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High-Efficiency Zinc-Metal Anode Enabled by Liquefied Gas Electrolytes

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ABSTRACT: The practical applications of rechargeable zinc metal batteries are prevented by poor Zn reversibility, which induces both inferior Coulombic efficiency (CE) and zinc dendrite growth that worsens at low temperatures because of deteriorated kinetics in both charge and mass transfer. Herein, a liquefied gas electrolyte based on a mixture of fluoromethane and difluoromethane is demonstrated, which displays an excellent conductivity (>3.4 mS cm⁻¹) across a broad temperature range (-60 to +20 °C) and enables highly reversible Zn cycling with no evidence of shorting behavior at both room temperature and -20 °C for over 200 cycles (>400 h) with an average CE of >99.3% and 20% Zn utilization per cycle. Density functional theory calculations showed that such improvements benefited from a ZnF₂-enriched interphase formed on the anode because of decomposition of the liquefied gas electrolyte. This electrolyte was verified in a ZnllNa₂V₆O₁₆·



1.63H₂O cell with stable performance, where a similar ZnF₂-rich interphase was also confirmed.

n ever-increasing demand for Li-ion batteries to power portable electronics, vehicles, and grid storage will eventually encounter supply limitations of the rare elements and materials such as lithium, cobalt, and nickel,^{1,2} which are either distributed or mined and processed in areas carrying geopolitical and ethical risks. Thus, it is urgent to develop alternative battery chemistries based on more sustainable and widely accessible elements and materials. Rechargeable Zn-metal batteries (RZMB) provide such an attractive alternative given a number of advantages possessed by Zn: nontoxicity, relatively high abundance and even distribution in the earth's crust, high volumetric and gravimetric capacities (5854 mAh cm^{-3} and 820 mAh g^{-1} , respectively),^{3,4} as well as moderate operating potentials (-0.763 V vs SHE). However, zinc metal (Zn^0) is an anode hardly reversible because of its parasitic reactivity with electrolytes that leads to low Coulombic efficiency (CE) and drives the formation of dendrite Zn⁰. Such irreversibility has kept Zn-based batteries nonrechargeable for over 200 years. The emergence of a practical RZMB depends on the resolution of Zn reversibility.⁵

The Zn deposition morphology and the properties of any possible solid-electrolyte-interphase (SEI) are closely correlated with the properties of the electrolyte (e.g., chemical composition, transport properties, electrochemical window, etc.), which are key to suppressing side reactions and dendrite growth, improving Zn plating/stripping CE, and enhancing cycling lifetime of the Zn metal anode. In aqueous electrolytes, parasitic hydrogen evolution occurs with the weak link being the strongly polarized Zn²⁺-bound waters. Previous efforts have considered the use of supporting salts (e.g., lithium bis-(trifluoromethylsulfonyl)imide (LiTFSI)⁶) or nonaqueous cosolvents (e.g., dimethyl sulfoxide (DMSO)⁷ and succinonitrile $(SN)^8$) to replace water in the Zn solvation sheath and form SEI from the solvation sheath chemistry so that water decomposition can be suppressed and CE improved. Alternatively, certain nonaqueous electrolytes (e.g., triethyl phosphate (TEP),⁹ eutectic ionic liquid,^{10,11} and N,Ndimethylformamide $(DMF)^{12}$ have also been investigated with the goal of improving Zn utilization per cycle and demonstrated superior Zn reversibility. However, specific capacity in a full cell setup is generally more limited for nonaqueous electrolytes because of the lack of a proton contribution and the slower kinetics of Zn cation desolvation.¹³

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Despite the numerous electrolytes developed in recent years, the degree of Zn reversibility is still far from the desired target for commercialization of a metal battery anode (5 mAh cm⁻², 10 mA cm⁻², 80% Zn utilization per cycle) in line with requirements for lithium metal batteries by Albertus et al.^{14,15} In addition, although the presence of both SEI and cathodeelectrolyte-interphase (CEI) have been confirmed in recent publications,^{5,7,8} the understanding of their formation mechanism is indispensable for developing state-of-the-art electrolytes capable of supporting commercially viable RZMBs.

Herein, a nonaqueous liquefied gas electrolyte based on fluoromethane (CH₃F, FM) and difluoromethane (CH₂F₂, DFM) that first saw success in previous work with safety testing (in an 18650 Form-Factor Cell)¹⁶ and Li metal anodes reversibility^{17,18} is transplanted to the Zn⁰ anode. The liquefied gas electrolyte supports superior ionic conductivity across a broad temperature range and enhances Zn reversibility even at 20% utilization, an important milestone which is approaching the commercial requirement for metal battery anodes. Additionally, thorough analyses of the Zn metal morphology and chemistries of the SEI and CEI are carried out to understand the origin of excellent Zn reversibility and stable full cell performance (paired with a Na₂V₆O₁₆·1.63H₂O (HNVO) cathode) achieved in this new liquefied gas system.

Because both FM and DFM demonstrate excellent chemical compatibility with Zn metal showing no sign of corrosion (Figure 1a–c), a solvent system of FM:DFM (1:1 by mol) was



Figure 1. Properties of Zn liquefied gas electrolyte. (a) Pristine Zn foil. (b) Pristine Zn foil after being immersed in FM for 3 days. (c) Pristine Zn foil after being immersed in DFM for 3 days. (d and e) Photographs of solubility tests in window cells after 1 h for 0.5 M Zn(TFSI)₂ (d) and 0.1 M Zn(TFSI)₂ (e) in FM:DFM:TMP (49.5:49.5:1 by mol). The red circle in panel d indicates the undissolved part. (f and g) Photographs of solubility tests in window cells after 24 h for 0.5 M Zn(TFSI)₂ (f) and 0.1 M Zn(TFSI)₂ (g) in FM:DFM:TMP (49.5:49.5:1 by mol). (h) Ionic conductivity of 0.1 M Zn(TFSI)₂ liquefied gas electrolyte. (i) Anodic stability of 0.1 M Zn(TFSI)₂ liquefied gas electrolyte compared with 0.1 M Zn(TFSI)₂ in AN during second cycle at room temperature from measurements at 1 mV s⁻¹ scan rate using a two-electrode coin cell containing glassy carbon as the working electrode and Zn foil as the counter electrode. The dashed line denotes 0.1 mA cm⁻².

selected as an exemplar solvent with $Zn(TFSI)_2$ salt to form the electrolyte. According to previous reports,^{17–19} salt solubility can be limited in FM-based electrolytes; thus, 1% (by mol in the solvent) trimethyl phosphate (TMP) was used as an entrainer to facilitate Zn salt dissolution in liquefied gas solvents with a possibility to tune the localized solvation structure (Figure S1). The high-pressure window cell clearly shows that there is no phase separation of these mixtures after a 24 h dissolution process (Figure 1f,g). However, some salt residue can be observed after only 1 h of dissolution in 0.5 M $Zn(TFSI)_2$ electrolyte (Figure 1d,e). With a focus on demonstrating the effect of liquefied gas solvent on Zn reversibility, only the concentration of 0.1 M $Zn(TFSI)_2$ (called 0.1 M $Zn(TFSI)_2$ liquefied gas electrolyte) was used for the electrochemical studies.

Ionic conductivity for the 0.1 M Zn(TFSI)₂ liquefied gas electrolyte is 4.17 mS cm⁻¹ at +20 °C (Figure 1h), which is comparable to that of most state-of-the-art, nonaqueous liquid Zn electrolytes (Table S1). Partially because of the exceptionally low melting point of FM ($T_m = -142$ °C) and DFM ($T_m =$ -136 °C) and high fluidity, an impressive conductivity of 3.37 mS cm⁻¹ is maintained at -60 °C, higher than that reported for a selection of competing Zn electrolytes (Table S1). This 0.1 M Zn(TFSI)₂ liquefied gas electrolyte also shows a remarkable anodic stability with an onset potential of ~2.6 V (vs Zn/Zn²⁺), slightly better than an acetonitrile (AN)-based electrolyte, if 0.1 mA cm⁻² is set as the onset threshold for major decomposition (Figure 1i).

Zn-metal plating/stripping in the liquefied gas electrolyte was examined using an "anodeless" CulZn (100 μ m) cell setup with an established galvanostatic procedure²⁰ at 20 °C, -10 °C, and -40 °C. The corresponding average CEs of duplicated cells (from eq S1) for each temperature were 99.2%, 99.18%, and 88.4%, respectively (Figure 2a-c), demonstrating a remarkable Zn reversibility within an unprecedentedly wide temperature range. The CE decay observed at -40 °C could be caused by a large overpotential as reported in previous work.²⁰

Working toward practical commercial conditions, a more rigorous long-term CE testing was applied using a "reservoir



Figure 2. Electrochemical performance of Zn metal in 0.1 M Zn(TFSI)₂ liquefied gas electrolyte at different temperatures. (ac) Voltage vs time for CulZn (100 μ m) cells at different temperatures as labeled in panels a-c. Cu was conditioned by plating (5 mAh cm⁻²) and stripping Zn (0.5 V) first. Then a Zn reservoir with a capacity of 5 mAh cm⁻² was plated on the Cu substrate with 0.5 mA cm⁻². The same current density was used for stripping and plating Zn during the following 9 cycles. A capacity of 1 mAh cm⁻² (Q_c) Zn was plated or stripped in each cycle. In the final step, a capacity was observed when plated Zn was stripped by charging to 0.5 V. Calculated Zn plating/stripping CEs are labeled in each panel. (d and e) Zn plating/stripping profiles and corresponding CE cycled using CulZn(10 μ m) cell setup at room temperature with 1.17 mA cm⁻² to an areal capacity of 1.17 mAh cm⁻² per cycle (d) and at -20 °C with 0.58 mA cm⁻² to an areal capacity of 1.17 mAh cm^{-2} per cycle (e).



Figure 3. Proposed interphasial chemistry for Zn-metal anode with 0.1 M Zn(TFSI)₂ liquefied gas electrolyte. XPS spectra of F 1s (a–c) for Zn metal. Ar⁺ sputtering for (a) 0 min, (b) 3 min, and (c) 5 min was conducted to generate depth profiles of F 1s. (d) TEM image of the cycled Zn anode surface. (e) SEM image of the cycled Zn anode. Zn anode samples for panels a–e were obtained from Zn|Zn symmetric cells at zero state of charge after 5 cycles (10 h of cycling with 0.5 mA cm⁻², 0.5 mAh cm⁻² per cycle) with 0.1 M Zn(TFSI)₂ liquefied gas electrolyte at room temperature. (f–k) Reduction potentials (in V vs Zn/Zn²⁺) for the CH₃F (f–h) and CH₂F₂ (i–k) containing clusters from PCM(dichloromethane)/M052X/6-31+G(d,p) DFT calculations. Brackets in panels f and i indicate averaging over the 2-electron transfer assuming the methyl radical products (the bottom left species in panels f and i) reduce again without chemical decomposition and release of HF (the middle species).



Figure 4. Electrolyte performance in an HNVO|Zn (100 μ m) full cell and chemical analysis of the cycled HNVO cathode. (a and b) Specific discharge capacity vs cycle number for different electrolytes: (a) 0.1 M Zn(TFSI)₂ in AN and (b) 0.1 M Zn(TFSI)₂ liquefied gas electrolyte tested with the HNVO (~3 mg cm⁻²)|Zn(100 μ m) cell setup at different current density (based on the active material mass of HNVO) at room temperature. (c) Discharge voltage profile at different current density corresponding to panel b. (d) CE and corresponding specific discharge capacity vs cycle number for 0.1 M Zn(TFSI)₂ liquefied gas electrolyte tested with the HNVO (~3 mg cm⁻²)|Zn(100 μ m) cell setup with 20 mA g⁻¹ at room temperature. (e–g) XPS spectra of F 1s for HNVO cathode. Ar⁺ sputtering for (e) 0 min, (f) 3 min, and (g) 5 min was conducted to generate depth profiles of F 1s. A peak at ~688 eV (C–F), assigned to polyvinylidene fluoride (PVDF) binder,²⁴ could also be due to a possible combination of liquefied gas solvent and PVDF binder decomposition according to a previous report;²⁵ each process results in similar products, though the relative immobility of PVDF may translate to a more minor role in CEI chemistry. (h) XRF results for the mass ratio of V/Zn in HNVO cathode after 10 cycles. (i) TEM image of the cycled HNVO cathode. HNVO samples for panels e–g and i were obtained from HNVO|Zn cells at 0.2 V (0% SOC) after 2 cycles at 20 mA g⁻¹ with 0.1 M Zn(TFSI)₂ liquefied gas electrolyte at room temperature. HNVO samples for panel h were obtained from HNVO|Zn cells at 0.2 V (0% SOC) after 10 cycles at 20 mA g⁻¹ with 0.1 M Zn(TFSI)₂ liquefied gas electrolyte at room temperature.

free" CulZn (10 μ m) cell setup at both room temperature (1.17 mA cm⁻², 1.17 mAh cm⁻², 20% Zn utilization per cycle) and -20 °C (0.585 mA cm⁻², 1.17 mAh cm⁻², 20% Zn utilization per cycle). In spite of the more aggressive conditions, a surprisingly small Zn plating overpotential (~0.25 V, Figure 2d,e) is maintained and high average CEs (from eq S2) are observed at room temperature (99.7%, 350 cycles, 700 h) and -20 °C (99.31%, 200 cycles, 800 h), respectively. The lack of "shorting behavior" was observed with the presence of normal electrochemical results (Figure 2d,e) during long-term cycling, demonstrating the ability of the liquefied gas electrolyte to support a highly reversible Zn metal anode with a high Zn utilization per cycle and the perspective

high energy density RZMBs operating within a wide temperature range.

Scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) depth profiles, transmission electron microscopy (TEM), and density functional theory (DFT) calculations were used to investigate Zn^0 morphology and the corresponding SEI chemistry. In the F 1s spectra, both ZnF_2 (at ~685 eV) and organic F (at ~688 eV) were detected on Zn^0 surface after 5 cycles (10 h cycling, Figure 3a). During sputtering, the ZnF_2 signal is consistently present while the organic F signal disappears with increasing Ar^+ etching time (Figure 3b,c), indicating that ZnF_2 is present throughout the SEI and organic F is most likely a signature of the residual salt

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on the SEI surface from the electrolyte. The lack of P signal (Figure S2) rules out a major SEI contribution from TMP according to a previous report,²¹ though its concentration in this work is probably too low to make a discernible contribution. TEM experiments (Figure 3d) complemented with energy-dispersive X-ray spectroscopy (EDX, Figure S3) were performed to image the Zn^{2+} -conducting interphase after 5 cycles (10 h cycling), revealing a \sim 60 nm surface layer. This thickness is much larger than most Li⁺-conducting interphases reported (~20 nm).²² A homogeneous Zn morphology without any observable dendrites is also observed by SEM (Figures 3e and S4), which is consistent with the electrochemical results (Figure 2) and could be attributed to the effect of the ZnF₂ enriched interphase. DFT calculations were used to explore the initial SEI formation steps as a result of reduction and decomposition of the representative Zn²⁺ solvates with FM and DFM (Figure 3f-k). Both FM and DFM solvents readily reduce through dimerization reactions well above the Zn potential, while TFSI reduction may occur closer to the Zn/Zn^{2+} potential¹⁰ (Figures S5 and S6). Propensity for solvent reduction displays dependence on solvation environment where $[ZnX_6]^{2+}$ (X = FM, DM) gas solvates reduce at a higher potential than $[Zn(TFSI)_2(X)_2]$ aggregates, though both species will participate in SEI formation on the anode. Solvent co-intercalation into the HNVO cathode may also allow [ZnX₆]²⁺ or partially solvated species (Figure 3f,i) to reduce as well. DFT calculations predict ZnF₂ and fluorinated alkyl compounds as major contributors to the SEI in accordance with XPS results (Figures 3a-c and S5). Thus, the liquefied gas electrolyte plays a critical role in forming the ZnF2-rich SEI that stabilizes the metal anode interphase in accordance with earlier reports.^{17,18} As an aside, the SEI evolution as a function of time and temperature is worth further study.

The performance of this 0.1 M $Zn(TFSI)_2$ liquefied gas electrolyte was further verified in a full cell with HNVO as the cathode and Zn metal foil as the anode. Here HNVO was used only for demonstration as vanadium is both toxic and rare and hence would not make an ideal cathode for Zn chemistry. Compared to a widely used nonaqueous AN-based electrolyte (Figure 4a), the liquefied gas electrolyte demonstrates much better rate capability at room temperature (Figure 4b,c). Surprisingly, a high specific capacity (~100 mAh g^{-1}) is still maintained after 100 cycles with 20 mA g^{-1} at room temperature (Figure 4d). It should be mentioned that, as an intercalation-type cathode,²³ HNVO rarely delivers such high capacity even in a nonaqueous electrolyte, including TMP (Figure S7). Thus, with a focus on identifying the source of such high specific capacity, sputtering XPS, X-ray fluorescence spectroscopy (XRF), TEM-EDX, and DFT calculations were used to examine the interphase chemistry of the HNVO cathode recovered from cycled cells. Again, the signature of ZnF_2 (~685 eV) is observed in the sputtering F 1s spectra for the HNVO cathode after only two cycles (Figures 4e-g, S8, and S9), which is consistent with DFT calculation results (Figure 3f-k). The high reduction potentials from Figure 3f,g,i,j suggest that the reduction of liquified gas clusters leads to a formation of ZnF_2 and protons, thus providing a possible explanation for the unexpected surge in capacity. To probe the contribution of Zn cations to cell capacity, XRF was used to test the mass ratio of V/Zn in the HNVO electrode in the charged (100% state-of-charge (SOC)) and discharged (0% SOC) states after 10 cycles (Figures 4h, S10, and S11 and

Table S2). The difference between two ratios could be ascribed to a capacity contribution from the Zn cation of ~25 mAh g⁻¹ (Table S2), which makes up only a small fraction of the full capacity (~110 mAh g⁻¹, Figure 4d). Intercalated Zn in HNVO is also indicated by the spatial separation of Zn and F in TEM-EDX (Figures 4i and S12). The hybrid intercalation occurring here highlights the necessity and urgency to seek new and practical Zn intercalation cathode materials.

In summary, a 0.1 M Zn(TFSI)₂ liquefied gas electrolyte was found to enable a highly reversible Zn⁰ anode. Benefiting from the formation of a ZnF_2 enriched interphase on the anode, the electrolyte yielded uniform Zn⁰ deposition morphology and a "shorting-free" cell behavior with a high average CE (>99.3%) over 200 cycles (>400 h) at both room temperature and -20°C, even with a high 20% Zn utilization per cycle. An uncharacteristically high specific capacity for a nonaqueous electrolyte was observed when Zn was coupled with an HNVO intercalation cathode. DFT calculations, XRF, and TEM-EDX point to capacity contributions from both Zn cations and other charge carriers, which are most likely protons evolved as a result of solvent reduction. The liquefied gas electrolyte concept is highly adaptable, and further investigation (e.g., electrolyte composition optimization and capacity decay mechanism) could see additional improvements in the performance at different temperatures, especially at a low temperature range, pending the development of new cathode materials. This unique approach provides a promising path toward high-energy RZMBs as well as other rechargeable multivalent metal batteries.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.1c02084.

Experimental details, supplementary characterization, and supporting data, as noted in the main text (PDF)

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Notes

The authors declare no competing financial interest.

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