Oxidation stability of electrolytes.

with increasing EG content, suggesting the slower reaction kinetics in the high-EG electrolytes due to the lower ionic conductivity [26]. Fig. 1e suggests that all of the electrolytes are stable below 2.1 V [33].

Zn/Zn symmetrical cells were assembled to study the reversibility of the Zn anode in these $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG}-x$ electrolytes. As shown in Fig. 2a and Fig. S3, the aqueous $\text{ZnSO}_4/\text{H}_2\text{O}$ electrolyte displays the lowest plating/stripping overpotential at a current density of 0.5 mA cm^{-2} and an areal capacity of 0.5 mA h cm^{-2} . As the EG content increases in the $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG}-x$ electrolytes, the overpotential is gradually enlarged, which is due to the decrease in ionic conductivity [27]. Nevertheless, for the

$\text{ZnSO}_4/\text{H}_2\text{O}$ electrolyte, a short circuit occurs in the symmetrical cells after 192 h. However, the cycle life is improved significantly with the addition of EG. For the $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG}-50$ electrolyte, the symmetrical cells can be cycled for 2878 h and then fail by a short circuit. When the EG content increases to 65% ($\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG}-65$), the cycle life is further prolonged, and the Zn plating/stripping processes remain stable for 5400 h without a short circuit. Such remarkable stability is more than 28 times that in the $\text{ZnSO}_4/\text{H}_2\text{O}$ electrolyte. However, for the $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG}-80$ and ZnSO_4/EG electrolytes with a higher EG content, the symmetrical cells exhibit a decrease in cyclability. Unlike the aqueous $\text{ZnSO}_4/\text{H}_2\text{O}$

Figure 2 Zn/Zn symmetrical cells: (a) galvanostatic cycling of Zn/Zn symmetrical cells in different electrolytes at 0.5 mA cm^{-2} . (b) Height distribution and (c–g) the corresponding 3D surface topographies at 500 $\times$ magnification of Zn foils after cycling in different electrolytes.

electrolyte, the symmetrical cells fail by a sharply increased overpotential instead of a short circuit in the $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG}-80$ and ZnSO_4/EG electrolytes. The above results demonstrate that the best cyclability is achieved in the $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG}-65$ electrolyte. The similar conclusion is also demonstrated at a current density of 1 mA cm^{-2} and an areal capacity of 1 mA h cm^{-2} (Fig. S4).

The surface morphology of the cycled zinc foils was explored in detail by a 3D digital microscope. The 3D surface topographies of Zn foils after cycling in different electrolytes are displayed in Fig. 2b–g. These pictures were obtained by scanning the surface of the zinc foils through the movement of the lens, collecting data from different positions, and finally converting them into a 3D model. Clearly, the surface of the zinc foil after cycling in the $\text{ZnSO}_4/\text{H}_2\text{O}$ electrolyte becomes very uneven, and a large number of dendrites can be observed (Fig. 2c). Such uncontrollable dendrite growth may induce the short circuit [37]. In contrast, the dendrite growth is significantly inhibited in the $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG}-x$ electrolytes. As shown in Fig. 2d, upon cycling in the $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG}-50$ electrolyte, the big dendrites disappear, but some small dendrites are still inevitable. These small dendrites would also eventually pierce the separator, causing a short circuit in the symmetrical cells. Surprisingly, the surface of the zinc foil is very smooth without the generation of the dendrites after cycling in the $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG}-65$ electrolyte (Fig. 2e). For the electrolytes with a higher EG content (e.g., $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG}-80$ or ZnSO_4/EG), the dendrite-free zinc anode can also be achieved (Fig. 2f, g). The corresponding roughness of the zinc foils and the size of dendrites can be estimated by the height distributions (Fig. 2b). Fig. S5 shows the low-magnification SEM images for the zinc anodes. After cycling in the $\text{ZnSO}_4/\text{H}_2\text{O}$ electrolyte, the zinc foil becomes fluffy and thick (Fig. S5a), suggesting the formation of dendrites in a large quantity [18]. However, the surface of the zinc foil gets denser after cycling in the $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG}-50$ electrolyte (Fig. S5b). For a higher EG content ($\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG}-65$, $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG}-80$, ZnSO_4/EG), the cycled zinc foils remain dense and smooth (Fig. S5c–e). The dendrites are effectively suppressed, which agrees well with 3D microscope observations.

The microstructures of the deposited zinc were further investigated by SEM. As shown in Fig. 3a, bulky dendrites are formed after cycling in the $\text{ZnSO}_4/\text{H}_2\text{O}$ electrolyte, and the dendrites grow vertically upwards. Meanwhile, some fibrous substances embedded in the zinc dendrites can be observed clearly. Detailed analysis in Figs S6, S7

show that these glass fibers are detached from the separator. These results reveal that massive dendrites are formed on the zinc anode and have penetrated the separator. For the $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG}-50$ electrolyte (Fig. 3b), big and vertical dendrites are not found. Nevertheless, some small dendrites still exist and have pierced the separator. As expected, the surface of the cycled zinc is quite clean, and the deposited zinc is parallel to the zinc foil without dendrite growth when the EG content reaches 65% (Fig. 3c). For the $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG}-80$ electrolyte (Fig. 3d) and the ZnSO_4/EG electrolyte (Fig. 3e), similar results can be obtained. Besides, the size of the deposited zinc becomes finer as the EG content increases in the electrolytes. Fig. 3f display the XRD patterns of zinc foils after cell failure. The diffraction peaks at 36.3° and 39.0° correspond to the (002) and (100) planes of zinc, respectively [13]. After cycling in the $\text{ZnSO}_4/\text{H}_2\text{O}$ electrolyte, the (002)/(100) ratio of zinc is relatively small, indicating that the deposited zinc tends to grow perpendicular to the surface of the zinc foil [14]. However, in the electrolyte containing EG, especially in the ZnSO_4/EG electrolyte using pure EG as the solvent, the (002)/(100) ratios increase significantly, revealing that zinc tends to deposit parallelly to the surface of zinc foil [50]. These results are consistent with the SEM results. Besides, distinct XRD diffraction peaks of $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot 3\text{H}_2\text{O}$ and $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot 4\text{H}_2\text{O}$ by-products can be seen after cycling in the $\text{ZnSO}_4/\text{H}_2\text{O}$ electrolyte, resulting from the severe side reactions in the aqueous electrolyte [19]. When the EG content is higher than 65%, only the weak peaks of $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot 4\text{H}_2\text{O}$ appear. With the further increase of the EG content, the intensity of the peaks decreases obviously, suggesting that the side reactions are significantly reduced in the electrolytes containing EG. Therefore, the electrolytes play a crucial role in inhibiting the dendrite growth and suppressing the side reactions. With the increase of the EG content, the dendrite growth is gradually suppressed. When the EG content is higher than 65%, dendrite-free deposition can be achieved. However, an excess of EG in the $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG}-80$ and ZnSO_4/EG electrolytes will lead to low ionic conductivity and reduce the cycle life [26]. Therefore, the optimal $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG}-65$ electrolyte combining the merits of the dendrite resistance and high ionic conductivity can achieve the best cyclability.

The underlying mechanism of inhibiting the dendrite growth in the $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG}-65$ electrolyte has been studied. *In-situ* optical microscope was firstly performed to monitor the zinc deposition process. Fig. S8 shows the galvanostatic discharge curve for a Zn/Zn symmetrical

Figure 3 (a–e) SEM images for Zn foils after cycling in different electrolytes. (f) XRD patterns of the zinc foils after cell failure.

cell based on the ZnSO₄/H₂O electrolyte. The corresponding morphology evolution of the zinc anode during this process is shown in Fig. 4a. It is found that the zinc foil is relatively flat in the initial state. After 20 min of deposition, a few small dendrites appear. As the deposition time increases, these dendrites gradually grow, leading to the uneven surface of the zinc foil. However, as expected, the zinc foil in the ZnSO₄/H₂O/EG-65 electrolyte remains smooth during the entire deposition process without the formation of dendrites (Fig. 4b and Fig. S9). The wettability of the electrolytes to the zinc foils significantly influences the deposition process. As shown in Fig. S10, the contact angle in the ZnSO₄/H₂O electrolyte is 86.9°, indicating that the electrolyte has poor wettability to the zinc foil [51]. In contrast, the wettability is im-

proved in the ZnSO₄/H₂O/EG-65 electrolyte, with a contact angle of 50.3°. The improved wettability of the ZnSO₄/H₂O/EG-65 electrolyte is in favor of reducing the Gibbs free energy of the nucleation process [24]. The nucleation overpotential of zinc deposition was further studied by CV measurements in a three-electrode system. The glass carbon electrode, Zn foil, and saturated calomel electrode (SCE) were used as the working, counter, and reference electrodes, respectively. As shown in Fig. S11, the nucleation overpotential in the ZnSO₄/H₂O/EG-65 electrolyte is 63 mV, which is higher than that in the ZnSO₄/H₂O electrolyte (26 mV). A higher nucleation overpotential implies a smaller critical nucleus size for nucleation [52]. Therefore, the size of the deposited zinc is finer in the ZnSO₄/H₂O/EG-65 electrolyte, which is

Figure 4 *In-situ* study of Zn deposition by an optical microscope (a) in the $\text{ZnSO}_4/\text{H}_2\text{O}$ electrolyte, and (b) in the $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG-65}$ electrolyte. (c) CA curves of Zn deposition in $\text{ZnSO}_4/\text{H}_2\text{O}$ and $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG-65}$ electrolytes at an overpotential of -150 mV. (d) Schematics of Zn deposition behaviors in $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG-65}$ (left) and $\text{ZnSO}_4/\text{H}_2\text{O}$ electrolytes (right). In the $\text{ZnSO}_4/\text{H}_2\text{O}$ electrolyte, Zn^{2+} tends to aggregate and grow into dendrites through 2D diffusion. However, 2D diffusion is limited in the $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG-65}$, resulting in a dendrite-free deposition.

consistent with the SEM results. The better wettability together with a higher nucleation overpotential in the $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG-65}$ electrolyte suggests that the zinc deposition positions are not the energetically favorable sites (surface of dendrites). CA was further conducted to study the zinc deposition behaviors. As shown in Fig. 4c, in the $\text{ZnSO}_4/\text{H}_2\text{O}$ electrolyte, the current density continues to increase rapidly for more than 300 s. This suggests that the zinc deposition process is a 2D diffusion process, in which the adsorbed zinc ions can diffuse laterally along the surface of zinc foil to the protruding sites and then deposit into dendrites [17]. The increase in current density indicates that the continuous growth of dendrites leads to a higher surface area [19]. For the $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG-65}$ electrolyte, the 2D diffusion process only occurs within about 40 s, which corresponds to the initial nucleation process [32]. Then, the current density becomes stable, indicating that a 3D diffusion process is in progress. At this stage, zinc can be deposited stably without dendrite growth [53]. Based on the above results, the zinc deposition behaviors can be described in Fig. 4d. For the $\text{ZnSO}_4/\text{H}_2\text{O}$ electrolyte, in the initial stage of deposition, a small number of crystal nucleus are formed on the surface

of the zinc foil and then evolve into protrusions. To minimize the surface energy, zinc ions tend to diffuse (including a 2D diffusion process) to these protrusions, then eventually grow into dendrites [54]. For the $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG-65}$ electrolyte, on the one hand, the better wettability to the zinc foil can reduce the Gibbs free energy of the nucleation process [24]. On the other hand, the bulky $\text{Zn}^{2+}(\text{H}_2\text{O})_m(\text{EG})_n$ solvated ions and the high viscosity of the electrolyte will increase the energy barrier for 2D diffusion [41]. Once the 2D diffusion barrier is higher than the nucleation energy in their initial adsorption positions (which are not the energetically favorable sites), the 2D diffusion is limited and zinc can only be deposited evenly on these sites without aggregations [17]. Therefore, the nucleation overpotential is higher and the size of deposited zinc is smaller than that in the $\text{ZnSO}_4/\text{H}_2\text{O}$ electrolyte. After deposition for a period, a smooth and dense zinc layer can be obtained eventually.

Coulombic efficiency is another critical parameter that determines the cycle life of zinc anodes [7]. The Zn/Ti cells were then assembled for evaluating the Coulombic efficiency of both electrolytes at a current density of

0.5 mA cm^{-2} . As can be seen from Fig. S12, the Coulombic efficiency gradually increases and remains stable at about 98% in the $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG-65}$ electrolyte. The enhanced Coulombic efficiency is probably ascribed to the activation and stabilization process of the Ti/electrolyte interface [17]. The average Coulombic efficiency from the 1st to 200th cycles is as high as 95.5%. On the contrary, in the $\text{ZnSO}_4/\text{H}_2\text{O}$ electrolyte, the voltage curves jitter obviously during the zinc plating/stripping process, which is mainly caused by the dendrite growth and water decomposition [29]. Moreover, the Coulombic efficiency fluctuates greatly during cycling. The Coulombic efficiency higher than 100% is probably because of the dendrites formed in the previous cycles that participate in the subsequent stripping processes [26]. The Coulombic efficiency suddenly drops to zero, suggesting that the dendrite growth induces a short circuit [27]. Furthermore, the average Coulombic efficiency is only 89.2%. Therefore, a higher and much stable Coulombic efficiency in the $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG-65}$ electrolyte is demonstrated.

Besides, corrosion is also an important factor affecting the cycle life of zinc anodes [55]. As shown in Fig. S13, the corrosion potential of the aqueous $\text{ZnSO}_4/\text{H}_2\text{O}$ electrolyte is -1.041 V . In contrast, a higher corrosion potential of -1.016 V can be achieved in the $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG-65}$ electrolyte. Also, the $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG-65}$ electrolyte exhibits a smaller corrosion current than that in the $\text{ZnSO}_4/\text{H}_2\text{O}$ electrolyte. The above results indicate that the $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG-65}$ electrolyte is capable of corrosion resistance, which is probably due to the better thermodynamic stability of zinc in organic solutions [27].

ZHSCs have been further assembled to demonstrate the practical application of the $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG-65}$ electrolyte. The anode is a Zn foil, and the cathode is commercially available activated carbon (YP-50F). The SEM image in Fig. S14 shows that the activated carbon particles with irregular shapes have an average size of about

$10 \mu\text{m}$. Tens of thousands of cycles in ZHSCs can be achieved in previous reports. It is mainly because their mass loading of cathode materials is relatively low (usually less than 2 mg cm^{-2}). Thus, the severe dendrite growth at the Zn anode would be avoided. However, in practical applications, a higher mass loading is compulsory to meet the energy-density requirements. In this regard, the problem of zinc dendrites cannot be ignored [37]. In our study, therefore, the mass loading of approximately 7 mg cm^{-2} was applied to compare the cycling stability in the $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG-65}$ electrolyte and the aqueous $\text{ZnSO}_4/\text{H}_2\text{O}$ electrolyte. Fig. 5a displays the representative galvanostatic charge/discharge curves of the ZHSCs at a current density of 0.2 A g^{-1} . Compared with the $\text{ZnSO}_4/\text{H}_2\text{O}$ electrolyte, the ZHSC in the $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG-65}$ electrolyte displays a higher iR drop and lower specific capacity (56 mA h g^{-1}), which may be due to the lower ionic conductivity [4]. Nevertheless, its cycling performance is greatly improved. As shown in Fig. 5b, c, for the aqueous $\text{ZnSO}_4/\text{H}_2\text{O}$ electrolyte, a dramatic decrease in Coulombic efficiency and capacity occurs within 4100 cycles, which is probably caused by the dendrite growth and short circuit (Figs S15, S16) [12]. It should be noted that the increased capacity in the initial cycles may be attributed to the improved wettability between the electrolyte and the electrode [6,10]. However, in the $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG-65}$ electrolyte, it can be cycled stably for 10,000 times with a Coulombic efficiency of nearly 100%. The postmortem analysis reveals that the Zn anode is quite smooth after cycling (Fig. S17), which plays a significant role in the long cycle life.

Under some extreme environments of low temperatures (e.g., polar exploration and aerospace), there is an increasing demand for the use of electrochemical energy storage devices [56–61]. For the $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG-65}$ electrolyte, considering that the hydrogen bonding network in the H_2O molecules is destroyed, it may offer an

Figure 5 Electrochemical performances of the as-assembled ZHSC. (a) Galvanostatic charge/discharge curves of ZHSCs at a current density of 0.2 A g^{-1} . Cycling performances (b) and the corresponding Coulombic efficiencies (c) of ZHSCs in $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG-65}$ and $\text{ZnSO}_4/\text{H}_2\text{O}$ electrolytes at a current density of 1 A g^{-1} after 10 cycles of activation at 0.2 A g^{-1} .

ideal anti-freezing feature for ZHSCs. Therefore, the low-temperature properties of the $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG-65}$ electrolyte were further investigated. Fig. 6a are digital photos of the $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG-65}$ and $\text{ZnSO}_4/\text{H}_2\text{O}$ electrolytes at low temperatures. It can be seen that the $\text{ZnSO}_4/\text{H}_2\text{O}$ electrolyte is frozen at -10°C , while the $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG-65}$ electrolyte remains liquid after being placed at -50°C for more than 12 h. This result suggests that the $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG-65}$ electrolyte possesses low-temperature tolerance. The ionic conductivity of the electrolytes at different temperatures is shown in Fig. 6b and Fig. S18. The $\text{ZnSO}_4/\text{H}_2\text{O}$ electrolyte exhibits a relatively high ionic conductivity at 25°C . However, it drops strikingly at low temperatures. This is probably because the electrolyte freezes at a low temperature, which suppresses ion migration [62]. In contrast, the $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG-65}$ electro-

lyte has a high ionic conductivity at extremely low temperatures (for example, 0.16 mS cm^{-1} at -40°C). The Zn/Zn symmetrical cells were cycled at -20°C and the galvanostatic cycling curves are shown in Fig. 6c. Zinc can be reversibly deposited/stripped for 1000 h without short circuit or rising overpotential at 0.5 mA cm^{-2} under such a low temperature. These results demonstrate dendrite-free depositions of Zn foils upon cycling under low-temperature environments (Fig. S19). As shown in Fig. 6d and Fig. S20, the ZHSC delivers a specific capacity of 61.3 mA h g^{-1} at 25°C . When the temperature drops to 0, -10 , -20 and -30°C , the specific capacities are 51.7, 47.2, 41.9, and 33.6 mA h g^{-1} , respectively. Encouragingly, the ZHSC can work even at -40°C , and delivers a specific capacity of 17.9 mA h g^{-1} . Moreover, when the temperature returns to 25°C , the specific capacity can be re-

Figure 6 Low-temperature properties of electrolytes. (a) The physical state of $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG-65}$ and $\text{ZnSO}_4/\text{H}_2\text{O}$ electrolytes at low temperatures. (b) Ionic conductivities of $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG-65}$ and $\text{ZnSO}_4/\text{H}_2\text{O}$ electrolytes at different temperatures. (c) Galvanostatic cycling of Zn/Zn symmetrical cells at -20°C . The voltage drop at around 277 and 580 h is caused by the temperature rise due to power failure of the temperature-controlled equipment. (d) Charge/discharge curves of the ZHSC at different temperatures. (e) Cycling performance of the anti-freezing ZHSC at -20°C . (f) Demonstration of the practical application of the anti-freezing ZHSC by charging the cell phone at extremely low temperatures.

covered to 61.0 mA h g^{-1} , which guarantees its practical application. The rate performance of the ZHSC at low temperatures is important. At -20°C , the capacities of 45.0, 39.1, 29.3 and 13.7 mA h g^{-1} can be achieved at the current density of 0.1, 0.2, 0.5 and 1 A g^{-1} , respectively (Fig. S21). The cycling performance of the ZHSC at -20°C is shown in Fig. 6e. The capacity retention is as high as 97.8% after 1000 cycles, and the Coulombic efficiency remains nearly 100% throughout the entire life. For comparison, the ZHSC using the $\text{ZnSO}_4/\text{H}_2\text{O}$ electrolyte cannot work at low temperatures, for its specific capacity is approximately 0 mA h g^{-1} (Fig. S22). Evidently, the $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG}-65$ electrolyte endows the ZHSC with remarkable low-temperature performance. It is worth noting that there is still room for improving the low-temperature performance of ZHSCs if the electrode materials and electrode structures are further optimized. To verify the freeze-resistant ability of the ZHSC at low temperatures, three coin cells of ZHSCs in series were put into water, then frozen at -40°C in a constant temperature water-bathing, and finally taken out for the demonstration. As shown in Fig. S23 and Movie S1, the ZHSC wrapped in ice cubes can still power a light-emitting diode. Soft-packed ZHSCs were further assembled to demonstrate their practical applications under extremely low temperatures. As shown in Fig. S24, the capacity of the soft-packed ZHSC is about 0.7 mA h . Five soft-packed ZHSCs in series and a thermocouple were frozen at -40°C and then taken out for characterization. Impressively, the soft-packed ZHSC can still charge a mobile phone under such an extremely low temperature (Fig. 6f and Movie S2). In contrast, the ZHSCs using the $\text{ZnSO}_4/\text{H}_2\text{O}$ electrolyte fail to charge the cell phone at low temperatures (Fig. S25 and Movie S3). It is expected that the low-temperature tolerance endows the $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG}-65$ electrolyte with broad applications at extremely low temperatures.

CONCLUSIONS

In summary, we successfully fabricated low-temperature-tolerant and highly reversible aqueous ZHSCs via synergistic modulation of cation solvation and co-solvent molecular interaction. The high content of EG in the electrolyte effectively restricts the 2D diffusion of Zn^{2+} ions, thereby suppressing the dendrite growth. Benefitting from the combination of dendrite-resistant ability and high ionic conductivity, the $\text{ZnSO}_4/\text{H}_2\text{O}/\text{EG}-65$ electrolyte endows zinc anodes with remarkable cyclability. The Zn/Zn symmetrical cells can be reversibly cycled for 1000 h at -20°C , without short circuits or overpotential

increases. ZHSCs also display excellent capacity retention under low temperatures. The practical application of the low-temperature-tolerant ZHSC is demonstrated by charging a cell phone under an extremely low temperature. It is expected that the zinc-based devices with long lifespans at extremely low temperatures may find new applications in the fields of energy storage devices.

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

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基于共溶剂分子间相互作用和阳离子溶剂化的耐低温、长寿命锌离子电容器

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摘要 近年来, 水系锌基储能器件引起了人们极大的关注. 然而, 锌负极中不可控的枝晶生长限制了其循环寿命. 另外, 水系电解液在零度以下冻结导致较差的低温性能, 限制了其在寒冷地区的实际应用. 以锌离子混合电容器为例, 本文报道了通过调节水/乙二醇共溶剂电解液来构建耐低温、长寿命的锌离子混合电容器. 通过调控共溶剂的组分, 系统探索了水和乙二醇分子间的氢键作用以及阳离子溶剂化对电化学性能的影响. 结果表明, 硫酸锌/水/乙二醇(65%)电解液在低温下具备较高的离子电导率, 并且可以有效地防止锌负极中枝晶的形成. 组装的锌离子混合电容器具有长循环稳定性, 能够在零下 40°C 的极端低温条件下工作. 该锌离子混合电容器成本低, 具有较好的抗冻特性, 有望应用于下一代电化学储能领域.