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Eutectic Electrolyte with Unique Solvation Structure for High-Performance Zinc-Ion Batteries

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Abstract: Zinc-ion battery (ZIB) presents great potential in energy storage due to low cost and high safety. However, the poor stability, dendrite growth, and narrow electrochemical window limit its practical application. Herein, we develop a new eutectic electrolyte consisting of ethylene glycol (EG) and ZnCl₂ for dendrite-free and long-lifespan ZIBs. The EG molecules participate in the Zn2+ solvation via coordination and hydrogen-bond interactions. Optimizing the ZnCl₂/EG molar ratio (1:4) can strengthen intermolecular interactions to form [ZnCl(EG)]⁺ and [ZnCl(EG)₂]⁺ cations. The dissociation-reduction of these complex cations enables the formation of CI-rich organic-inorganic hybrid solid electrolyte interphase film on Zn anode, realizing highly reversible Zn plating/stripping with long-term stability of ~3200 h. Furthermore, the polyaniline||Zn cell manifests decent cycling performance with ~78 % capacity retention after 10,000 cycles, and the assembled pouch cell demonstrates high safety and stable capacity. This work opens an avenue for developing eutectic electrolytes for high-safety and practical ZIBs.

Introduction

Zinc-ion battery (ZIB) is regarded as a potential candidate for large-scale energy storage, due to the relatively high theoretical capacity (820 mAh g⁻¹), low redox potential (-0.76 V vs. standard hydrogen electrode), abundant reserves of Zn, and environmental friendliness.^[1,2] However, its further practical application is hindered by the poor reversibility, dendrite formation, and narrow electrochemical window caused by the decomposition of free water in aqueous electrolyte.^[3] To address the above-mentioned issues, extensive efforts have been devoted to developing novel electrolytes. Organic electrolytes,^[4], ionic liquids (ILs),^[5], gel electrolytes,^[6], and quasi-solid/all-solid electrolytes^[7] have been proposed. Wang et al. reported a ZnCl₂/H₂O/DMSO (dimethyl sulfoxide) electrolyte, where DMSO limits the activity of water by forming hydrogen bonds with water, thereby realizing dendrite-free Zn anode.^[8] Cheng et al. found that the Zn(CF₃SO₃)₂/Al(CF₃SO₃)₃ electrolyte can enable ZIBs with a high discharge voltage of 1.7 V.^[9] Although the above electrolytes demonstrate certain advantages compared to traditional aqueous electrolytes, the overall electrochemical performances still need further optimization. An ideal electrolyte should possess high ionic conductivity, good electrode material compatibility, and good thermal/electrochemical stability, and be economical and environmentally friendly.^[10,11]

Deep eutectic solvents (DESs), first proposed by Abbott et al. in 2003,^[12] has aroused extensive research attention in electrochemical energy storage due to the simple synthesis and eco-friendliness.^[13] DESs are usually binary and ternary component solvents, mainly containing hydrogen bond donors and hydrogen bond acceptors. The most significant physical feature of DESs is that the freezing point of the whole system is lower than that of each component.^[14] When DESs is applied as the electrolyte for batteries, it is usually called eutectic electrolyte.[15,16] Unlike conventional electrolytes with solvated cations and anions through simple dissolving, the eutectic electrolytes contain complex anions and cations, which are formed through the strong interactions between the components.^[17-19] For example, 2.0 M ZnCl₂ aqueous electrolyte contains solvated Zn2+ cations and Cl- anions, while AICI₃/acetamide (AcA) eutectic electrolyte has AICI₄- and AI₂CI₇anions and [AICl₂(AcA)₂]⁺ cations.^[20] Compared with the traditional electrolytes, the eutectic electrolytes possess many as structural characteristics. such flexibility good thermal/chemical stability, low vapor pressure, and wide potential windows.^[21] Such unique features make the eutectic electrolytes very promising for advanced batteries. Chen's group reported а eutectic electrolyte based lithium on bis[(trifluoromethyl)sulfonyl]imide (LiTFSI), lithium difluoro(oxalato)borate (LiDFOB), and succinonitrile (SN) with non-flammable properties, which could realize stable cathodeelectrolyte interface (CEI) and solid electrolyte interphase (SEI) in LIBs.^[22] Boisset et al. found the eutectic electrolyte composed of LiTFSI and MAc (N-methylacetamide) could widen the electrochemical window up to ~5.3 V for LIBs.^[23] However, there are few reports on eutectic electrolytes for ZIBs. Cui et al. reported a Zn(TFSI)₂/acetamide eutectic electrolyte, which realized a dendrite-free Zn anode through in-situ SEI formation.^[24] However, the price of Zn(TSFI)₂ salt is relatively high. In addition, because amide is a solid (melting point: 80 °C) with low conductivity at room temperature, the Zn(TFSI)₂/acetamide eutectic electrolyte has relatively high viscosity and low ion conductivity.

Herein, we develop a brand new eutectic electrolyte composed of EG (ethylene glycol) and ZnCl₂, which realizes dendrite-free Zn anode and long-lifespan ZIBs. Optimizing the ZnCl₂/EG molar ratio could strengthen the intermolecular interactions, facilitating the coordination between EG and Zn²⁺ to form [ZnCl(EG)]⁺ and [ZnCl(EG)₂]⁺ cations. The decomposition of these complex cations leads to the formation of a Cl-rich organic-inorganic hybrid SEI on Zn anode, thereby realizing reversible and stable Zn plating/stripping. With the obtained

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Figure 1. (a) Viscosity and ion conductivity of various DES; (b) ¹H NMR spectra, (c) FTIR spectra, and (d) Raman spectra of various DES and pure EG; (e) schematic illustration of the Zn-Cl polynuclear aggregate; (f) LSV curves of ZC, ZS, and DES-4 at a scan rate of 0.1 mV s⁻¹.

eutectic electrolyte, the polyaniline (PANI)||Zn cell manifests good rate capability and decent cycling performance, and the assembled pouch cell also demonstrates stable capacity and high safety.

Results and Discussion

Physicochemical Properties and Solvation Structure of Eutectic Electrolytes

The EG molecule with two O-H bonds and relatively high polarity is a hydrogen bond donor and a good solvent for various salts.^[25] ZnCl₂, a low-cost zinc salt, is a strong Lewis acid and hydrogen bond acceptor.^[26,27] Therefore, the EG and ZnCl₂ are ideal components to construct a low-cost DES. To optimize the performance, the ZnCl₂/EG molar ratio is varied from 1:2, to 1:16. With ZnCl₂/EG ratios of 1:2, 1:4, 1:8, and 1:16, the zinc salt concentration in turn reaches 8.9, 4.45, 2.25 and 1.125 M, and the corresponding DES is designated as DES-8, DES-4, DES-2, and DES-1, respectively. Due to the interactions between EG and ZnCl₂, all the DES are homogeneous and colorless liquid at room temperature, and they remain liquid at -20 °C (Figure S1). This temperature is lower than the melting point of pure EG (-12.9 °C) and ZnCl₂ (283 °C). Among all DES, the DES-4 has the highest conductivity (1.15 mS cm⁻¹) and a moderate viscosity (126.73 cp) (Figure 1a).

To study the specific intermolecular interactions of DES, nuclear magnetic resonance (NMR) was employed (Figure 1b). The ¹H resonances from OH and CH₂ of pure EG are located at 4.7 and 3.4 ppm, respectively.^[28] Compared with pure EG, the ¹H OH peaks of DES-2, DES-4, DES-8 undergo an obvious chemical shift and become wider, and the corresponding ¹H CH₂ peaks show an incremental increase in intensity. However, the ¹H NMR spectrum of DES-1 shows negligible difference. The results indicate the strong interactions between ZnCl₂ and EG, which may contain coordination (Zn²⁺ … O⁵⁻ in EG) and hydrogen bond (Cl⁻ …H⁵⁺-O⁵⁻ in EG). Furthermore, with the increase of zinc salt concentration, such interactions can be strengthened. The OH stretching of pure EG is located at 3000~3500 cm⁻¹ in the Fourier transform infrared (FTIR) spectra (Figure 1c and Figure S2a). After introducing ZnCl₂, the OH

stretching peak becomes slightly wider and weaker, especially for the DES-2, DES-4, and DES-8, which is caused by the coordination and hydrogen bond interactions between $ZnCl_2$ and EG.^[29,30]

Raman spectra of the DES and pure EG are presented in Figure 1d and Figure S2b. Compared to pure EG, all DES display two new peaks, one from ZnCl₄²⁻ at 260~310 cm⁻¹ and the other from Zn-Cl polynuclear aggregate at 200~240 cm⁻ ^{1.[31,32]} The other Raman bands of DES all comes from EG, indicating that the introduction of ZnCl₂ does not destroy the intramolecular bonds of EG.[33] The Zn-Cl polynuclear aggregate is the aggregate form of ZnCl₂ via coordination (Figure 1e).^[34,35] As expected, the peaks of ZnCl42- and Zn-Cl polynuclear aggregate intensify gradually with the increase of zinc salt concentration. The above results indicate that the DES contains free ZnCl42- anions whose concentration increases with the ZnCl₂ feeding amount. Notably, the results also indicate that DES with ZnCl4²⁻ complex anions differs substantially from the simple dissolving system such as 2.0 M ZnCl₂ aqueous electrolyte (ZC) with almost completely dissociated Zn²⁺ and Cl⁻ (Figure S3).^[36] Benefiting from the strong interactions between EG and ZnCl₂, the DES possesses a wide electrochemical stability window (ESW). As shown in the linear sweep voltammetry (LSV, Figure 1f) curves, the DES-4 is stable to a high potential of ~2.15 V vs. saturated calomel electrode (SCE). In contrast, the ZC electrolyte and traditional 2.0 M ZnSO₄ aqueous electrolyte (ZS) are stable to a potential of only 1.0 -1.1 V vs. SCE.[37]

To explore the solvation structure of DES, molecular dynamics (MD) simulations were performed. For all DES, the Zn^{2+} ions are coordinated with EG and Cl⁻ (Figure 2a and Figure S4-S6). With the increase of zinc salt concentration, the numbers of Cl⁻ and EG coordinated to each Zn^{2+} (termed as coordination number, CN) both increase (Figure 2b), indicating that the coordination ability of Cl⁻ and EG with Zn^{2+} strengthens. These results agree with the aforementioned spectroscopy analysis. According to the previous reports^[38], the coordination of Cl⁻ and EG with Zn^{2+} could result in the formation of [ZnCl(EG)]⁺ and [ZnCl(EG)2]⁺ complex cations. Herein, density functional theory (DFT) calculations are performed to elucidate the detailed coordination structures of such cations. Considering

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Figure 2. (a) MD simulation snapshot of DES-4; (b) diffusion coefficient of Zn^{2+} calculated from MSD simulations and coordination numbers of Cl⁻ and EG around each Zn^{2+} of various DES; (c) schematic diagram showing the interactions between $ZnCl_2$ and EG; energy profiles of the dissociation-reduction reactions of (d) $[ZnCl(EG)]^{+}$ and (e) $[ZnCl(EG)_2]^{+}$; electrostatic potential maps of (f) $[ZnCl(EG)]^{+}$ and (g) $[ZnCl(EG)_2]^{+}$ in DES-4.

that each EG molecule contains two hydroxyl groups (-OH), there are two coordination modes for each complex cation. The first mode is that only one -OH of EG coordinates with Zn2+ (Figure S7), while the second mode is that both -OH groups of EG simultaneously coordinate with Zn2+ through the rotation of C-C bond (Figure S8). For the formation of [ZnCl(EG)]*, the Gibbs free energy changes (ΔG) of the first mode and second mode are -2.35 and -3.33 eV (Figure S9 and S10), respectively. For the formation of $[ZnCl(EG)_2]^+$, the ΔG of the first mode and second mode are -3.69 and -4.44 eV, respectively. Although the formation of both coordination modes are spontaneous, the DFT calculation results suggest that the second coordination model is energetically preferred. Figure 2c depicts the interactions between EG and ZnCl₂ in DES: (I) the EG molecules tend to provide two -OH groups to chelate with the central Zn2+ to form [ZnCl(EG)]⁺ and [ZnCl(EG)₂]⁺ cations; (II) the Cl⁻ ions interacts with the -OH group of EG through hydrogen bonds.

Although the dissociation of [ZnCl(EG)]⁺ and [ZnCl(EG)₂]⁺ to Zn, Cl⁻, and EG requires extra energy (Δ G of -1.34 and -1.56 eV, respectively), the process becomes thermodynamically feasible when coupled with the reduction of Zn²⁺ to Zn (Figure 2d and 2e). Therefore, the [ZnCl(EG)]⁺ and [ZnCl(EG)₂]⁺ can spontaneously undergo dissociation-reduction to form a series of organic and inorganic products. Under the same energy scale bar, the electrostatic potential on the surface of [ZnCl(EG)₂]⁺ is lower than that of [ZnCl(EG)]⁺, suggesting the [ZnCl(EG)₂]⁺ can well shield the repulsion between Zn²⁺ cations (Figure 2f and 2g).^[39]

of $[ZnCl(EG)_2]^+$ is more kinetically favored. As expected, due to the strong coordination $(Zn^{2+} \cdots O^{\delta-} \text{ in EG})$ and hydrogen-bond $(Cl^- \cdots H^{\delta+} - O^{\delta-} \text{ in EG})$ interactions, large quantities of $[ZnCl(EG)_2]^+$ cations enable DES-4 with the highest diffusion coefficient (Figure 2b and Figure S11). Nevertheless, due to lager viscosity, DES-8 with strong intermolecular interactions has the lowest diffusion coefficient.

Electrochemical Performance of Zn Anode in Eutectic Electrolytes

To explore the reversibility of Zn plating/stripping process, TillZn coin cells were assembled. Figure 3a and Figure S12 show the SEM images of Zn plating on Ti foil in DES-4, ZC, and ZS at a capacity of 1 mAh cm⁻². In ZC and ZS aqueous electrolytes, large and non-uniform zinc flakes with hexagonal shape can be observed on the Ti foil. In practical ZIBs, such large flakes would penetrate the separator and cause short circuit.^[40] In contrast, much smaller and more uniform Zn flakes grow on the Ti foil in DES-4. Figure 3b presents the Coulombic efficiency (CE) of Zn plating/stripping at a current density of 1 mA cm⁻² and capacity of 1 mAh cm⁻². With ZC and ZS electrolytes, the CE of TillZn cell fluctuates with a relatively low average value of ~93.9 % and ~90.1 %, respectively, which could be ascribed to the concurrent side reactions, such as hydrogen evolution.^[41] In contrast, the cell with DES-4 electrolyte manifests a much more stable and higher average CE of 99.7 %. Under the same conditions, the TillZn cells with DES-1, DES-2, and DES-8 also deliver higher average CE than those with ZC

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Figure 3. (a) SEM image of Zn plated on Ti foil at 1 mAh cm⁻² though the Ti||Zn cell with DES-4 electrolyte; (b) Coulombic efficiency of Zn plating/stripping with DES-4, ZC, and ZS at 1 mA cm⁻² and 1 mAh cm⁻²; galvanostatic Zn plating/stripping in Zn||Zn symmetrical cells with (c) DES-4 and ZS electrolytes at 0.5 mA cm⁻² and 0.5 mAh cm⁻² and (d) DES-4 electrolyte at 1 mA cm⁻² and 1 mAh cm⁻²; (e) comparison of eutectic electrolytes for ZlBs. Radar plots: the properties of various eutectic electrolytes. The values (distances from the center) range from 0 to 5, where 5 presents the best property, 0 means the worst property.

and ZS electrolytes (Figure S13 and S14). Therefore, it is safe to conclude that the DES electrolytes are able to enable more reversible Zn plating/stripping than conventional ZC and ZS aqueous electrolytes. Nevertheless, due to the relatively sluggish ion diffusion kinetics caused by the high viscosity and large size of $[ZnCl(EG)]^+$, $[ZnCl(EG)_2]^+$, and $ZnCl_4^2$ - complex ions, the polarization voltage in DES is higher than those in ZC and ZS (Figure S15 and S16).^[42]

To explore the stability of Zn anode, symmetrical Zn||Zn cells were fabricated with DES, ZC and ZS electrolytes. At a capacity of 0.5 mAh cm⁻² and current density of 0.5 mA cm⁻², the cell with DES-4 exhibits a hysteresis voltage of ~55 mV and an ultralong cycle life of 2000 h, which is about 16.6 and 28.5 times to those with ZS (~120 h) and ZC (~70 h), respectively (Figure 3c). Under the same conditions, the cells with DES-1, DES-2, and DES-8 also show an excellent stability (640 - 1000 h) (Figure S17a-c). Notably, at a higher capacity of 1.0 mAh cm⁻² and current density of 1.0 mA cm⁻², the DES-4 enables a more stable cycle life of 3200 h (Figure 3d). The results indicate that the DES electrolyte can enable highly reversible Zn plating/stripping and thus excellent cycling stability, which lays the foundation for developing long cycle-life ZIBs. Compared with other water-free and water-involved eutectic electrolytes,[24,43-46] the DES-4 manifests obvious merits in ESW, Zn anode stability, and cost (Figure 3e, Figure S18, and Table S1). Although the DES-4 shows a lower ionic conductivity than water-involved eutectic electrolytes (Zn(ClO₄)₂·6H₂O-SN and Zn(ClO₄)₂·6H₂O-SL), the ionic conductivity of DES-4 (1.15 ms cm⁻¹) is sufficient for practical ZIBs,^[21] and it is better than those of water-free eutectic electrolytes.

To explore the compatibility of Zn anode in the DES and aqueous ZS electrolyte, the Zn plating process was monitored by in-situ optical microscopy (Figure 4a, 4b, Video S1, and S2). The cells were constructed with transparent glass window for optical observation (Figure S19). In conventional aqueous ZS electrolyte. Zn protrusions start to form randomly on the surface of Zn plate after 10 mins plating, and they grow into tree-like Zn dendrite in the subsequent 20 mins. In contrast, the Zn plate in DES-4 presents a relatively smooth surface without visible dendrite in the whole plating (30 mins) process. SEM images of the Zn anode after 50 plating/stripping cycles are also collected. In ZC, and ZS electrolytes, rough and flake-like dendrites fully cover the surface of Zn plate (Figure S20), while in DES-4 electrolyte, a dendrite-free smooth surface is observed. In addition, the DES-1, DES-2, and DES-8 eutectic electrolytes also realize dendrite-free Zn anode (Figure S17d-f).

X-ray photoelectron spectroscopy (XPS) spectra of the Zn anode after 50 plating/stripping cycles were collected to reveal the reason for dendrite-free Zn anode in DES electrolytes (Figure S21). The Cl 2p spectra of Zn plate after cycling in DES-4 (Figure 4c) presents two chlorine species, inorganic chlorine (Cl-Zn) and organic chlorine (Cl-C). After 600 s Ar⁺ sputtering, the two species still exist. In the C 1s spectrum (Figure S22), signals for organic C-Cl and EG can be detected, suggesting that EG molecules could be absorbed on the surface of Zn anode. Energy dispersive spectrometer (EDS) mappings of the Zn anode after plating/stripping in DES-4 show the uniform

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Figure 4. *In-situ* observation of Zn plating in Zn||Zn cells with (a) aqueous ZS electrolytes, and (b) DES-4 by optical microscopy (the current density is 5 mA cm⁻² and the images are collected at the Zn-electrolyte interface region); (c) Cl 2p XPS spectra of the SEI formed on Zn anode after 50 cycles in DES-4 (current density: 0.5 mA cm⁻²; capacity: 0.5 mAh cm⁻²); (d) schematic illustrations of Zn plating/stripping in aqueous electrolytes (top) and DES-4 (bottom).

distribution of Zn, Cl, O, and C (Figure S23). The above results indicate the formation of a stable Cl-rich organic-inorganic hybrid SEI on the surface of Zn anode in DES-4. The dissociation-reduction of $[ZnCl(EG)]^*$ and $[ZnCl(EG)_2]^*$ cations may play a significant role in the formation of the stable Cl-rich organic-inorganic hybrid SEI, which in turn contribute to the dendrite-free feature of Zn anode in DES-4.

Electrochemical impedance spectroscopy (EIS) was performed to detect the Zn-electrolyte interface stability (Figure S24). The charge-transfer resistance of symmetric Zn||Zn cells using ZC and ZS electrolytes experiences a sharp increase from the 1st cycle to 50th cycle. In contrast, the charge-transfer resistance is much more steady in DES-4. The results indicate that a stable Zn-electrolyte interface can be obtained in DES-4, which may stem from the stable Cl-rich SEI. Although the initial charge-transfer resistance of the cell in DES-4 is a bit higher than those in ZC and ZS electrolytes owing to the slightly larger viscosity of DES-4, it is beneficial to increase the Zn deposition potential for dense Zn deposition (Figure S25).^[39]

The difference in Zn plating/stripping behavior can be ascribed to the different chemical makeup, especially the solvation structures of aqueous electrolyte and DES (Figure 4d). In aqueous electrolyte, the Zn^{2+} is coordinated with six water molecules to form $[Zn(H_2O)_6^{2+}]$. During Zn plating, the desolvated and free water molecules may undergo hydrogen

evolution reaction (HER) *via* deprotonation process. The generation of H₂ bubbles, formation of by-products, and corrosion of Zn anode by the weak acidic electrolyte would cause the uneven distribution of electric field on the Zn anode, eventually leading to Zn dendrite accumulation.^[47] In DES-4, the EG molecules participate in the Zn²⁺ solvation structure, forming [ZnCl(EG)]⁺ and [ZnCl(EG)₂]⁺ cations. During the initial Zn plating, the dissociation-reduction of complex cations enables the formation of a Cl-rich organic-inorganic hybrid SEI. The stable SEI acts as a protective layer to mediate the Zn²⁺ flow for uniform Zn plating and complete Zn stripping, leading to a high average CE (99.7%).

Electrochemical Performance of PANI||Zn Cells in Eutectic Electrolytes

To explore the efficacy of eutectic electrolytes, ZIBs composed of Zn anodes and PANI cathodes were assembled. XPS spectra of the PANI cathode were collected to investigate the charge/discharge mechanism. During discharge, the appearance of Zn signal in the PANI cathode indicates the Zn²⁺ insertion (Figure S26 and Figure S27a). During charge, signals for CI-Zn are detected, suggesting the insertion of ZnCl₄²⁻ species in PANI cathode (Figure S26 and S27b). CV curves of the PANI||Zn cells with DES-4 electrolyte show two pairs of

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Figure 5. Electrochemical performance of PANI||Zn cells: (a) CV curves of the PANI || Zn cell with DES-4 electrolyte at a scan rate of 5 mV s⁻¹; (b) charge/discharge curves of the PANI||Zn cells with DES-4 and ZS electrolytes at 0.1 A g⁻¹; cycling performances of the cells with DES-4 and ZS electrolytes at (c) 0.1 A g⁻¹ and (d) 2 A g⁻¹; (e) rate performances at various current densities of 0.05 A g⁻¹ to 1 A g⁻¹. Electrochemical performance of PANI||DES-4||Zn pouch cells: (f) digital photo showing the open-circuit voltage; (g) cycling performance of PANI||DES-4||Zn pouch cell at 0.05 A g⁻¹. (h) pouch cells powering LEDs; (i – j) nail test; (k – I) cut test.

redox peaks at around 0.5/1.45 V and 1.35/2.2 V, respectively (Figure 5a). Compared to DES-4, the cells with DES-1, DES-2, and DES-8 electrolytes display much weaker redox peaks (Figure S28), which could be attributed to the relatively low ionic conductivity. With the DES-4 electrolyte, except for the nonoverlapping of the first loop due to SEI formation, the CV profiles overlap quite well, indicating the high reversibility. To find out an appropriate voltage window for the PANI||Zn cells with DES electrolyte, galvanostatic (0.5 A g-1) discharging/charging tests were performed in two voltage windows of 0.5 - 1.45 V and 0.5 - 2.2 V (Figure S29). When cycled at 0.5 - 1.45 V, the cell manifests high CE, good reversibility, and excellent stability. In contrast, when cycled at 0.5 - 2.2 V, the cell shows relatively low CE and poor reversibility. The poor electrochemical performance in wide operating voltage window is caused by the decomposition of PANI at high voltage.[48] Although the PANI||Zn cells with ZS electrolytes shows a slightly wider operating voltage window (0.5 - 1.6 V), the cells with DES-1, DES-2, and DES-4 electrolytes demonstrate significantly higher capacity as well as higher average discharge voltage (Figure 5b and Figure S30). Notably, PANI||Zn cell with ZC cannot work properly due to the corrosion (Figure S31).[49]

At 0.1 A g⁻¹, the cyclability and CE of the PANI||Zn cells with various DES outperform those of the cells with ZS electrolyte (Figure 5c and Figure S32). Especially, the cell with DES-4 electrolyte delivers the highest capacity (~180 mAh g⁻¹). Besides, at 2 A g⁻¹, the cell with DES-4 electrolyte demonstrates a high capacity retention of ~78% over 10,000 cycles (Figure 5d and Figure S32). In sharp contrast, the capacity of the cell with ZS electrolyte decays from 54 to 15 mAh g⁻¹ after 3700 cycles (capacity retention < 40%). In addition, the PANI||Zn cells with various DES electrolytes also manifest better rate performance (from 0.05 to 1.0 A g⁻¹) than the cell with ZS electrolyte (Figure 5e and Figure S34).

The excellent electrochemical performance of PANI||Zn coin cells with DES electrolytes can be transferred to PANI||Zn pouch cells. The cells can be easily assembled in atmospheric environment. The assembled PANI||DES-4||Zn pouch cell (4cm \times 4cm) has an open circuit voltage of 1.076 V (Figure 5f). At a current density of 0.05 A g⁻¹, the pouch cell shows a reversible capacity of 130 mAh g⁻¹ and demonstrates negligible capacity decay over 50 cycles (Figure 5g and Figure S35). The pouch cells can power the LEDs, demonstrating its effectiveness (Figure 5h). To evaluate the safety, the pouch cells were subjected to nail test and cut test (Video S3). Interestingly, after

piercing and several cuts, the pouch cell can still work without short circuit or burning, demonstrating the excellent safety of such cells (Figure 5i - 5I). From the electrochemical tests, it can be concluded that the optimized eutectic electrolyte (DES-4) can enable not only decent ZIB electrochemical performances but also excellent safety for practical applications.

Conclusion

In summary, a novel eutectic electrolyte composed of EG and ZnCl₂ was successfully developed, achieving dendrite-free Zn anode and long-lifespan ZIBs. Optimizing the ZnCl₂/EG molar ratio could enable a eutectic electrolyte (DES-4) with maximized ion conductivity. The EG molecules participate in the solvation of Zn²⁺, leading to the formation of [ZnCl(EG)]⁺ and [ZnCl(EG)₂]⁺ complex cations. The dissociation-reduction of complex cations enable the formation of a CI-rich organic-inorganic hybrid SEI, which realizes highly reversible and ultra-stable 7n plating/striping. With the optimized DES-4 eutectic electrolyte, the PANIIIZn cell manifests excellent cycling stability and the assembled pouch cell also demonstrates stable high capacity as well as excellent safety. This work will promote the development of low-cost eutectic electrolytes for large-scale energy storage and advance the practical application of ZIBs.

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RESEARCH ARTICLE

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The brand new eutectic electrolyte consisting of EG and ZnCl₂ has a unique solvation structure and could enable the formation of a Cl-rich organic-inorganic hybrid solid electrolyte interphase film on Zn anode, realizing highly reversible Zn plating/stripping.