# Fluorinated interphase enables reversible aqueous zinc battery chemistries

Longsheng Cao<sup>®</sup><sup>1,6</sup>, Dan Li<sup>1,6</sup>, Travis Pollard<sup>®</sup><sup>2,6</sup>, Tao Deng<sup>1</sup>, Bao Zhang<sup>1</sup>, Chongyin Yang<sup>®</sup><sup>1</sup>, Long Chen<sup>1</sup>, Jenel Vatamanu<sup>2</sup>, Enyuan Hu<sup>®</sup><sup>3</sup>, Matt J. Hourwitz<sup>4</sup>, Lin Ma<sup>1,2</sup>, Michael Ding<sup>2</sup>, Qin Li<sup>1</sup>, Singyuk Hou<sup>1</sup>, Karen Gaskell<sup>1</sup>, John T. Fourkas<sup>4,5</sup>, Xiao-Qing Yang<sup>®</sup><sup>3</sup>, Kang Xu<sup>®</sup><sup>2</sup><sup>\infty</sup>, Oleg Borodin<sup>®</sup><sup>2</sup><sup>\infty</sup> and Chunsheng Wang<sup>®</sup><sup>1,4</sup><sup>\infty</sup>

Metallic zinc is an ideal anode due to its high theoretical capacity ( $820 \text{ mAh g}^{-1}$ ), low redox potential (-0.762 V versus the standard hydrogen electrode), high abundance and low toxicity. When used in aqueous electrolyte, it also brings intrinsic safety, but suffers from severe irreversibility. This is best exemplified by low coulombic efficiency, dendrite growth and water consumption. This is thought to be due to severe hydrogen evolution during zinc plating and stripping, hitherto making the in-situ formation of a solid-electrolyte interphase (SEI) impossible. Here, we report an aqueous zinc battery in which a dilute and acidic aqueous electrolyte with an alkylammonium salt additive assists the formation of a robust,  $Zn^{2+}$ -conducting and waterproof SEI. The presence of this SEI enables excellent performance: dendrite-free zinc plating/stripping at 99.9% coulombic efficiency in a Ti||Zn asymmetric cell for 1,000 cycles; steady charge-discharge in a Zn||Zn symmetric cell for 6,000 cycles (6,000 h); and high energy densities (136 Wh kg<sup>-1</sup> in a Zn||VOPO<sub>4</sub> full battery with 88.7% retention for >6,000 cycles, 325 Wh kg<sup>-1</sup> in a Zn||O<sub>2</sub> full battery for >300 cycles and 218 Wh kg<sup>-1</sup> in a Zn||MnO<sub>2</sub> full battery with 88.5% retention for 1,000 cycles) using limited zinc. The SEI-forming electrolyte also allows the reversible operation of an anode-free pouch cell of Ti||Zn<sub>x</sub>VOPO<sub>4</sub> at 100% depth of discharge for 100 cycles, thus establishing aqueous zinc batteries as viable cell systems for practical applications.

he lithium-ion (Li-ion) battery has become a ubiquitous commodity in portable electronics, transportation and grid-storage applications. However, our growing reliance on the lithium-ion battery in these industries has exposed its shortcomings in safety, energy density and cost driven by limited reserves of crucial elements<sup>1,2</sup>. Zinc metal (Zn<sup>0</sup>) batteries have emerged as a promising alternative because of their high volumetric capacity (5,855 mAh cm<sup>-3</sup> versus 2,061 mAh cm<sup>-3</sup> for Li)<sup>3,4</sup>, non-toxicity, relatively high abundance and low cost<sup>5</sup>. Coupling Zn<sup>0</sup> with aqueous electrolytes offers fast kinetics and high safety compared with non-aqueous counterparts<sup>6,7</sup>.

Most efforts in rechargeable Zn batteries have been dedicated to identifying cathode materials serving as hosts for either Zn ion  $(Zn^{2+})$  intercalation<sup>8-10</sup> or oxygen/air conversion<sup>11,12</sup>. However, the Znº electrode suffers from severe irreversibility during repeated plating/stripping across a broad pH range, as evidenced by low coulombic efficiency (CE)<sup>3,8,9</sup> stemming from the attraction between Zn<sup>2+</sup> and water<sup>13</sup> even at high ZnCl<sub>2</sub> concentrations<sup>14,15</sup>. Water decomposition forms Zn(OH)4<sup>2-</sup> (zincate) in the local high pH regions, which subsequently converts to insoluble and electrochemically inert ZnO (ref. 7). Moreover, the inhomogeneous morphology of Zn(OH)2- and ZnO-based depositions on Zn induces the dendrite growth that compromises cycle life and safety<sup>8,9,16</sup>. Large excesses of Zn and electrolyte are required to mitigate anode and water consumption during cycling, which decrease the overall energy density and cycle life of the batteries.

An effective method to suppress the side reactions on  $Zn^0$  is to form in situ a  $Zn^{2+}$ -conducting solid–electrolyte interphase (SEI) in non-aqueous electrolytes<sup>17,18</sup>, and water-in-salt electrolytes (WiSE)<sup>3,19</sup>. However, WiSE suffer from intrinsic disadvantages (for example, high viscosity and high cost), necessitating the use of lower concentration aqueous electrolytes to form an interphase on  $Zn^0$ . Recently, it was reported that a dilute aqueous electrolyte based on hydrophobic trifluoromethanesulfonate (OTF<sup>-</sup>) anions enabled a two-electron oxygen chemistry on the cathode surface by removing water from the inner Helmholtz layer<sup>20</sup>. However, on the anode side, Zn plating/stripping in this dilute aqueous electrolyte still suffers from irreversibility (CE <90%). Since the Zn<sup>0</sup> anode is the essential component for all Zn<sup>0</sup> chemistries including Zn–air batteries, improving Zn<sup>0</sup> reversibility marks a crucial hurdle for commercialization of Zn batteries.

Here, we enhanced Zn plating/stripping CE in aqueous zinc trifluoromethanesulfonate (Zn(OTF)<sub>2</sub>) electrolyte from 87.6% to 99.9% with trimethylethyl ammonium trifluoromethanesulfonate (Me<sub>3</sub>EtNOTF) as an additive, which engenders in-situ formation of a fluorinated and hydrophobic interphase that conducts Zn<sup>2+</sup> while suppressing the hydrogen evolution reaction. This in-situ-formed interphase suppresses dendrite growth for up to 6,000 cycles. More importantly, 4 m Zn(OTF)<sub>2</sub>+0.5 m Me<sub>3</sub>EtNOTF + H<sub>2</sub>O (where m is molality, mol kg<sup>-1</sup>) electrolytes also enable the stable cycling of both vanadium phosphate (VOPO<sub>4</sub>) and O<sub>2</sub> cathodes. The Zn||VOPO<sub>4</sub> full cell delivers 136 Whkg<sup>-1</sup> and retains 88.7% of its capacity for >6,000 cycles, while the Zn||O<sub>2</sub> delivers 325 Whkg<sup>-1</sup> for >300 cycles

<sup>&</sup>lt;sup>1</sup>Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, MD, USA. <sup>2</sup>Battery Science Branch, Energy Science Division, Sensor and Electron Devices Directorate, US Army Research Laboratory, Adelphi, MD, USA. <sup>3</sup>Chemistry Division, Brookhaven National Laboratory, Upton, NY, USA. <sup>4</sup>Department of Chemistry and Biochemistry, University of Maryland, College Park, MD, USA. <sup>5</sup>Institute for Physical Science and Technology, University of Maryland, College Park, MD, USA. <sup>6</sup>These authors contributed equally: Longsheng Cao, Dan Li, Travis Pollard. <sup>Ka</sup>e-mail: conrad.k.xu.civ@mail.mil; oleg.a.borodin.civ@mail.mil; cswang@umd.edu



**Fig. 1** [Electrochemical properties of different electrolytes. a-c, The electrochemical stability window of aqueous electrolytes measured using polarization scanning at  $1 \text{mV s}^{-1}$  on non-active Ti electrodes between -0.2 V and 3.0 V versus  $2\text{n}/2\text{n}^{2+}$ : the overall electrochemical stability window (**a**) and magnified views of the regions outlined near anodic (**b**) and cathodic (**c**) extremes in **a**. Purple arrows in **b** show the hydrogen evolution current at 0.4 V. **d**,**e**, Zn-metal plating/stripping profiles on a Ti electrode cycled in  $4 \text{ m Zn}(\text{OTF})_2$  (**d**) and  $4 \text{ m Zn}(\text{OTF})_2 + 0.5 \text{ m Me}_3\text{EtNOTF}$  (**e**) with magnified views of selected cycles in the regions outlined between 0.18 V and 0.22 V at a current density of  $0.5 \text{ mA cm}^{-2}$ . **f**, Zn plating/stripping CE with magnified views of selected cycles between 800th cycle to 1,000th cycle in different electrolytes at  $0.5 \text{ mA cm}^{-2}$  and  $0.5 \text{ mA cm}^{-2}$ . **g**, Galvanostatic Zn plating/stripping in a Zn||Zn symmetric cell at  $0.5 \text{ mA cm}^{-2}$  and  $0.25 \text{ mA cm}^{-2}$ .



**Fig. 2** | **SEM** and **TEM** imaging of Zn metal after 50 plating/stripping cycles in different electrolytes in a Zn||Zn symmetric cell at 0.5 mA cm<sup>-2</sup> and 0.25 mAh cm<sup>-2</sup>. **a**-**f**, SEM images after 50 plating/stripping cycles in 4 m  $Zn(OTF)_2$  at scales of 50 µm (**a**), 20 µm (**b**) and 10 µm (**c**) and in 4 m  $Zn(OTF)_2 + 0.5$  m Me<sub>3</sub>EtNOTF at scales of 50 µm (**d**), 20 µm (**e**) and 10 µm (**f**). Insets in **a** and **d** show optical images of Zn foils after cycling. In **c** and **f**, red lines indicate the etching depth. **g**,**h**, TEM images of the cycled Zn anode surface in 4 m  $Zn(OTF)_2 + 0.5$  m Me<sub>3</sub>EtNOTF (**g**) and 4 m  $Zn(OTF)_2$  (**h**). In **g**, red lines indicate the thickness of the interphase.

since Me<sub>3</sub>EtNOTF further enhances the reversibility of the twoelectron reaction of the O<sub>2</sub> cathodes. Its merits were further evidenced by the extremely high energy density of 218 Wh kg<sup>-1</sup> demonstrated by a Zn||MnO<sub>2</sub> full battery, with 88.5% capacity retention achieved after 1,000 cycles using limited Zn. The electrolyte also enables reversible operation of an anode-free Ti||Zn<sub>x</sub>VOPO<sub>4</sub> pouch cell at 100% depth of discharge for 100 cycles.

### **Results and discussion**

**Zn plating/stripping reversibility.** The electrochemical stability windows of various aqueous electrolytes at almost identical pH (Supplementary Table 1) were evaluated on non-active titanium (Ti) electrodes (Fig. 1a–c), where  $0.5 \text{ m Me}_3$ EtNOTF salt in  $4 \text{ m Zn}(\text{OTF})_2 + \text{H}_2\text{O}$  electrolytes was found to extend the cathodic limit. Closer examination showed that Me<sub>3</sub>EtNOTF drove the onset potential for water reduction from 358 mV down to 157 mV (versus Zn/Zn<sup>2+</sup>) before a minor reduction occurred at -64 mV. Zn plating occurred at -108 mV (Fig. 1a,b). The hydrogen evolution current of  $63 \mu \text{A cm}^{-2}$  at 0.4 V in  $4 \text{ m Zn}(\text{OTF})_2$  electrolytes was eliminated with the addition of Me<sub>3</sub>EtNOTF (purple arrows, Fig. 1b). The negatively shifted potential for both Zn deposition and hydrogen evolution (Fig. 1a,b) originated from the protection by the ammonium cation adsorption and SEI formation from reduction of OTF<sup>-</sup> anions on the anode surface (Supplementary Fig. 1).

On the cathode side (Fig. 1c), oxygen evolution was further suppressed by Me<sub>3</sub>EtNOTF, increasing the oxidation onset potential from 2.55 V to 2.6 V. Overall, a wider stability window of ~2.7 V was achieved (Fig. 1a) with both cathodic  $(-0.1 \text{ V versus } \text{Zn}/\text{Zn}^{2+})$ and anodic (2.6V versus Zn/Zn<sup>2+</sup>) limits expanded. The reversibility of the Zn<sup>0</sup> electrode in 4 m Zn(OTF)<sub>2</sub> electrolytes with and without Me<sub>3</sub>EtNOTF was compared in Zn||Zn or Zn||Ti cells (Fig. 1d-g and Supplementary Fig. 2). The addition of Me<sub>3</sub>EtNOTF increased the overpotential of Zn plating/stripping on the Ti surface (Fig. 1d,e) due to the increased interphasial resistance and the reduction in ionic conductivity (38.2 mS cm<sup>-1</sup>) as compared with alkylammonium-free electrolyte (46.7 mS cm<sup>-1</sup>) at room temperature (Supplementary Fig. 3). Even so, the resulting ionic conductivity was still higher than WiSE (12.7 mS cm<sup>-1</sup>) by a factor of three<sup>10</sup>. Although Me<sub>3</sub>EtNOTF slightly decreases the conductivity at room temperature, the low-temperature (below -32 °C) conductivity was improved (Supplementary Fig. 3), and the Zn<sup>2+</sup>-transference number  $(t_+)$  was increased to ~0.4 on the basis of Bruce–Vincent methodology and 0.32-0.36 from molecular dynamics (MD) simulations (Supplementary Fig. 4, Supplementary note 1 and Supplementary Table 2). Me<sub>3</sub>EtNOTF also increases thermal stability by 31 °C according to thermogravimetric analysis (Supplementary Fig. 5). Most importantly, the presence of 0.5 m Me<sub>3</sub>EtNOTF promotes SEI formation, improving Zn plating/stripping efficiency to >99.0%

NATURE NANOTECHNOLOGY



**Fig. 3 | XPS spectra of F1s and C1s for Zn metal after 50 plating/stripping cycles in 4 \text{ m Zn}(\text{OTF})\_2 + 0.5 \text{ m Me}\_3\text{EtNOTF} at a current density of <b>0.5 mA cm**<sup>-2</sup>. **a**-**f**, Depth profiles of F1s generated after Ar<sup>+</sup> sputtering for 0 min (**a**), 2 min (**b**) and 10 min (**c**) and of C1s after 0 min (**d**), 2 min (**e**) and 10 min (**f**). **g**, Composition of SEI after various durations of Ar<sup>+</sup> sputtering on Zn metal cycled in  $4 \text{ m Zn}(\text{OTF})_2 + 0.5 \text{ m Me}_3\text{EtNOTF}$ . **h**, Fourier-transformed extended X-ray absorption fine structure data of ZnF<sub>2</sub>·4H<sub>2</sub>O and Zn electrode recovered from  $4 \text{ m Zn}(\text{OTF})_2 + 0.5 \text{ m Me}_3\text{EtNOTF}$ . **h**, Fourier-transformed extended X-ray absorption coefficient; *R*, the phase-shift-adjusted bond distance between absorbing atom and its neighbouring atom. **i**, Cartoon of proposed Zn<sup>2+</sup>-conducting SEI, characterized by small nodular particles embedded in a polymeric framework (see Fig. 2g). a.u., arbitrary units.

within the initial 15 cycles, with an average CE of 98.0% at a current of  $0.5 \,\mathrm{mA}\,\mathrm{cm}^{-2}$  and a capacity of  $0.5 \,\mathrm{mAh}\,\mathrm{cm}^{-2}$ . CE further increased to 99.9% after 100 cycles, averaging to 99.8% across 1,000 cycles (Fig. 1f) (for a comparison with other reported anodes, see Supplementary Table 3). By contrast, Zn plating/stripping in 4 m Zn(OTF)<sub>2</sub> electrolytes demonstrated a low CE of 87.6%, failing at the 20th cycle at  $0.5 \,\mathrm{mA}\,\mathrm{cm}^{-2}$  and  $0.5 \,\mathrm{mAh}\,\mathrm{cm}^{-2}$  (Fig. 1f). When areal capacity is increased to  $1.0 \,\mathrm{mAh}\,\mathrm{cm}^{-2}$  at  $0.5 \,\mathrm{mA}\,\mathrm{cm}^{-2}$ , Zn plating/ stripping CE in 4 m Zn(OTF)<sub>2</sub> + 0.5 m Me<sub>3</sub>EtNOTF electrolyte still reached >99.6%, while in 4 m Zn(OTF)<sub>2</sub> electrolyte, it deteriorated to 80.9%, failing at the tenth cycle (Supplementary Fig. 6). Note that CE increases with increasing currents for identical capacity of Zn plating/stripping (Supplementary note 2). Me<sub>3</sub>EtNOTF rendered excellent  $Zn^{2+}$  reversibility in Zn||Zn for over 6,000 cycles, while the Me<sub>3</sub>EtNOTF-free electrolyte failed after 194 cycles (Fig. 1g). The effectiveness of this alkylammonium salt in forming an SEI was also found in another electrolyte (1 m ZnCl<sub>2</sub> in water). Without Me<sub>3</sub>EtNOTF, the Zn||Ti cell showed a low CE (~90%) and short circuit within 52 cycles. With Me<sub>3</sub>EtNOTF, CE increased to 99.0% and supported cycling beyond 100 cycles (Supplementary Fig. 7).



**Fig. 4 | Proposed mechanism demonstrating synergistic reactions between triflate and trimethylethyl ammonium to deposit predominantly fluoride and carbonate-based SEI.** Alkylammonium decomposes in the presence of a strong base (B:) such as  $OH^-$  or  $CF_3^-$ , produced by triflate reduction and decomposition, to form an amine that is reactive with dissolved  $CO_2$  from ambient air to precipitate  $ZnCO_3$  SEI (in parentheses). The released ethylene scavenges reduction products of triflate to precipitate a protective and conducting polyanion species as well as a  $ZnF_2$ -rich SEI (in parentheses). Reaction energies and additional details are given in Supplementary Figs. 23–29.

An in-house device (Supplementary Fig. 8a–c) demonstrated a rapid decrease in  $H_2$  evolution during Zn plating/stripping with Me<sub>3</sub>EtNOTF present (Supplementary Fig. 8d,e).

Zn plating/stripping morphology. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to investigate the Zn surface after 50 cycles in a Zn||Zn cell containing 4 m Zn(OTF)<sub>2</sub> electrolyte at 0.5 mA cm<sup>-2</sup>. Substantial cracking and dendritic growth were detected on the cycled Zn surface (Fig. 2a,b). The large thickness of deposited  $Zn (5 \mu m)$  is attributed to the highly porous/mossy structure (between the red lines in Fig. 2c), which was also confirmed by the non-uniform distribution of the elements in energy-dispersive X-ray spectroscopy mapping (Supplementary Fig. 9). By contrast, Zn deposited from Me<sub>3</sub>EtNOTF-containing electrolyte is smooth and compact (Fig. 2d,e), as supported by a thin deposited Zn layer (2µm) in cross-sectional imaging (red line range in Fig. 2f) and the uniform distribution of elements in energy-dispersive X-ray spectroscopy mapping (Supplementary Fig. 10). As revealed by TEM, a 64 nm ZnF<sub>2</sub>-rich interphase was observed on the deposited Zn surface when Me<sub>3</sub>EtNOTF was present (Fig. 2g) and resulted in the emergence of semicircles at high frequencies in the electrochemical impedance spectra for Me<sub>3</sub>EtNOTF-containing electrolyte (red line in Supplementary Fig. 11). This SEI serves as an electron barrier preventing the reduction of water while allowing Zn<sup>2+</sup> to migrate. No such interphase was found on the Zn surface recovered from 4 m Zn(OTF)<sub>2</sub> electrolyte after 50 plating/stripping cycles (Fig. 2h).

**ZnF<sub>2</sub>-rich SEI chemistry.** The SEI chemistry was investigated using X-ray photoelectron spectroscopy (XPS). Inorganic  $ZnF_2$  was detected at ~684.7 eV, and the ratio of inorganic fluorine to organic fluorine increased with etching by Ar<sup>+</sup> (Fig. 3a–c and Supplementary Fig. 12). The total percentage increased from 22% on the surface to 35% at 2 min and remained relatively steady at 10 min (Fig. 3g).

Time-of-flight secondary-ion mass spectrometry additionally confirmed the formation of a ZnF<sub>2</sub>-rich interphase (Supplementary Fig. 13). X-ray absorption spectroscopy (Fig. 3h) revealed that the interphase is not simply ZnF<sub>2</sub>, although the exact composition cannot be determined at this time. However, we can clearly identify Zn species therein as Zn<sup>2+</sup> rather than Zn<sup>0</sup>. A ZnF<sub>2</sub>-rich interphase allows Zn<sup>2+</sup> to diffuse through while shielding the Zn surface from water and preventing parasitic reactions. Equally important is the high ZnF<sub>2</sub>/Zn interface energy, which suppresses dendrite growth by promoting lateral rather than vertical Zn<sup>2+</sup> migration and deposition<sup>5</sup>. This is similar to how the LiF/Li interface works<sup>21</sup>, although the 64 nm interphase observed in the mixed electrolyte is much thicker than typically observed on graphitic or lithium-metal anodes<sup>22,23</sup>. By contrast, no ZnF<sub>2</sub> was found in F1s high-resolution spectroscopy of the Zn electrode recovered from the baseline electrolyte (Supplementary Figs. 14 and 15).

In addition to ZnF<sub>2</sub>, CO<sub>3</sub><sup>2-</sup> (~288.6 eV) was also observed in C1s spectra on the Zn electrode recovered from Me<sub>3</sub>EtNOTF-containing electrolyte (Fig. 3d-f and Supplementary Fig. 16), consistent with a previous report<sup>24</sup>. Trimethylamine evolved from decomposition of the alkylammonium assists in this conversion (Fig. 4 and Supplementary Fig. 17). A mixture of Zn(OTF)<sub>2</sub> and Me<sub>3</sub>EtNOTF powders was used as a reference for peak assignments of ~292.5 eV for CF<sub>3</sub>, ~286.4 eV for C-O/C-N and ~284.8 eV for C-H/C-C (Supplementary Fig. 18a). Etching the surface by Ar<sup>+</sup> bombardment exposed an underlying interphase consisting of ZnCO<sub>3</sub>, which remained after prolonged (10 min) sputtering (Fig. 3d-f and Supplementary Fig. 16). Such resistance against sputtering could come only from a very dense surface interphase (Fig. 3i), similar to LiF observed in WiSE<sup>19</sup>. The presence of ZnCO<sub>3</sub> could also contribute to high CE, as CO<sub>3</sub><sup>2-</sup> was absent on the Zn surface recovered from the baseline electrolyte or in the original salts (Supplementary Figs. 18 and 19). The same conclusion applies to the detected SO<sub>3</sub><sup>2-</sup> (Supplementary Figs. 16 and 20), also missing

## **NATURE NANOTECHNOLOGY**



**Fig. 5 | Electrochemical performances of Zn-oxygen and Zn-ion batteries. a**,**b**, Cycling performance of the  $Zn||O_2$  batteries in 4 m Zn(OTF)<sub>2</sub> (**a**) and 4 m Zn(OTF)<sub>2</sub> + 0.5 m Me<sub>3</sub>EtNOTF (**b**) with selected cycle number at 50 mA g<sup>-1</sup> under 1,000 mA h g<sup>-1</sup> (the areal capacity of the cathode was 0.7 mAh cm<sup>-2</sup>). **c**,**d**, Rate performance (**c**) and cycling stability and CE (**d**) of the Zn||VOPO<sub>4</sub> coin cell in different electrolytes at 2.0 A g<sup>-1</sup>. **e**,**f**, Schematic (**e**) and digital picture (**f**) of the anode-free 50 mAh pouch cell. **g**, Cycling performance of the anode-free pouch cells at a charge-discharge rate of 0.5 mA cm<sup>-2</sup>. Specific capacity was calculated based on the electrode mass.

on the Zn electrode recovered from the baseline electrolyte or in the original salts (Supplementary Figs. 19 and 21). The decreasing peak ratio of  $Me_3EtN^+$  to electrically neutral ( $R^1R^2R^3$ )N ( $R^1$ ,  $R^2$  and  $R^3$  denote different attached groups in the typical chemistry context) with sputter time indicated the apparent decomposition of  $Me_3EtN^+$  (Supplementary Fig. 22).

Initial reduction of triflate was found to favour cleavage of C–F or C–S bonds (Supplementary Fig. 23) in accord with previous reports<sup>19,25</sup>. Density functional theory calculations show that the defluorination reaction generates a  $(SO_3)F_2C$ . species that reacts with the ethylene in a highly exergonic polymerization reaction (Supplementary Fig. 24). The reaction shifts the radical to H<sub>2</sub>C., which is stabilized through adsorption to Zn at the interface or in solution until a second reduction product is added. One possible product is shown in Supplementary Fig. 25, where  $ZnF_2$  is also

generated. It is expected that any radical species generated from triflate decomposition could be added to ethylene. The polyanion species may precipitate on the anode surface and, together with  $ZnCO_3$ and  $ZnF_2$ , provide kinetic protection against  $H_2$  evolution by repelling water from  $Zn^0$ .

Density functional theory calculations suggest that downstream reactions resulting from alkylammonium decomposition are responsible for the formation of ZnCO<sub>3</sub> (Fig. 4). The alkylammonium decomposes through Hofmann elimination, with the base generated as a result of hydrogen evolution reaction (OH<sup>-</sup>) or triflate reduction (CF<sub>3</sub><sup>-</sup>) (ref. <sup>26</sup>) (Supplementary Figs. 26a and 27). A similar mechanism has been observed previously<sup>27-29</sup> on Li<sup>0</sup> where alkylammonium decomposes through one- or two-electron reduction and the radical or carbanion is subsequently deprotonated to generate the alkene. The amine readily reacts with

## **NATURE NANOTECHNOLOGY**

## ARTICLES



**Fig. 6 | Fabrication and electrochemical performances of aritificial ZnF<sub>2</sub> SEL a**, Schematic illustration of the in-situ formation of a ZnF<sub>2</sub>-rich SEI layer (red dashed lines). **b**, Chemical structure and reaction of the KFSI. R, nitrogen containing moiety. **c**, XPS spectra of F1s for Zn metal after plating/stripping in  $2 \text{ m Zn}(\text{OTF})_2 + 0.02 \text{ m KFSI}$  at a current density of  $0.5 \text{ mA cm}^{-2}$ . **d**, Electrochemical performance of the Zn||MnO<sub>2</sub> battery enabled by  $2 \text{ m Zn}(\text{OTF})_2 + 0.05 \text{ m Mn}(\text{OTF})_2 + 0.02 \text{ m KFSI}$  at 5.0 C.

 $CO_2$  or  $H_xCO_3$  (x = 1, 2) in an aqueous environment, leading to the formation of  $CO_3^{2-}$  (Supplementary Fig. 17) and is consistent with other reports<sup>30,31</sup>. Hydroxides in zincates generated locally near the electrode surface may also decompose the alkylammonium through a Hofmann elimination (Supplementary Fig. 26b), where the preferred product is  $Zn(OH)_2(Me_3N)_2$  (Supplementary Fig. 26c). This metastable product (Supplementary Fig. 26d) may be the source of trace nitrogen observed in the SEI (Fig. 3g).

It was also suggested that anion species may be chemically decomposed through nucleophilic attack by bases such as hydroxide generated at the anode surface<sup>32,33</sup>. Several mechanisms of OH<sup>-</sup>/CF<sub>3</sub><sup>-</sup> attacking carbon and/or sulfur in OTF<sup>-</sup> are explored (Supplementary Figs. 28 and 29). It is observed that all of the reactions considered are exergonic, favouring the formation of several products, although mostly with barriers in excess of 2 eV. A more reasonable barrier of 1.09 eV was found for the formation of HCF<sub>3</sub>+SO<sub>4</sub><sup>2-</sup>. Destabilizing the reactant as described in ref. <sup>33</sup> with OH<sup>-</sup> generated via hydrogen evolution reaction on the anode surface may further decrease the barrier with ZnSO<sub>x</sub> (*x* = 3, 4) products generated near the anode surface.

The formation of SEI is often correlated with the cation solvation structure. The <sup>1</sup>H nuclear magnetic resonance chemical shifts observed in the electrolytes with and without  $Me_3EtNOTF$  versus pure water (Supplementary Fig. 30) suggest that  $4 \text{ m } Zn(OTF)_2$ strongly affects water structure. The effect of  $Me_3EtNOTF$  is negligible. A joint Raman spectroscopy, MD simulation and density functional theory analysis of OTF<sup>-</sup> bands (Supplementary Figs. 31–35) in  $4 \text{ m } Zn(OTF)_2 + Me_3EtNOTF$  showed that  $Zn^{2+}$ is solvated by six waters with little Zn–OTF contact ion pair formation (Supplementary Fig. 33). The interfacial adsorption/ desorption behaviour of ions on Zn was investigated using electrochemical impedance spectroscopy at different potentials. An inductive arc emerged at low frequency at open circuit potential for Zn<sup>0</sup> in  $Me_3EtNOTF$ -containing electrolyte, but was absent on Zn<sup>0</sup> in the baseline electrolyte (black line in Supplementary Fig. 36a,b). This indicates desorption of alkylammonium ions on Zn electrodes<sup>34,35</sup>. When the electrode potential is shifted to -20 mV versus Zn/Zn<sup>2+</sup> from open circuit voltage, polarization due to mixed kinetic (plating) and diffusion (Zn<sup>2+</sup>) control was observed. The increased interfacial impedance is attributed to the SEI. The hydrophobicity of the electrolytes on the Zn surface was also investigated through measurement of the contact angle at open circuit potential and when polarized (Supplementary Fig. 37a–d). The angle is large for Me<sub>3</sub>EtNOTF-containing electrolyte and becomes larger once polarized due to the formation of SEI. The combined effect makes water molecules unwelcome at Zn surfaces.

Electrochemical performance of Zn-metal full cells. Full  $Zn||O_2$  cells were assembled using  $Zn^0$  as the anode and carbon black coated carbon paper as the air cathode. This  $Zn||O_2$  cell has a theoretical energy density of 1,218 Wh kg<sup>-1</sup> and has been widely proposed as a candidate for automotive and grid-storage applications<sup>12,31,36</sup>. Although air cathodes could be stabilized by a fast and reversible two-electron oxygen redox reaction using  $Zn(OTF)_2 + H_2O$  electrolyte<sup>20</sup>,  $Zn^0$  reversibility has remained an issue that we address with the Me<sub>3</sub>EtNOTF-containing electrolyte. Comparing the previously reported  $Zn||O_2$  (Supplementary Table 4) and Zn||O<sub>2</sub> with 4 m Zn(OTF)<sub>2</sub> electrolyte (Fig. 5a), Zn||O<sub>2</sub> batteries with Me<sub>3</sub>EtNOTF-containing electrolyte and limited Zn anode excess (Fig. 5b) display notable cycle life (300 cycles). Cycling was conducted under a constant-capacity mode of 1,000 mAhg-(based on the cathode), corresponding to a full-cell energy density of 325 Whkg<sup>-1</sup> (based on the cathode and anode). The remarkable depth of discharge<sup>37</sup> of 68% for the Zn electrode during the Zn||O<sub>2</sub> cycling is attributed to the highly reversible Zn plating/ stripping chemistry. Me<sub>3</sub>EtNOTF in 4m Zn(OTF)<sub>2</sub> electrolytes enable smooth Zn surfaces to be recovered from prolonged cycling (Fig. 2d,e), substantially reducing voltage hysteresis in Zn||O<sub>2</sub> batteries (Fig. 5b) and suppressing  $H_2$  evolution potential (Fig. 1b), all of which are in sharp contrast to  $4 \text{ m Zn}(\text{OTF})_2$  electrolytes, which display poor performance and high overpotential (Fig. 5a). The decreased polarization in the Zn $||O_2$  full cell and increased polarization in the observed anode (Supplementary Fig. 11) demonstrate that Me<sub>3</sub>EtNOTF also accelerates the oxygen oxidation– reduction reactions. Further improvement of the round-trip energy efficiency can be achieved by adopting proper bifunctional catalysts or redox mediators.

To further demonstrate the versatility of Me<sub>3</sub>EtNOTF, VOPO<sub>4</sub> with a theoretical capacity of 165 mAhg<sup>-1</sup> was also used as the cathode to couple with the Znº electrode. Most previous work has adopted impractical half-cell configurations using a large Zn<sup>0</sup> excess to maintain decent but deceptive cycling stability, leading to substantial underutilization of the Znº theoretical capacity. When calculating cell energy density, the mass of excess Zn<sup>0</sup> was excluded, resulting in a high 'apparent' energy density (Supplementary Table 5). Here, a Ti plate pre-deposited with quantitative Zn<sup>0</sup> in the twofold excess needed for the cathode (negative-to-positive electrode capacity (N/P) ratio of 3.0) was chosen as the anode, so that we could investigate the effect of Zn loss on cell performance. This loading represents a rigorous test for electrolyte stability because it requires high Zn-metal utilization and low parasitic reactions in each cycle. The high potential (1.9V) and highly catalytic surface of VOPO<sub>4</sub> present an additional challenge to the anodic stability of the electrolyte. In Me<sub>3</sub>EtNOTF-containing aqueous electrolytes, discharge capacities of 163.1 mAh g<sup>-1</sup>, 147.1 mAh g<sup>-1</sup>,  $125.3 \text{ mAh } g^{-1}$ ,  $102.7 \text{ mAh } g^{-1}$  and  $84.9 \text{ mAh } g^{-1}$  were recorded at  $0.05 \text{ A } g^{-1}$ ,  $0.15 \text{ A } g^{-1}$ ,  $0.7 \text{ A } g^{-1}$ ,  $1.5 \text{ A } g^{-1}$  and  $2.0 \text{ A } g^{-1}$ , respectively (Fig. 5c and Supplementary Fig. 38a). When the rate was shifted back to 0.05 A g<sup>-1</sup>, the capacity recovered to 163.3 mAh g<sup>-1</sup>, showing a resilience to the rapid Zn<sup>2+</sup> insertion/extraction and stripping/ plating. At  $0.05 \,\mathrm{A\,g^{-1}}$ , the energy density based on the cathode mass is 160 Wh kg<sup>-1</sup>, and 100 Wh kg<sup>-1</sup> with the anode weight included. In the absence of Me<sub>3</sub>EtNOTF, the rate performance did not experience an obvious change (Fig. 5c and Supplementary Fig. 38b). However, the two electrolytes differed in long-term cycling stability, with the Me<sub>3</sub>EtNOTF-containing electrolyte retaining 88.7% of the original reversible capacity after 6,000 cycles at 2.0 A g<sup>-1</sup> with an average CE of ~99.9% (Fig. 5d) (for a comparison of performance for VOPO<sub>4</sub>-based Zn-ion batteries, see Supplementary Table 5). By contrast, the cell with 4 m Zn(OTF)<sub>2</sub> electrolyte retained <25% capacity within 2,000 cycles (Fig. 5d). Even at small rate  $(0.15 \text{ A g}^{-1})$ , Me<sub>3</sub>EtNOTF improved capacity retention up to 92.0% after 200 cycles, compared with 48.8% in the baseline (Supplementary Fig. 39). The most challenging evaluation of the electrolytes was performed using an anode-free configuration in a 50 mAh pouch cell consisting of Ti $||Zn_v VOPO_4|$  (Fig. 5e-g), where all Zn are pre-stored at the cathode side. This cell maintains 80% of its capacity after 90 cycles at 0.5 mA cm<sup>-2</sup> when Me<sub>3</sub>EtNOTF was used, demonstrating an unprecedented 100% depth-of-discharge performance, while the cell with baseline electrolyte falls below <80% capacity within 15 cycles.

Artificial ZnF<sub>2</sub> SEI. To exclude the influence of ZnCO<sub>3</sub> and polyanions on SEI, we designed a neat ZnF<sub>2</sub> SEI. Since bis(fluorosulfonyl) imide anion (FSI<sup>-</sup>) decomposes gradually in aqueous solution<sup>38</sup>, it was chosen as the fluorine source (Fig. 6a,b) in an electrolyte saturated with ZnF<sub>2</sub>. Formation of ZnF<sub>2</sub> SEI was identified from XPS (Fig. 6c). In contrast to short circuits observed for the Zn||Ti and Zn||Zn cells without FSI, remarkable CE of >99.1% was achieved in the presence of only 0.02 m potassium bis(fluorosulfonyl) imide (KFSI) in 2 m Zn(OTF)<sub>2</sub> (Supplementary Fig. 40a–d). Based on depth profiling of the fluorine distribution (Supplementary Fig. 41), it is shown that the surface of the Zn<sup>0</sup> electrode recovered from the 2 m Zn(OTF)<sub>2</sub>+0.02 m KFSI electrolyte is ZnF<sub>2</sub> rich (high fluorine ionicity). This pure  $ZnF_2$  SEI also dramatically improved the cycling stability of the  $Zn||MnO_2$  cell from 38.2% to 95.3% during 100 cycles at 0.5 C (Supplementary Fig. 42). Furthermore, the  $Zn||MnO_2$  cell with an N/P ratio of 2.0 exhibited good long-term cycling stability (88.5% after 1,000 cycles at 5.0 C) (Fig. 6d) and rate performance (Supplementary Fig. 43). The high CE of Zn plating/stripping and limited  $Zn^0$  enable a high energy density of 350 Wh kg<sup>-1</sup> (218 Wh kg<sup>-1</sup> based on the weight of the cathode and anode). The in-situ-formed  $ZnF_2$  SEI helped to preserve a smooth Zn anode surface (Supplementary Fig. 44) and a uniform fluorine dispersion (Supplementary Fig. 45).

### Conclusions

A dilute and acidic aqueous Zn electrolyte was formulated with Me<sub>3</sub>EtNOTF, which enabled highly reversible and dendrite-free Zn plating/stripping at CE of 99.9% via in-situ formation of a composite interphase consisting of ZnF<sub>2</sub>, ZnCO<sub>3</sub>, ZnSO<sub>3</sub> and polyanions. This Zn<sup>2+</sup>-conducting SEI suppresses H<sub>2</sub> evolution and increases the electrochemical stability window of the electrolyte. Leveraging this high reversibility, serval Zn battery chemistries were demonstrated, all of which outperform their counterparts using an electrolyte without Me<sub>3</sub>EtNOTF. The challenging  $Zn||O_2$  system delivered high reversibility for 300 cycles, while the Zn||VOPO<sub>4</sub> battery delivered excellent cycling stability, retaining ~88.7% of its original capacity during 6,000 cycles at CE of ~100% despite limited Zn supply. Even in the most challenging anode-free configuration, 50 mAh pouch cells demonstrated 80% of capacity retention for 90 cycles. To further prove the effectiveness of ZnF<sub>2</sub> in improving Zn reversibility, an artificial ZnF<sub>2</sub> SEI was deposited on Zn<sup>0</sup> and demonstrated in a Zn||MnO<sub>2</sub> battery using limited Zn<sup>0</sup>, which displayed an extremely high energy density of 350 Wh kg<sup>-1</sup> and 88.5% capacity retention after 1,000 cycles. The identification of this electrolyte and fundamental understanding about the role of alkylammonium opens up an avenue to the development of emerging Zn chemistries.

### Online content

Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at https://doi.org/10.1038/ s41565-021-00905-4.

Received: 23 December 2020; Accepted: 17 March 2021; Published online: 10 May 2021

#### References

- 1. Turcheniuk, K., Bondarev, D., Singhal, V. & Yushin, G. Ten years left to redesign lithium-ion batteries. *Nature* **559**, 467–470 (2018).
- 2. Xu, K. Electrolytes and interphases in Li-ion batteries and beyond. *Chem. Rev.* **114**, 11503–11618 (2014).
- Wang, F. et al. Highly reversible zinc metal anode for aqueous batteries. *Nat. Mater.* 17, 543–549 (2018).
- Parker, J. F. et al. Rechargeable nickel-3D zinc batteries: an energy-dense, safer alternative to lithium-ion. Science 356, 415–418 (2017).
- Zheng, J. & Archer, L. A. Controlling electrochemical growth of metallic zinc electrodes: toward affordable rechargeable energy storage systems. *Sci. Adv.* 7, eabe0219 (2021).
- Kundu, D. et al. Aqueous vs. nonaqueous Zn-ion batteries: consequences of the desolvation penalty at the interface. *Ener. Env. Sci.* 11, 881–892 (2018).
- Bayer, M. et al. Influence of water content on the surface morphology of zinc deposited from EMImOTf/water mixtures. J. Electrochem. Soc. 166, A909–A914 (2019).
- Higashi, S., Lee, S. W., Lee, J. S., Takechi, K. & Cui, Y. Avoiding short circuits from zinc metal dendrites in anode by backside-plating configuration. *Nat. Commun.* 7, 11801 (2016).
- Zhao, Z. et al. Long-life and deeply rechargeable aqueous Zn anodes enabled by a multifunctional brightener-inspired interphase. *Energy Environ. Sci.* 12, 1938–1949 (2019).

## NATURE NANOTECHNOLOGY

- Zhang, L. et al. ZnCl<sub>2</sub> 'water-in-salt' electrolyte transforms the performance of vanadium oxide as a Zn battery cathode. *Adv. Funct. Mater.* 29, 1902653 (2019).
- 11. Luo, M. et al. PdMo bimetallene for oxygen reduction catalysis. *Nature* 574, 81–85 (2019).
- 12. Fu, J. et al. Electrically rechargeable zinc-air batteries: progress, challenges, and perspectives. Adv. Mater. 29, 1604685 (2017).
- Chang, N. et al. An aqueous hybrid electrolyte for low-temperature zinc-based energy storage devices. *Energy Environ. Sci.* 13, 3527–3535 (2020).
- Zhang, C. et al. A ZnCl<sub>2</sub> water-in-salt electrolyte for a reversible Zn metal anode. *Chem. Commun.* 54, 14097–14099 (2018).
- 15. Zhang, Q. et al. Modulating electrolyte structure for ultralow temperature aqueous zinc batteries. *Nat. Commun.* **11**, 4463 (2020).
- Xie, X. et al. Manipulating the ion-transfer kinetics and interface stability for high-performance zinc metal anodes. *Energy Environ. Sci.* 13, 503–510 (2020).
- 17. Qiu, H. et al. Zinc anode-compatible in-situ solid electrolyte interphase via cation solvation modulation. *Nat. Commun.* **10**, 5374 (2019).
- Cao, L., Li, D., Deng, T., Li, Q. & Wang, C. Hydrophobic organic-electrolyte-protected zinc anodes for aqueous zinc batteries. *Angew. Chem. Int. Ed.* 59, 19292–19296 (2020).
- 19. Suo, L. et al. 'Water-in-salt' electrolyte enables high-voltage aqueous lithium-ion chemistries. *Science* **350**, 938–943 (2015).
- 20. Sun, W. et al. A rechargeable zinc-air battery based on zinc peroxide chemistry. *Science* **371**, 46–51 (2021).
- Liu, Z. et al. Interfacial study on solid electrolyte interphase at Li metal anode: implication for Li dendrite growth. J. Electrochem. Soc. 163, A592–A598 (2016).
- Nie, M. et al. Role of solution structure in solid electrolyte interphase formation on graphite with LiPF<sub>6</sub> in propylene carbonate. *J. Phys. Chem. C* 117, 25381–25389 (2013).
- Cao, X. et al. Monolithic solid-electrolyte interphases formed in fluorinated orthoformate-based electrolytes minimize Li depletion and pulverization. *Nat. Energy* 4, 796–805 (2019).
- 24. Winiarski, J., Tylus, W., Winiarska, K., Szczygieł, I. & Szczygieł, B. XPS and FT-IR characterization of selected synthetic corrosion products of zinc expected in neutral environment containing chloride ions. *J. Spectrosc.* **2018**, 1–14 (2018).
- 25. Suo, L. et al. 'Water-in-salt' electrolyte makes aqueous sodium-ion battery safe, green, and long-lasting. *Adv. Energy Mater.* **7**, 1701189 (2017).
- Chen, Y., Cao, Y., Shi, Y., Xue, Z. & Mu, T. Quantitative research on the vaporization and decomposition of [EMIM][Tf<sub>2</sub>N] by thermogravimetric analysis–mass spectrometry. *Ind. Eng. Chem. Res.* 51, 7418–7427 (2012).

- Kroon, M. C., Buijs, W., Peters, C. J. & Witkamp, G.-J. Decomposition of ionic liquids in electrochemical processing. *Green Chem.* 8, 241–245 (2006).
- Markevich, E. et al. In situ FTIR study of the decomposition of N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)amide ionic liquid during cathodic polarization of lithium and graphite electrodes. *Electrochim. Acta* 55, 2687–2696 (2010).
- Preibisch, Y., Horsthemke, F., Winter, M., Nowak, S. & Best, A. S. Is the cation innocent? An analytical approach on the cationic decomposition behavior of N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl) imide in contact with lithium metal. *Chem. Mater.* https://doi.org/10.1021/acs. chemmater.9b04827 (2020).
- Chowdhury, F. A., Yamada, H., Higashii, T., Goto, k & Onoda, M. CO<sub>2</sub> capture by tertiary amine absorbents: a performance comparison study. *Ind. Eng. Chem. Res.* 52, 8323–8331 (2013).
- Kortunov, P. V., Siskin, M., Paccagnini, M. & Thomann, H. CO<sub>2</sub> reaction mechanisms with hindered alkanolamines: control and promotion of reaction pathways. *Energy Fuels* **30**, 1223–1236 (2016).
- Yi, Y. et al. Instability at the electrode/electrolyte interface induced by hard cation chelation and nucleophilic attack. *Chem. Mater.* 29, 8504–8512 (2017).
- Nicolas, D. et al. The role of the hydrogen evolution reaction in the solid-electrolyte interphase formation mechanism for 'water-in-salt' electrolytes. *Energy Environ. Sci.* 11, 3491–3499 (2018).
- 34. Cao, C.-N. On the impedance plane displays for irreversible electrode reactions based on the stability conditions of the steady-state. I. One state variable besides electrode potential. *Electrochim. Acta* 35, 831–836 (1990).
- Zhang, D., Li, L., Cao, L., Yang, N. & Huang, C. Studies of corrosion inhibitors for zinc-manganese batteries: quinoline quaternary ammonium phenolates. *Corros. Sci.* 43, 1627–1636 (2001).
- McKubre, M. C. H. & Macdonald, D. D. The dissolution and passivation of zinc in concentrated aqueous hydroxide. *J. Electrochem. Soc.* 128, 524–530 (1981).
- Parker, J. F., Ko, J. S., Rolison, D. R. & Long, J. W. Translating materials-level performance into device-relevant metrics for zinc-based batteries. *Joule* 2, 2519–2527 (2018).
- Liu, L. et al. In situ formation of a stable interface in solid-state batteries. ACS Energy Lett. 4, 1650–1657 (2019).

**Publisher's note** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

© The Author(s), under exclusive licence to Springer Nature Limited 2021

# ARTICLES

### **NATURE NANOTECHNOLOGY**

### Methods

**Materials.**  $Zn(CF_3SO_3)_2$  ( $Zn(OTF)_2$ ) was purchased from Tokyo Chemical Industry.  $Mn(CF_3SO_3)_2$  ( $Mn(OTF)_2$ ) (5% metallic Mn),  $V_2O_5$  powder (99.99%),  $H_3PO_4$  (85%), acetone (99.9%),  $KMnO_4$  (99.0%),  $MnSO_4H_2O$  (99.0%) and ethanol were from Sigma-Aldrich. ( $CH_3CH_2$ )( $CH_3$ )<sub>3</sub>N( $CF_3SO_3$ ) ( $Me_3ENOTF$ ) was synthesized at the Army Research Laboratory. De-ionized (DI) water (HPLC grade) was purchased from Sigma-Aldrich. Zn foil, Ti foil and Ti gauze were purchased from Alfa Aesar. Carbon paper was purchased from Fuel Cell Store.

VOPO<sub>4</sub>·2H<sub>2</sub>O powder was synthesized according to the previous literature<sup>39,40</sup>. In detail, the mixture of 24 g of V<sub>2</sub>O<sub>5</sub> powder in 140 ml of 85% H<sub>3</sub>PO<sub>4</sub> and 400 ml of DI water was refluxed at 110 °C for 20 h. The VOPO<sub>4</sub>·2H<sub>2</sub>O powder with a yellow-green colour was centrifuged, washed with acetone and kept under ambient conditions. The VOPO<sub>4</sub> was obtained by calcining the as-synthesized VOPO<sub>4</sub>·2H<sub>2</sub>O powder at 500 °C for 6 h in air. The colour of resulting VOPO<sub>4</sub> powder was yellow.  $\beta$ -MnO<sub>2</sub> nanoparticles were prepared via a hydrothermal method. To be specific, 15.8 g of KMnO<sub>4</sub> in 40 ml DI water and 101.4 g of MnSO<sub>4</sub>·H<sub>2</sub>O in 20 ml DI water was transferred into an 80 ml Teflon-lined autoclave and maintained at 140 °C for 24 h. The product above was centrifuged, then washed thoroughly using water and/or ethanol several times before drying at 60 °C for 24 h.

Material characterizations. The morphologies of the samples were investigated by SEM (Hitachi SU-70) equipped with an energy-dispersive X-ray spectroscopy detector and TEM (JOEL 2100F). All of the samples for ex-situ SEM and TEM were recovered from a full aqueous battery in a 2032 coin-cell configuration after electrochemical cycling. Contact angles between the electrolyte and electrode surface were measured at room temperature using the sessile drop method<sup>41</sup>. Using a contact-angle goniometer (Ramé-Hart, 250-00), a drop of electrolyte was dispensed from a syringe onto the Zn electrode surface, and a drop image was captured. The contact angle was measured between the solid/liquid interface and the tangent line to the drop shape at the liquid/ vapour interface. Gas chromatography was performed on an Agilent 7890B gas chromatograph. 1H nuclear magnetic resonance spectra were acquired on a Bruker DRX 500 spectrometer at a <sup>1</sup>H frequency of 500 MHz, using the chemical shift of the <sup>1</sup>H nucleus in pure water as 4.7 ppm reference. All nuclear magnetic resonance measurements were conducted at 298 K. Fourier-transform infrared spectroscopy was performed with a Nicolet 6700 spectrometer and a Golden Gate single-reflection monolithic diamond attenuated-total-reflection sample cell. Raman spectra were collected with a Horiba Jobin Yvon Labram Aramis using a 532 nm diode-pumped solid-state laser between 2,600  $\rm cm^{-1}$  and 100  $\rm cm^{-1}$ Laser power was set at ~150-450 mV, and 400 scans were accumulated with a resolution of 2 cm<sup>-1</sup>. XPS data were collected using a high-sensitivity XPS (Kratos AXIS 165, Mg Ka radiation). The C1s peak (284.6 eV) was used as the reference to calibrate other binding energy values. The electrodes were rinsed and dried under vacuum before characterizations. The contents of different species in the SEI layers were obtained by fitting the whole XPS spectra using Casa XPS software. The depth-reaching rate for the Ar sputtering is estimated to be ~1.0 nm s<sup>-1</sup>. The distribution of the constituent elements at different depths in the cycled Zn metal was analysed using time-of-flight secondary-ion mass spectroscopy attached to a Ga+ focused-ion beam SEM (Tescan GAIA3) at an accelerated voltage of 20 kV and 1 nA current. Thermogravimetric analysis experiments were performed with a TA Q600 differential scanning calorimeter. X-ray absorption spectroscopy measurements were performed at the 7-BM beamline of the National Synchrotron Light Source II at Brookhaven National Laboratory in the fluorescence mode.

Electrochemical measurements. The VOPO4 or MnO2 cathode was prepared by compressing active material, carbon black and polytetrafluoroethylene at a weight ratio of 8/1/1 onto the Ti mesh. For the anode-free pouch cells, the cathode was fabricated by blending VOPO4 powder, Super P carbon and polyvinylidene fluoride in a weight ratio of 8/1/1 using N-methyl-2-pyrrolidone as solvent. The obtained slurry was pasted onto a Ti foil and vacuum dried at 100 °C for 12 h. The loading mass of active material was ~3 mg cm<sup>-2</sup>. Filter paper was employed as the separator. We used  $4 \text{ m Zn}(\text{OTF})_2$  and  $4 \text{ m Zn}(\text{OTF})_2 + 0.5 \text{ m Me}_3\text{EtNOTF}$  aqueous solutions as electrolytes. Ti plate with pre-deposited Zn served as the anode. All Zn from the anode was discharged to the cathode before cycling. A higher energy density of ~136 Wh kg<sup>-1</sup> was achieved. For air batteries, the O<sub>2</sub> cathode was prepared by mixing 70% carbon black and 30% polyvinylidene difluoride in *N*-methylpyrrolidone, and the slurry mixture was then coated on carbon paper. After coating, the electrodes were dried at 80 °C for 10 min to remove the solvent before pressing. The electrodes were cut into 1  $\rm cm^2$  sheets, vacuum dried at 100  $^{\rm o}\rm C$ for 24 h and weighed before assembly. The mass of zinc and air electrode for the Zn||O<sub>2</sub> cell are 1.238 mg and 0.7 mg, respectively. Cyclic voltammetry was carried out using a GAMRY interface 1000E electrochemical work station. The chargedischarge experiments were performed on a Land BT2000 battery test system at room temperature.

**Ab initio calculations.** Cluster calculations for reaction energies and free energies were performed with Gaussian 16 rev. C.01 using M05-2X/6-31++ $G(d_p)$ , M05-2X/6-311++ $G(3d_{f,2}pd)$ , M06-2X/6-311++ $G(3d_{f,2}pd)$ , wB97XD/6-311++ $G(3d_{f,2}pd)$ 

and CBS-QB3 model chemistries (refs.  $^{42-47}$ ). All complexes were immersed in implicit solvent represented using the polarizable continuum model (water) solvation model unless otherwise stated<sup>48</sup>. Raman spectra were computed at the M05-2X/6-31++G(*d*,*p*) level.

**MD** simulations. MD simulations were performed on 4 m Zn(OTF)<sub>2</sub> and 4 m Zn(OTF)<sub>2</sub> + 0.5 m Me<sub>3</sub>EtNOTF electrolytes using a simulation cell shown in Supplementary Fig. 33a. Composition of the simulation cells and lengths of the simulation trajectories are given in Supplementary Table 2 together with the predicted transport properties. The double layer of 4 m Zn(OTF)<sub>2</sub> + 0.5 m Me<sub>3</sub>EtNOTF electrolyte at the model graphite electrode was studied in a separate set of MD simulations as a function of applied electrode potential using the set-up shown in Supplementary Fig. 46. The electrodes comprised of three graphene layers, each layer having 336 carbon atoms and a cross-sectional area of 29.88 Å × 29.57 Å. The distance between electrodes was 85.6 Å. It was chosen such that the electrolyte density in the middle of the simulation cell matched that from a bulk MD simulation. The equilibration runs were performed at 363 K for 8 ns.

The equations of motion were solved with a time-reversible<sup>49</sup> (reference system propagator algorithms) integrator over the following time resolutions: (1) the contribution from bonds and angles to the forces were calculated every 0.5 fs, (2) the contribution of dihedrals and non-bonded forces within 7.5 Å cut-off were updated every 1.5 fs and (3) the remainder of the forces (reciprocal space Ewald and non-bonded forces within 11 Å cut-off for double layer simulations and 16 Å for bulk simulations) were updated every 3 fs. A Nosé–Hoover<sup>50</sup> thermostat was used for temperature control. An archive containing all input files needed to perform bulk MD simulations is included in the Supplementary Information.

The electrolyte was modelled using APPLE&P (ref. <sup>51</sup>) polarizable force field with induced point dipoles dumped at short distance via the Thole<sup>52</sup> model and a dampening parameter  $a_{\text{Thole}} = 0.4$ . The electrode layer closest to the electrolyte was charged at a constant potential using the Siepmann and Reed charge equilibration technique<sup>53,54</sup> for electronic conductors. This charge equilibration method calculates on the fly the electrode charges such that they minimize the total electrostatic energy of the system under the constraints of a constant electrostatic potential imposed on the position of each electrode atom. The fluctuating electrode charges were calculated numerically via self-consistent iterations every 150 fs (50 time steps). The electrode charges were Gaussian-distributed with widths of 0.5 Å (refs. <sup>54,55</sup>). The position of the electrode atoms was constrained during simulations.

### Data availability

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

### References

- Yamamoto, N., Okuhara, T. & Nakato, T. Intercalation compound of VOPO<sub>4</sub>·2H<sub>2</sub>O with acrylamide: preparation and exfoliation. *J. Mater. Chem.* 11, 1858–1863 (2001).
- Wang, F. et al. How water accelerates bivalent ion diffusion at the electrolyte/ electrode interface. Angew. Chem. Int. Ed. 57, 11978–11981 (2018).
- Horng, P., Brindza, M. R., Walker, R. A. & Fourkas, J. T. Behavior of organic liquids at bare and modified silica interfaces. *J. Phys. Chem. C* 114, 394–402 (2010).
- 42. Frisch, M. J. et al. Gaussian 16, Revision C.01 (Gaussian, Inc., 2016).
- Frisch, M. J., Pople, J. A. & Binkley, J. S. Self-consistent molecular orbital methods. 25. Supplementary functions for Gaussian basis sets. *J. Chem. Phys.* 80, 3265–3269 (1984).
- 44. Zhao, Y., Schultz, N. E. & Truhlar, D. G. Design of density functionals by combining the method of constraint satisfaction with parametrization for thermochemistry, thermochemical kinetics, and noncovalent interactions. *J. Chem. Theory Comput.* **2**, 364–382 (2006).
- 45. Zhao, Y. & Truhlar, D. G. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.* **120**, 215–241 (2008).
- Chai, J.-D. & Head-Gordon, M. Long-range corrected hybrid density functionals with damped atom-atom dispersion corrections. *Phys. Chem. Chem. Phys.* 10, 6615–6620 (2008).
- Montgomer, J. A. Jr., Frisch, M. J., Ochterski, J. W. & Petersson, G. A. A complete basis set model chemistry. VI. Use of density functional geometries and frequencies. J. Chem. Phys. 110, 2822–2827 (1999).
- Scalmani, G. & Frisch, M. J. Continuous surface charge polarizable continuum models of solvation. I. General formalism. *J. Chem. Phys.* 132, 114110 (2010).
- Martyna, G. J., Tuckerman, M. E., Tobias, D. J. & Klein, M. L. Explicit reversible integrators for extended systems dynamics. *Mol. Phys.* 87, 1117–1157 (1996).

## NATURE NANOTECHNOLOGY



- 50. Hoover, W. G. Canonical dynamics: equilibrium phase-space distributions. *Phys. Rev. A* **31**, 1695–1697 (1985).
- Borodin, O. Polarizable force field development and molecular dynamics simulations of ionic liquids. J. Phys. Chem. B 113, 11463–11478 (2009).
- Thole, B. T. Molecular polarizabilities calculated with a modified dipole interaction. *Chem. Phys.* 59, 341–350 (1981).
- Siepmann, J. I. & Sprik, M. Influence of surface topology and electrostatic potential on water/electrode systems. *J. Chem. Phys.* 102, 511–524 (1995).
- Reed, S. K., Lanning, O. J. & Madden, P. A. Electrochemical interface between an ionic liquid and a model metallic electrode. *J. Chem. Phys.* 126, 084704 (2007).
- Vatamanu, J., Borodin, O. & Smith, G. D. Molecular dynamics simulations of atomically flat and nanoporous electrodes with a molten salt electrolyte. *Phys. Chem. Chem. Phys.* 12, 170–182 (2010).

### Acknowledgements

C.W. acknowledges funding support from the US Department of Energy (DOE) through ARPA-E grant DEAR0000389 and the Center of Research on Extreme Batteries. Modelling and experimental work at Army Research Laboratory was supported by the Joint Center for Energy Storage Research, an Energy Innovation Hub funded by the US Department of Energy under cooperative agreement no. W911NF-19-2-0046. E.H. and X.-Q.Y. are supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Vehicle Technology Office of the US DOE through the Advanced Battery Materials Research Program under contract no. DE-SC0012704. This research used beamline 7-BM of the National Synchrotron Light Source II, a US DOE Office of Science User Facility operated for the DOE Office of Science by Brookhaven National Laboratory under contract no. DESC0012704.

### Author contributions

L. Cao and D.L. designed the experiments and analysed data. K.X. synthesized the asymmetric ammonium salt. T.P., O.B. and J.V. conducted the calculations. T.D., C.Y., L. Chen, L.M., Q.L. and S.H. assisted with the material synthesis and characterizations. E.H. and X.-Q.Y. did X-ray absorption spectroscopy measurement and data analysis. M.D. performed conductivity and differential scanning calorimetry measurements. K.G. assisted with XPS analysis. M.J.H. and J.T.F. assisted with contact-angle testing. K.X., O.B. and C.W. conceived and supervised the project. All authors contributed to interpretation of the results.

### **Competing interests**

The authors declare no competing interests.

### Additional information

**Supplementary information** The online version contains supplementary material available at https://doi.org/10.1038/s41565-021-00905-4.

Correspondence and requests for materials should be addressed to K.X., O.B. or C.W.

**Peer review information** *Nature Nanotechnology* thanks the anonymous reviewers for their contribution to the peer review of this work.

Reprints and permissions information is available at www.nature.com/reprints.