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Ammonium enables reversible aqueous Zn battery chemistries by tailoring the interphase

Graphical abstract



Highlights

- A new aqueous Zn electrolyte with ammonium-TFSI salt is demonstrated
- Zn reversibility is enhanced by suppressing hydrogen evolution and dendrite growth
- The Zn interphasial chemistries are investigated via modeling and experiments
- The interphase chemistry allows a $Na_2V_6O_{16}\cdot$ 1.63H_2O/Zn cell with >1,000 cycle lifetime

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In brief

Aqueous electrolyte-based rechargeable Zn metal batteries have emerged as a promising energy storage solution for grid storage applications, but their commercialization has been hindered by the irreversibility of Zn anode cycling. It remains unclear how electrolyte structure, transport, and interphasial chemistries affect Zn reversibility. Here, we demonstrate reversable potential by experimentally examining structure and transport in ZnTFSI₂ ammonium-TFSI dual-salt aqueous electrolytes. Reaction pathways toward interphasial chemistry formation (including ZnF₂, ZnCO₃, and fluoro-polymeric species) are illustrated through advanced modeling.





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Ammonium enables reversible aqueous Zn battery chemistries by tailoring the interphase

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SCIENCE FOR SOCIETY The wide adoption of renewable energy requires reliable and affordable storage options like batteries. Aqueous rechargeable zinc (Zn) metal batteries (RZMBs) are gaining popularity for grid-scale applications due to their low cost, high energy density, safety, and reduced dependence on unsustainable critical metals. However, the commercialization of RZMBs is hindered by unfavorable reactions during battery operation between the Zn electrode and electrolytes. These reactions can rapidly exhaust electrolytes, the media that connect electrodes for converting stored energy into electricity, via building up uneven Zn microstructures and eventually result in battery failure. To overcome this problem, we report an aqueous electrolyte design that enables the formation of a stable interphase on the Zn electrode—a layer that inhibits unfavorable reactions. Our examination of the interphase formation mechanism offers a guide for better electrolyte design to extend Zn electrode lifetime and enhance RZMBs' cyclability, contributing to the development of more reliable and stable energy-storage options.

SUMMARY

Aqueous rechargeable Zn metal batteries (RZMBs) are promising candidates for coupling with intermittent renewable energy sources to realize a carbon-neutral energy transition. However, irreversible issues of Zn metal anodes and a poor understanding of the interphasial chemistry severely limit the viability of RZMBs. Here, we demonstrate that the addition of an asymmetric alkylammonium cation, trimethylethyl ammonium-bis(trifluoromethylsulfonyl)imide (Me₃EtN-TFSI), as a supporting salt into a traditional aqueous electrolyte results in improved Zn anode reversibility. Performance improvements are attributed to the formation of interphasial chemistries including ZnF_2 , $ZnCO_3$, and fluoro-polymeric species, especially when combined with CO_2 . By tailoring the Zn interphase, this electrolyte exhibited excellent stability in $Na_2V_6O_{16} \cdot 1.63H_2O$ (HNVO)/Zn full cells, with a high specific capacity sustained (>100 mAh g⁻¹) over 1,000 cycles at 300 mA g⁻¹. A combination of experiments and modeling showed the importance of tuning interphases to further improve Zn reversibility and RZMBs.

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INTRODUCTION

The transition toward a carbon-neutral energy future requires extensive deployment of renewable energy. Due to the intermittent nature of many renewable sources such as solar, wind, or ocean waves, achieving significant levels of integration requires reliable and affordable energy-storage systems on the utility scale of gigawatts.^{1,2} Lithium-ion batteries (LIBs) are currently the predominant chemistry employed for electric vehicles (EVs) and grid-scale battery storage due to existing manufacturing capacity, declining costs, and a favorable balance of achievable power and energy densities.³ However, the supply-chain risk of LIBs induced by rare elements (e.g. lithium, cobalt, and nickel) available in earth crust as well as geopolitical and ethical concerns have become increasingly pronounced.⁴ This, coupled with the continuing rapid growth in demand from other technology sectors (e.g., mobile electronics), necessitates the development of complementary battery chemistries to avoid potential resource crises in the future,^{5,6} especially when the available resources are used in LIBs for EV and grid technology.⁷ Rechargeable Zn metal batteries (RZMBs)8-11 stand out as a potential complementary chemistry to LIBs because of the unique advantages of Zn metal as a negative electrode of high volumetric capacity (5,854 mAh cm⁻³),¹² relatively high abundance,¹³ and natural compatibility with aqueous electrolytes. However, Zn metal suffers from irreversible plating/stripping in aqueous electrolytes, which leads to Zn dendrite formation and growth in aqueous electrolytes and hydrogen evolution from water. Specifically, the dendrites could penetrate the separator and short a cell immediately. Hydrogen evolution leads to electrolyte dry out, disabling a cell in addition to swelling a cell excessively. A combination of these issues associated with Zn irreversibility severely impedes the practical deployment of aqueous RZMBs.14-18

Recent efforts to improve Zn metal reversibility in aqueous electrolytes have achieved varying successes using modified electrolyte formulations.¹⁹⁻²¹ Wang et al.²⁰ and Zhang et al.²¹ suppressed water decomposition by increasing the salt concentration (e.g., lithium bis(trifluoromethylsulfonyl)imide [LiTFSI], ZnCl₂) to extreme levels in order to alter the Zn solvation-sheath structure. Bayaguud et al.²² demonstrated the use of tetrabutylammonium sulfate as an electrolyte additive in 2M ZnSO₄ aqueous electrolytes to impede dendrite growth by modifying the Zn cation deposition direction on the interphase. Yang et al.²³ prevented Zn dendrite growth and improved Zn plating/ stripping Coulombic efficiency (CE) by forming an aqueous Zn(ClO₄)₂-succinonitrile (SN) eutectic electrolyte. This system forced the replacement of water molecules by SN in the Zn solvation sheath to minimize water decomposition. However, the relationship between electrolyte composition modification and solid-electrolyte interphase (SEI) formation is poorly understood despite its importance as the bridge linking bulk electrolytes and electrodes that determines the battery electrochemical performance.24,25

Here, we explored the effect of ammonium bis(trifluoromethylsulfonyl)imide (Me₃EtN-TFSI; Figure S1) synthesized in our lab as a supporting salt on the traditional, mildly acidic aqueous $Zn(TFSI)_2$ electrolyte.²⁶ The 4m $Zn(TFSI)_2$ electrolyte was selected as an advanced baseline over those diluted baselines

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(1m Zn(TFSI)₂, 1M ZnSO₄, etc.) usually adopted in literature because it provides a more rigorous and stringent standard of comparison than electrolytes of diluted salt concentrations.^{26,27}

Our study revealed that this system generates a unique SEI on the anode consisting of polymeric species and ZnF₂, which enhanced Zn reversibility by suppressing both hydrogen evolution and dendrite formation/growth. Spectroscopic and modeling results also suggested that dissolved CO₂ led to the formation of ZnCO₃ as a supporting species in the SEI, which extended the Zn/Zn symmetric-cell lifetime. This illustrates the process of SEI formation and its benign effect on Zn reversibility. The positive effects of ammonium cation were further demonstrated in a Na₂V₆O₁₆ · 1.63H₂O (HNVO)/Zn full-cell chemistry, which retained a high specific discharge capacity (>100 mAh g⁻¹) even after 1,000 cycles at 30°C.

RESULTS AND DISCUSSION

Bulk and transport properties

Liquid electrolyte properties were evaluated using molecular dynamics (MD) simulations combined with Fourier transform infrared (FTIR) spectroscopy. MD-simulation results suggest that in an electrolyte consisting of 4m Zn(TFSI)₂ + 4m Me₃EtN-TFSI, Zn²⁺ is coordinated by six oxygen atoms primarily contributed from water rather than TFSI⁻ anions (Figure S2), which is consistent with a high degree of salt dissociation. A rather uniform distribution of room temperature ionic liquid (RTIL) and zinc hexahydrate solvates $Zn^{2+}(H_2O)_6$ was observed (Figure 1A). A closer examination, taken around a Me₃EtN⁺ cation (within 2.5 Å), reveals that each Me₃EtN⁺ cation is loosely bound to 3 TFSI⁻ anions, forming a transient negatively charged cluster (Figure 1B) that favorably interacts with positively charged Zn²⁺(H₂O)₆ located nearby. Formation of such negatively charged [Me₃EtN(TFSI)₃]²⁻ and Zn²⁺(H₂O)₆ assists the dissolution of Me₃EtN-TFSI in Zn containing an aqueous electrolyte, considering that Me₃EtN-TFSI is barely soluble in neat water.²⁸ In the FTIR spectra, the broad O-H stretching band is a feature of particular interest (Figure 1C) since it indicates the degree of hydrogen bonding. According to previous work, the broad O-H stretching band (Figure 1C) can be deconvoluted to three populations of water molecules (Figure S3) based on the strength of the hydrogen-bonding network around²⁹⁻³¹ "network water" $(\sim 3,205 \text{ cm}^{-1})$, "intermediate water" $(\sim 3,433 \text{ cm}^{-1})$ and "multimer water" (\sim 3,560 cm⁻¹). Generally, more extensive hydrogen bonding leads to longer O-H stretching and a shift to lower wavenumbers. A quantitative deconvolution on these three components (Figure S3) shows that the addition of 4m Me₃EtN-TFSI continuously increased the fraction of multimer water, which suggests that the hydrogen-bonding network is further disrupted compared with an aqueous 4m Zn(TFSI)₂ baseline electrolyte. The temperature dependences of bulk conductivity for these selected aqueous electrolytes are shown in Figure 1D. Even with high concentrations of the supporting salt (4m Me₃EtN-TFSI), this aqueous electrolyte exhibits an approximate conductivity of 10 mS cm⁻¹ with a Zn²⁺ transference number of 0.45 (Table S1) at 25°C, which is comparable with that of the standard carbonate formulation (1m LiPF₆ in ethylene carbonate/ethyl methyl carbonate [EC/EMC 3/7 w/w]) widely used in LIBs and state-of-the-art Zn electrolytes (Table S2).





Zn metal anode reversibility

The electrochemical stability window of these electrolytes was measured using cyclic voltammetry (CV) with stainless steel (SS) as the working electrode (Figure 2A). Compared with the baseline 4m Zn(TFSI)₂ electrolyte, the addition of 4m Me₃EtN-TFSI reduced the onset potential of parasitic reactions (e.g., hydrogen evolution) from \sim 0.6 down to \sim 0.2 V (versus Zn/Zn²⁺), while the onset for major Zn plating occurred at around -0.14 V (Figure 2B). The anodic stability was also improved in the presence of 4m Me₃EtN-TFSI, as shown by the suppression of parasitic reaction (e.g., oxygen evolution) currents (Figure 2C). Benefitting from these effects, if using 0.1 mA cm⁻² as a threshold, a stable electrochemical window of \sim 2.48 V (-0.14-2.34 V versus Zn/Zn²⁺) was achieved in the electrolytes due to the presence of 4m Me₃EtN-TFSI as the supporting salt. In addition to hydrophobicity introduced by the supporting salt (Figures 2D-2E), this expanded electrochemical stability window could be mainly ascribed to a change in SEI composition resulting from the addition of Me₃EtN-TFSI, which is discussed in the next section.

To evaluate the electrolytes' stability in a longer time frame and in an environment closer to actual Zn-battery operation, Zn|Zn (100 μ m) symmetric cells were tested under galvanostatic conditions (Figures 2F, 2G, S4, and S5) with the most commonly published testing parameters (0.5 mA cm⁻², 0.5 mAh cm⁻², and 1 mA cm⁻², 1 mAh cm⁻² per cycle) at room temperature. For these cells, electrolyte preparation and cell fabrication were carried out in an Ar-filled glovebox (to suppress CO₂). As shown in Figures 2F and 2G, the addition of 4m Me₃EtN-TFSI noticeably suppressed Zn dendrite formation/growth and extended the cell-cycle lifetime (~270 h; Figure 2G) compared with a lower concentration of Me₃EtN-TFSI (~190 h; Figure S5) and the 4m Zn(TFSI)₂ baseline (~100 h; Figure 2F), despite its trivial effect on Zn plating/stripping CE (Figure S6).

Figure 1. Bulk and transport properties of Zn aqueous electrolyte systems

(A) A snapshot of the MD simulation box of aqueous $4m \text{ Zn}(\text{TFSI})_2 + 4m \text{ Me}_3\text{EtN}-\text{TFSI}$ highlighting Zn atoms (purple) and Me}_3\text{EtN}^+ cations (in green); (B) showing only Me}_3\text{EtN}^+ first solvation shell (within 2.5 Å) with TFSI⁻ anions (C) FTIR spectra of OH stretching band.

(D) Temperature-dependent conductivities for selected electrolytes from impedance measurements. Colors: hydrogen (white), nitrogen (blue), carbon (cyan), oxygen (red), fluorine (pink), sulfur (yellow), and zinc (purple).

Mechanism and Zn surface analysis

X-ray photoelectron spectroscopy (XPS; Figures 3A and 3B, F 1s) and transmission electron microscopy (TEM; Figure 3C) were used in combination with density functional theory (DFT; Figure 3D) calculations to investigate the underlying mechanism for improvements from the perspective of interphasial chemistry, which is regarded as one of the predominant factors dictating electrode reversibility and the subsequent cell lifetime.²⁵ Results

from this investigation expose that the interphase is composed of chemical ingredients from both Me_3EtN^+ cation and $TFSI^-$ anion decomposition.

DFT calculations have shown that the Me_3EtN^+ cation is susceptible to nucleophilic attack from base (A⁻) generated by localized water splitting (OH⁻) or TFSI⁻ anion reduction (e.g., CF_3^-), which forms an amine and ethylene through a Hofmann-type elimination.³² An additional mechanism is highlighted in Figure 3D (with additional details in Figure S7), where the native ZnO film deprotonates Me_3EtN^+ to generate the amine and ethylene with a reaction free energy of -43.5 kJ mol⁻¹. This chemical process is independent of hydrogen evolution or anion decomposition and, as shown below, plays an integral role in the formation of SEI.

Electrochemical evolution of the amine and ethylene has been considered previously as well,33 though the reduction potential computed here is -1.16 V versus Zn/Zn²⁺ (Figure S8), meaning that only the chemical generation through base attack or surface deprotonation are relevant on Zn. Amines formed through these two routes readily react with acid species such as carbonic acid and bicarbonate, which were derived from the dissolved CO₂, and form ZnCO3 as a supportive species in the SEI (reaction energy of -28.3 kJ mol⁻¹ for conversion of carbonic acid to bicarbonate; Figure S7).^{34,35} In support of this proposed mechanism, we deliberately prepared the electrolyte and subsequently fabricated cell in a dry room (dew point -30°C or better) instead of an Ar-filled glovebox so that more CO₂ could be dissolved in the electrolyte. Indeed, more pronounced ZnCO3 features were observed on the surface of Zn (Figure S9), which is consistent with previous work.³² Considering the higher shear modulus of ZnCO₃ (49GPa) compared with Zn (37GPa), addition of this interphasial component could further mechanically suppress Zn dendrite growth by resisting Zn volume change (Figure S10).







Figure 2. Electrochemical testing and Zn metal anode reversibility

(A) Overall electrochemical stability window testing results for selected electrolytes during second cycle.

(B and C) Enlarged view of the regions outlined near cathodic and anodic regions, respectively.

(D and E) Images of droplets of (D) $4m Zn(TFSI)_2$ (contact angle: 55°) and (E) $4m Zn(TFSI)_2 + 4m Me_3EtN-TFSI$ (contact angle: 60°) on a Zn electrode surface. (F and G) Galvanostatic Zn plating/stripping using a Zn|Zn(100 μ m) symmetric cell setup at 25°C with a current density and areal capacity of 0.5 mA cm⁻² and 0.5mAh cm⁻² per cycle for (F) $4m Zn(TFSI)_2$ in H₂O and (G) $4m Zn(TFSI)_2 + 4m Me_3EtN-TFSI$ in H₂O.

Fluorinated interphasial contributions were also observed in XPS (Figures 3A and 3B) and could be ascribed to decomposition of the TFSI⁻ anion on the Zn electrode. There are two suspected possible origins for the anion decomposition in aqueous electrolytes: (1) direct reduction of the anion and/or (2) chemical decomposition involving OH⁻ ions generated from hydrogen evolution at the electrode surface.^{26,36} In the current study, we focus on the decomposition resulting from electrochemical reduction of TFSI⁻ at the anode surface (Figure 3D; see additional details in Figures S11 and S12). Figure S11 is largely illustrative and features an overly simplified cluster model that generally overestimates reduction potentials with respect to the more realistic first solvation-shell model in Figure S12. Thus, we focus on the data presented in Figure S12 in which reduction of [ZnTFSI(H₂O)₅]⁺ clusters occurred at potentials of 0.30, -0.14, and -0.15 V (versus Zn/Zn²⁺) for S-N, C-S, and C-F cleavages, respectively. The reduction potential computed for S-N bond cleavage in this hydrated cluster is comparable to the \sim 0.3 V potential computed for the hydrogen evolution reaction (HER) from [Zn(H₂O)₆]²⁺ clusters. Hydrogen evolution in [ZnTFSI(H₂O)₅]⁺ clusters is also predicted to occur at ~0.3 V versus Zn/Zn²⁺, suggesting that the net +1 charged cluster remains susceptible to HER. This leads to simultaneous and continuous parasitic hydrogen evolution and SEI growth, leading to a compromised cycle life in the 4m Zn(TFSI)₂ electrolyte. Clearly, the formation of ZnCO₃ accelerated by the amine released from ammonium decomposition is essential to early SEI growth and improves the overall cycle life.

We subsequently considered the reduction process coupled with binding to ethylene generated by ammonium decomposition, which forms a polyfluorinated species. In each case, the reactions are highly exergonic (Figures S11 and S12), indicating that shifting the radical to \cdot CH₂ may stabilize the reduction products. Figure S13 shows one of the possible polyfluorinated species, in which a ZnF₂ is also produced. TEM analysis (Figure 3C), complemented with energy-dispersive X-ray spectroscopy (EDX; Figure S14), of the Zn anode surface after cycling in Zn symmetric cells confirmed the existence of this interphase. Based on characterization and DFT calculations, a combination of polymeric species, ZnF₂, and ZnCO₃ are expected to provide a protection layer to temper hydrogen evolution and Zn dendrite growth.

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Full-cell demonstration

Finally, the performance of the 4m Zn(TFSI)₂ + 4m Me₃EtN-TFSI aqueous electrolyte was assessed in a RZMB full-cell chemistry with an HNVO cathode, which only serves as a test platform for the new electrolytes here. For these builds, the electrolytes and cells were prepared in an Ar-filled glovebox. Figure 4 shows CEs (Figure 4A) and the corresponding specific discharge capacity (Figure 4B) versus cycle number for HNVO|Zn (100 µm) cells with different electrolytes tested at a rate of 300 mA g⁻¹ (based on HNVO mass) between 0.2 and 1.6 V at 30°C. Compared with the 4m Zn(TFSI)₂ baseline, the 4m Zn(TFSI)₂ + 4m Me₃EtN-TFSI aqueous electrolyte achieved better cycling stability without cell shorting and a high specific discharge capacity (>100 mAh g^{-1}), even after 1,000 cycles, which is comparable with state-of-theart Zn-battery systems (Table S3). In contrast, 4m Zn(TFSI)₂ displayed poor capacity retention and exhibited "roll-over" failure behavior after ~200 cycles, which is attributed to the severe

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Figure 3. Proposed mechanism on Zn surface chemistry

(A and B) XPS spectra of F 1s for Zn metal at zero state of charge in Zn|Zn symmetric cells with (A) $4m Zn(TFSI)_2$ in H₂O and (B) $4m Zn(TFSI)_2 + 4m Me_3EtN-TFSI$ in H₂O after 80 h of cycling (0.5 mA cm⁻², 0.5 mAh cm⁻²) at room temperature.

(C) TEM image for Zn metal interphase obtained from Zn|Zn symmetric cells with $4m Zn(TFSI)_2 + 4m Me_3EtN-TFSI$ in H₂O after 80 h of cycling (0.5 mA cm⁻², 0.5 mAh cm⁻²) at room temperature.

(D) Me_3EtN^+ cation decomposes in the presence of a strong base (A⁻, e.g., OH⁻ or CF₃⁻). The amine can react with dissolved CO₂ to form ZnCO₃ finally. The TFSI⁻ anion decomposes through either C–F breaking or S–N breaking. Then, the decomposed species scavenges ethylene derived from the Me_3EtN^+ cation to form a \cdot CH₂ radical-containing species for further precipitating of a protective polymeric species as well as a ZnF₂-rich SEI. Reaction energies and additional details are given in Figures S7, S8, and S11–S13. Colors: hydrogen (white), nitrogen (blue), carbon (gray), oxygen (red), fluorine (green), sulfur (yellow), and zinc (blueish gray).

Zn dendrite formation reported in previous work.²⁶ Based on these observations, the full-cell results were consistent with the dendrite suppression benefit of Me₃EtN-TFSI shown in Figure 2.

Conclusion

In this work, we explored the effects of an asymmetric ammonium cation Me₃EtN⁺ on Zn reversibility in a mildly acidic, Zn(TFSI)₂-based aqueous electrolyte. In addition to observing an expanded electrochemical stability window and high conductivity in these hybrid electrolytes, we examined the underlying mechanism from the interphasial chemistry perspective via spectroscopic and computational methods. These efforts revealed that the presence of the Me_3EtN^+ cation supports formation of new interphase chemistry in addition to the typical TFSI⁻ anion decomposition products. Thanks to this modified SEI constructed upon species polymeric and inorganic ingredients ZnF_2 and $ZnCO_3$, hydrogen evolution and Zn dendrite formation/growth were effectively suppressed, which ensures Zn reversibility and extends the cell-cycle lifetime. The electrolyte was further demonstrated in an HNVO/Zn full cell, where the supporting salt electrolyte far outperformed the baseline system and achieved an excellent cycling stability over 1,000 cycles with an average CE of ~99.9%. Complementing previous work with the

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OTf-based salts, these results provide a comprehensive and atomistic insight into the interfacial electrochemistry and ways to improve Zn anode reversibility by tailoring both anion and cation chemistry, thus opening a new avenue to design highly reversible electrolytes for supporting Zn or other multivalent metal anodes.

EXPERIMENTAL PROCEDURES

Resource availability

Lead contact

Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Dr. Kang Xu (conrad.k. xu.civ@army.mil).

Materials availability

The Me_3EtN -TFSI salt generated in this study will be made available on request, but we may require a payment and/or a completed materials transfer agreement if there is potential for commercial application.

Data and code availability

All original data and code have been deposited at Mendeley Data: https://data. mendeley.com/datasets/5k89wwj4v9/1 (https://doi.org/10.17632/ 5k89wwj4v9.1) and are publicly available.

Materials preparation

Bis(trifluoromethanesulfonyl)imide (HTFSI; >99%) was purchased from TCI. Zinc bis(trifluoromethylsulfonyl)imide (Zn(TFSI)₂) hydrate was synthesized based on a previous report.¹ The water content was determined by using the Karl Fischer method in order to make further aqueous electrolytes with ac-

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Figure 4. HNVO|Zn full-cell performance with the baseline 4m Zn(TFSI)₂ in H₂O (black) and 4m Zn(TFSI)₂ + 4m Me₃EtN-TFSI in H₂O (red) electrolytes at 30° C

(A and B) CEs (A) and specific discharge capacity versus cycle number (B) for selected electrolytes tested with the HNVO(\sim 3 mg cm⁻²)|Zn(100 µm) cell setup at 300 mA g⁻¹.

curate salt concentrations. Trimethylethylammonium bis(trifluoromethylsulfonyl)imide (Me3EtN-TFSI) was prepared via a two-step reaction. In the first step, 58.51 g diethylammonium (Sigma-Aldrich), 72.06 g dimethyl carbonate (Gotion), and 50 mL methanol (Avantor) were added into a pressure reactor. Then, the pressure reactor was heated up to 120°C for 12 h with constant stirring inside. In the second step, 100 g trimethylammonium carbonate (the product of the first step) was slowly mixed with 0.5 M HTFSI aqueous solution with constant stirring to obtain the target product. 0.5 M HTFSI aqueous solution was added drop by drop until the pH became neutral. Then, reflux was carried out by mixing Me₃EtN-TFSI with \sim 10 g active carbon in an acetonitrile solution environment for 2 h to remove residue impurity of Me₂EtN-TFSI. Active carbon was removed by filtering the mixture afterward. The final pure product was obtained by drying the filtered mixture at 60°C under vacuum for 24 h. Figure S1 shows nuclear magnetic resonance (NMR) spectroscopy.

The electrolyte solutions were prepared by dissolving selected salts in de-ionized water (18 k Ω) according to different ratios, either in an Ar-filled glovebox or a dry room (dew point -30° C or better). The Zn foil (0.1 mm thick, 99.994%) electrode was

obtained from Alfa Aesar. Na₂V₆O₁₆ \cdot 1.63H₂O (HNVO) was selected as the active material in the positive electrode and was synthesized according to Silva.² The electrode slurries were prepared by mixing HNVO with Timical super C45, MTI) and polyvinylidene difluoride (PVDF; Kynar) in *N*-methylpyrrolidone (NMP; Alfa Aesar, >99%) solvent based on a weight ratio of active material:C45:PVDF of 70:20:10 and then were coated on a Ti current collector. The electrodes were dried at 80°C (open air) for 1 h and at 60°C (under vacuum) for 12 h sequentially to fully remove the NMP. The active material mass loading was ~3 mg cm⁻² for the positive electrode.

Materials characterization

Electrochemical characterization: the Cu|Zn and Zn|Zn cells were fabricated using 2032-type coin cell sets with glass fiber (Whatman GF/F) as separator and electrolyte (150 μ L/cell) in either an Ar-filled glovebox or a dry room (dew point -30° C or better). The charge-discharge testing was conducted on these cells at room temperature using a Maccor Series 4000 cycler.

The Zn plating/stripping CE measurement method follows the protocol reported by a previous work.¹ The average CE was calculated based on the following:

$$CE = \frac{9Qc + Qs}{9Qc + Qt}$$
. (Equation 1)

Zn|Zn symmetric cells were used to analyze Zn dendrite formation under 0.5 mA cm⁻² at room temperature. Each half cycle (charge or discharge) was set to 1 h.

lonic-conductivity results of the selected electrolytes were obtained from impedance scans from 20 Hz to 2 MHz with an amplitude of 20 mV with an Agilent E4980A precision LCR meter as reported by a previous work.²⁷ A YSI 3418 cell was used as the conductivity cell to fit into a polyethylene bottle for holding

the electrolyte samples. The cell constant (0.1 cm⁻¹ nominal) was calibrated with a 100 mS cm⁻¹ standard solution. The tests were applied in a Tenney Jr. Environmental Chamber with temperature change from 60° C to -20° C then back up at 0.1° C min⁻¹ while the impedance was continuously scanned.

The contact angle between selected electrolytes and Zn metal was measured at room temperature using the sessile-drop method with a contact-angle goniometer (Rame-Hart Instruments, 250-00). A drop of electrolyte was dispensed from a syringe onto the Zn electrode surface, and a drop image was captured.

XPS testing (PHI Versaprobe III) was applied on selected Zn electrode samples prepared in an Ar-filled glovebox, rinsed with anhydrous acetonitrile (AN), and dried in an antechamber under vacuum overnight. A sealed vacuum-transfer capsule was used to transfer all samples into the XPS testing system without air/moisture contamination. Survey scan (pass energy 224 eV, step size 0.4 eV) and high-resolution scan (pass energy 55 eV, step size 0.05 eV) were recorded. XPS peak deconvolution was performed using PHI's Multipak software v.9.6 using 70/30 Gaussian/Lorentzian line shapes on a Shirley background. All collected spectra were shifted relative to the binding energy of the carbon 1s sp3 (assigned to 284.8 eV) to compensate for any surface charging off-set during the measurement.

The electrochemical stability windows of selected electrolytes solutions were evaluated via CV at a scan rate of 0.5 mV s^{-1} using a Swagelok threeelectrode cell setup at room temperature. SS was used as a working electrode, active carbon was used as a counter electrode, and Ag/AgCl was used as a reference electrode. CV measurements were performed using a single-channel Gamry Potentiostat (Reference 3000).

TEM (JOEL 2100F) images were collected for Zn interphase of Zn metal foil electrodes obtained from Zn|Zn symmetric cells at zero state of charge after 80 h cycling (0.5 mA cm⁻², 0.5 mAh cm⁻²).

Computational details: MD

MD simulations were carried out using the package LAMMPS.³⁷ The general Amber force field (GAFF)³⁸ was used to describe Me₃EtN⁺ cation and TFSI- ions. For each isolated ion, electronic structure calculations were carried out to optimize the structure at the B3LYP/6-311++g(d,p) level of theory using Gaussian09[g09]. The atomic charges were then derived based on the optimized structure by fitting the electrostatic potential surface using the restrained electrostatic potential (RESP) method.³⁹ Zn²⁺ parameters were taken from the work by Babu et al.⁴⁰ The SPC/fw water model⁴¹ was used. To approximate the effect of charge transfer and polarizability in the bulk phase, the partial charges of ions were scaled uniformly by a factor of 0.8.42 The long-range electrostatic interactions were calculated using the particle-particle particle-mesh (PPPM) method⁴³ with a real-space cutoff of 12 Å. The same 12 Å cutoff was also used for van der Waals interactions. The Nose-Hoover thermostat⁴⁴ and the extended Lagrangian approach⁴⁵ were applied to control the temperature and pressure, respectively. A time constant of 100 fs was used in both the thermostat and barostat. All simulations were carried out at 293 K. The pressure was fixed at one atmosphere in all constant-pressure simulations with isotropic volume fluctuations. A timestep of 1 fs was used. The simulation box was built up by placing proper numbers (see Table S4) of Zn²⁺, Me₃EtN⁺, TFSI⁻, and water molecules randomly in a cubic box using Packmol. 46,47 The systems were then equilibrated for 2 ns in the isothermal-isobaric (NPT) ensemble followed by a 40 ns production run in the canonical ensemble (NVT). The periodic boundary conditions were applied in all directions, and a tail correction was applied to the van der Waals interaction.48

Apparent transference-number calculation

The Zn^{2+} apparent transference number was calculated assuming no ion correlations as

$$t_{Zn^{2+}} = \frac{q_{Zn^{2+}}^2 D_{Zn^{2+}}}{\sum q_i^2 D_i},$$
 (Equation 2)

where q_i and D_i are the total charge and self-diffusion coefficient of species *i*, respectively. The self-diffusion coefficient was calculated using the Einstein relation

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$$D = \frac{1}{6} \lim_{t \to \infty} \frac{d}{dt} \frac{1}{N} \sum_{i=1}^{N} |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2,$$
 (Equation 3)

where $r_i(t)$ is the center of mass position of species *i* at time *t*, and *N* is the number of individual species. A finite system-size correction was applied using the Yeh-Hummer method^{3,4} with the calculated viscosities. The viscosity-calculation procedure was detailed in our previous publications.^{5,6}

Computational details: Reactivity and reduction potentials

PCM(acetone)/M05-2X/6-311++G(3df,3pd) DFT calculations were used to predict reaction free energies and reduction potential calculations for complexes shown in Figure S11. Reduction potentials for [ZnTFSI(H₂O)₅]⁺ clusters were sampled using the same method but with the smaller 6-31++G(2d,2p) basis set. The reaction free energies for the Hofmann-like mechanism on (ZnO)12 were also computed with the same method but using the 6-31+G(d,p) basis set.⁴⁹⁻⁵² PCM using acetone parameters was used to simulate the reduced dielectric constant conditions common to moderately to highly concentrated battery electrolytes. For the $[\text{ZnTFSI}(\text{H}_2\text{O})_5]^+$ clusters, approximately 50 unique structures were sampled and considered reductive decomposition via C-F, C-S, and S-N cleavage. As a thermodynamic quantity, only the structures resulting in the highest reduction potentials (i.e., the most stable products) for each reaction product are shown. In all cases, Gaussian 16 rev. C was used to perform the calculations in conjunction with the Atomic Simulation Environment for file generation.^{53,54} Reaction free energies are computed as differences in the free energies for the optimized structures of [products] - [reactants], and the reduction potentials were computed from free energy differences in the optimized structures of the reduced species A⁻ and initial species A via

$$\mathsf{E}^{\mathsf{red}} = -\frac{[\Delta G(\mathsf{A}^{-}) - \Delta G(\mathsf{A})]}{\mathsf{n}\mathsf{F}} - 3.68, \qquad (\mathsf{Equation}\ 4)$$

where n is the number of electrons, F is Faraday's constant, the free energies are in units of Hartree, and the 3.68 V shift reflects a shift to the Zn scale, assuming 4.44 V for the absolute potential of the standard hydrogen electrode.⁵⁵ To compute hydrogen-evolution potentials in the hydrated clusters, one of the waters was converted to OH⁻, and a separate set of PCM(acetone)/M052X/6-31++G(2d,2p) DFT calculations was performed for the H₂ molecule. All geometries were optimized. The potential is computed as in the above expression but with the addition of +1/2 Δ G(H₂) inside the brackets. In the main text, the HER potentials are reported for the Zn-hexahydrate and Zn-pentahydrate + TFSI clusters as ~0.3 V; explicitly, these are 0.27 and 0.31 V, respectively. The water that decomposes in the cluster containing TFSI⁻ is opposite the anion (viz., the Zn-O(TFSI) and Zn-OH are in the axial positions).

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at https://doi.org/10.1016/j.oneear.2022.03.012.

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AUTHOR CONTRIBUTIONS

L.M., M.A.S., T.P.P., O.B., and K.X. conceived the idea. L.M. designed the experiments. L.M., T.P.P., O.B., and K.X. directed the project. L.M. prepared most of the experimental materials and performed the material characterizations (including SEM, XPS, and TEM), electrochemical measurements, and coin-cell testing. L.C., M.H., J.T.F., and C.W. performed contact-angle testing. M.S.D. performed the conductivity testing. T.P.P. conducted DFT calculations on surface reaction mechanisms. Y.Z. and E.J.M. performed IB experiments. M.A.S. assisted with the XPS measurements. X.R. performed IR experiments. T.B.A. conducted XRF experiments. All authors discussed and analyzed the data. L.M., T.P.P., M.A.S., O.B., and K.X. wrote and revised the manuscript

DECLARATION OF INTERESTS

The authors declare no competing interests.

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