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## **Design of a Solid Electrolyte Interphase for Aqueous Zn Batteries**

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Abstract: Aqueous Zn batteries are challenged by water decomposition and dendrite growth due to the absence of a dense Zn-ion conductive solid electrolyte interphase (SEI) to inhibit the hydrogen evolution reaction (HER). Here, we design a low-concentration aqueous  $Zn(OTF)_2$ - $Zn(NO_3)_2$ electrolyte to in situ form a robust inorganic  $ZnF_2$ - $Zn_5(CO_3)_2$ -(OH)<sub>6</sub>-organic bilayer SEI, where the inorganic inner layer promotes Zn-ion diffusion while the organic outer layer suppresses water penetration. We found that the insulating  $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$  layer is first formed on the Zn anode surface by the self-terminated chemical reaction of  $NO_3^-$  with  $Zn^{2+}$  and  $OH^{-}$  generated via HER, and then it transforms into Zn-ion conducting  $Zn_5(CO_3)_2(OH)_6$ , which in turn promotes the formation of  $ZnF_2$  as the inner layer. The organicdominated outer layer is formed by the reduction of OTF<sup>-</sup>. The in situ formed SEI enables a high Coulombic efficiency (CE) of 99.8% for 200 h in Ti || Zn cells, and a high energy density (168 Wh kg<sup>-1</sup>) with 96.5 % retention for 700 cycles in  $Zn \parallel MnO_2$  cells with a low  $Zn/MnO_2$  capacity ratio of 2:1.

### Introduction

The aqueous Zn battery is promising for large-scale energy storage owing to its high theoretical capacity (820 mAhg<sup>-1</sup>), the high abundance of Zn, and its intrinsic safety.<sup>[1]</sup> Since the reduction potential of Zn (-0.762 V vs. standard hydrogen electrode (SHE)) is more negative than that of hydrogen evolution reaction (HER), water is reduced to  $H_2$  during Zn deposition (Figure 1a), which changes the local pH to strongly alkaline.<sup>[2]</sup> The alkaline environment corrodes the Zn anode surface by formation of porous Zn(OH)<sub>2</sub> and ZnO.<sup>[3]</sup> The inhomogeneous morphology of the Zn(OH)<sub>2</sub> and ZnO-based layer on Zn anode surface induces the Zn dendrite growth, reducing the Coulombic efficiency (CE) of Zn plating/stripping and leading to rapid battery failure.[4]

To suppress water decomposition and Zn dendrite growth, extensive efforts are devoted to constructing artificial solid

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electrolyte interphase (SEI) by coating inorganic<sup>[5]</sup> or polymer<sup>[6]</sup> on Zn surface that allow Zn<sup>2+</sup> to transport but block water penetration to Zn surface. Unfortunately, these interphases suffer from crack and/or degradation during repeat volume changes of cycles.<sup>[7]</sup> Since these artificial SEI are not self-reparable as that of in situ formed SEI, they gradually lose the function of protection. Therefore, it is highly desired to form SEI by in situ decomposition of electrolyte components on electrode surface. The decomposition of organic triflate anion (OTF<sup>-</sup>)<sup>[8]</sup> in high-concentration aqueous 21 m LiTFSI + 7 m LiOTF electrolyte has been proved to form electrically insulating and ionically conductive fluorinated inorganic-organic composite SEI, effectively protecting anode and preventing electrolyte decomposition while allowing lithium ion to cross in lithium batteries. However, the in situ formation of robust fluorinated SEI in low-concentration aqueous Zn batteries has been challenged. Even if a SEI can be formed during Zn plating in a low-concentration aqueous electrolyte, the hydrogen gas evolution during SEI formation will blow the formed SEI away. To promote SEI formation while suppressing H<sub>2</sub> gas generation during Zn plating in lowconcentration aqueous electrolytes, additives with a high reduction potential are normally added. However, long Zn plating/stripping cycles are needed for forming a dense SEI since H<sub>2</sub> gas evolution cannot be completely inhibited by additives, which reduces the average CE.

Here, we completely prevented the H<sub>2</sub> gas evolution during Zn plating/stripping by adding 20 mM Zn(NO<sub>3</sub>)<sub>2</sub> additive into aqueous 3 M Zn(OTF)<sub>2</sub> electrolyte (denoted as  $Zn(OTF)_2$ - $Zn(NO_3)_2$ ) to chemically form a thin and dense  $Zn_{5}(OH)_{8}(NO_{3})_{2}$   $\cdot 2H_{2}O$  passivation layer upon the contact of Zn with electrolyte which blocks water penetration. Since the passivation layer is self-repairing, hydrogen evolution will be prevented even if the passivation layer cracks during Zn plating/stripping cycles. Upon contact of Zn with Zn(OTF)2- $Zn(NO_3)_2$  electrolyte, water reduces on Zn surface generating a local alkaline environment, which triggers the thermodynamically and kinetically favourable reaction between Zn and NO<sub>3</sub><sup>-/</sup>OH<sup>-</sup> and forms an electrically and ionically resistive  $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$  passivation layer<sup>[9]</sup> before Zn electrodeposition. The Zn<sub>5</sub>(OH)<sub>8</sub>(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O layer inhibits water penetration onto Zn surface, which allows reduction of OTFanion to form SEI on Zn surface. As an intermediate template layer, Zn<sub>5</sub>(OH)<sub>8</sub>(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O layer gradually transforms into a more stable Zn-ion conductive Zn<sub>5</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>6</sub> layer through metathesis reaction due to the lower solubility product  $(2.0 \times 10^{-15})$  of  $Zn_5(CO_3)_2(OH)_6$  than that  $(7.4 \times 10^{-15})_2(OH)_6$  $10^{-11}$ ) of Zn<sub>5</sub>(OH)<sub>8</sub>(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O<sup>[9]</sup> when CO<sub>3</sub><sup>2-</sup> forms from the reduction of  $Zn(OTF)_2$ . At the same time, the organic components out-layer forms from the reaction between  $(CF_3SO_3)^-$  and  $NO_3^-$  acting as flexible protection layer, and

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*Figure 1.* Illustration of surface evolution mechanism. a) Zn dendrite growth in aqueous electrolytes. The water-passivation-induced porous ZnO layer (purple) constantly breaks and reforms, leading to non-uniform Zn electrodeposition, dendrite formation, and dead Zn during Zn plating/ stripping. b) Formation mechanism of  $ZnF_2-Zn_5(CO_3)_2(OH)_6$ -organic SEI. The presence of  $NO_3^-$  promotes the formation of an electrically and ionically insulating  $Zn_5(OH)_8(NO_3)_2$ : 2H<sub>2</sub>O layer (red), which subsequently transforms into an electrically insulating but ionically conductive SEI in which the  $ZnF_2-Zn_5(CO_3)_2(OH)_6$  inner part is coated by the organic outer part.

the zinc ion conducting  $ZnF_2$  forms in the inner part (Figure 1 b). The highly flexible organic outer layer prevents SEI from crack due to volumetric change and facilitates solvated Zn ion to immigrate. The hydrophobic  $ZnF_2$  in the inner layer further removes solvated water and suppresses water decomposition and Zn dendrite growth by preventing direct contact of zinc with water but allows  $Zn^{2+}$  to transport through. This robust SEI enhanced the Zn plating/stripping CE to 99.8% in 200 h. The Zn || MnO<sub>2</sub> batteries show a high capacity stability with an extremely low capacity delay rate of only 0.005% per cycle for 700 cycles.

### **Results and Discussion**

#### In Situ Formation of SEI on Zn Anodes

The Zn surface passivation was formed by immersing Zn plate in Zn(OTF)<sub>2</sub>-Zn(NO<sub>3</sub>)<sub>2</sub> electrolyte (pH 3.8). After 4 h treatment in Zn(OTF)<sub>2</sub>-Zn(NO<sub>3</sub>)<sub>2</sub> electrolyte at room temperature, the color of Zn metal surface changed from light silver to gray (Supplementary Figure 1). X-ray powder diffraction (XRD) in Supplementary Figure 2 demonstrated that Zn<sub>5</sub>(OH)<sub>8</sub>(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O passivation layer was formed based on the chemical reaction<sup>[9]</sup> in Figure 1b. For comparison, Zn was also immersed in Zn(OTF)<sub>2</sub> reference aqueous electrolyte (pH 3.6). However, well-identified peaks of ZnO/  $Zn(OH)_2$  (Supplementary Figure 3) were observed. The Zn surface passivation layer morphologies were characterized using the scanning electron microscopy (SEM). Supplementary Figure 4 show that Zn<sub>5</sub>(OH)<sub>8</sub>(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O passivation layer presents a compact sheet stacking morphology, which can suppress water decomposition by separating water from Zn anode, confirmed by a smaller change of pH values (from 3.8 to 4.0 than that from 3.6 to 4.0 in  $Zn(OTF)_2$ ) electrolyte during Zn immersion test. However, the Zn plate surface after treatment in  $Zn(OTF)_2$  electrolyte showed cracked surface. The electrochemical behaviors of Zn electrode in different electrolytes were investigated using Zn || Ti cells with cyclic voltammetry (CV). As shown in the CV curves in  $Zn(OTF)_2$ - $Zn(NO_3)_2$  electrolyte (Figure 2a), in the first cathodic scan, the in situ formed  $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$  passivation layer suppressed Zn plating potential to a very low potential of -0.37 V, with a small Zn stripping peak at a very high potential of 0.31 V. The Zn plating/stripping overpotentials gradually reduced with charge/discharge cycles and show a normal Zn plating peak at -0.15 V and Zn stripping peak at +0.15 V at the 10th charge/discharge cycle. Therefore, the  $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$  layer gradually becomes a high Zn-ion conductor during Zn plating/stripping cycles. In contrast, Zn plating/stripping peaks at +0.15/-0.15 V were observed in the Zn(OTF)<sub>2</sub> reference electrolyte (Supplementary Figure 5) due to formation of porous ZnO/Zn(OH)<sub>2</sub> layer on Zn.

The formation of Zn<sub>5</sub>(OH)<sub>8</sub>(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O passivation layer is attributed to the unique Zn<sup>2+</sup> solvation sheath structure in bulk electrolyte. Nuclear magnetic resonance (NMR) demonstrated that only 20 mM NO<sub>3</sub><sup>-</sup> additive can move the  $^{65}$ Zn chemical shift from 2.0 ppm in Zn(OTF)<sub>2</sub> reference electrolyte to 0.7 ppm in  $Zn(OTF)_2$ - $Zn(NO_3)_2$ electrolyte (Supplementary Figure 6a), indicating a shielding effect of the solvation sheath on Zn nucleus. This is because that  $NO_3^{-1}$  is involved in solvation sheath and replaces some OTF<sup>-</sup> due to larger electron-donating ability of NO<sub>3</sub><sup>-</sup> than that of OTF<sup>-</sup>. Additionally, the <sup>17</sup>O chemical shift of OTF<sup>-</sup> showed a downshift with the addition of NO<sub>3</sub><sup>-</sup> (Supplementary Figure 6b), confirming that  $NO_3^-$  anions entered the Zn<sup>2+</sup> solvation sheath. Both <sup>65</sup>Zn and <sup>17</sup>O NMR spectroscopy demonstrated that  $Zn^{2+}$  preferentially coordinates with NO<sub>3</sub><sup>-</sup> instead of OTF<sup>-</sup>, which is beneficial for the generation of  $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O.$ 

During 10 activation cycles, insulating  $Zn_5(OH)_8$ -(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O layer gradually converts into Zn-ion conducting  $Zn_5(CO_3)_2(OH)_6$  SEI as evidenced by XRD (Supplementary Figure 2), which enables reversible Zn plating/stripping (Figure 2a), but suppresses water reduction. The conversion of  $Zn_5(OH)_8(NO_3)_2$ ·2H<sub>2</sub>O into  $Zn_5(CO_3)_2(OH)_6$  is attributed to the replacement of NO<sub>3</sub><sup>-</sup> by CO<sub>3</sub><sup>-</sup>, which are generated





**Figure 2.** a) CV curves of Zn || Ti half cells with Zn(OTF)<sub>2</sub>-Zn(NO<sub>3</sub>)<sub>2</sub> electrolyte. b) Galvanostatic Zn plating/stripping in the Zn/Zn symmetrical cell at 0.5 mA cm<sup>-2</sup> and 0.5 mA cm<sup>-2</sup>. c) Schematic illustration of the home-built system for in situ detection of hydrogen gas evolution with a gas chromatograph (GC). Peak of hydrogen gas released from Zn || Zn cells using d) Zn(OTF)<sub>2</sub>-Zn(NO<sub>3</sub>)<sub>2</sub> and e) Zn(OTF)<sub>2</sub> electrolytes before and after cycling. f) Interfacial impedance measured from Zn || Zn cells in Zn(OTF)<sub>2</sub>-Zn(NO<sub>3</sub>)<sub>2</sub> and Zn(OTF)<sub>2</sub> electrolytes under cycling. g) Zn plating/ stripping CE in different electrolytes (inset: magnified view of Zn plating/stripping CE in Zn(NO<sub>3</sub>)<sub>2</sub> electrolyte).



**Figure 3.** SEM images of surface and cross-section Zn electrodes recovered from Zn || Zn symmetrical cells after 100 plating/striping cycles in a–c) Zn(OTF)<sub>2</sub>, and d–f) Zn(OTF)<sub>2</sub>-Zn(NO<sub>3</sub>)<sub>2</sub> electrolytes. (a,b) and (d,e) are surface morphologies of Zn metal. Red lines in SEM images (c,f) indicated the etching depth of the Zn metal cycled in different electrolytes.

mainly from  $OTF^-$  reduction with minor contribution from dissolved CO<sub>2</sub>, because the solubility product  $(2.0 \times 10^{-15})$  of

 $Zn_5(CO_3)_2(OH)_6$  in water is three order of magnitude lower than that  $(7.4 \times 10^{-11})$  of  $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O^{[9]}$  To validate the conversion of  $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$  into  $Zn_5(CO_3)_2$ -(OH)<sub>6</sub> through reduction of OTF<sup>-</sup> into CO<sub>3</sub><sup>-</sup>, synthesized Zn<sub>5</sub>(OH)<sub>8</sub>(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O<sup>[10]</sup> powers were coated on inert Ti electrode and scanned using CV in an inert electrolyte, that is, 1 M NaCl aqueous electrolyte (Supplementary Figure 7 a-d). Since the insulative  $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$  cannot transit into Zn-ion conductive Zn<sub>5</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>6</sub> in 1 M NaCl aqueous electrolyte, the Zn-ion insulating Zn<sub>5</sub>(OH)<sub>8</sub>(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O layer on Ti shifted the Zn plating and water reduction potential to -0.6 V vs.  $Zn/Zn^{2+}$ , while the Zn can be normally stripped at a low potential of 0.15 V due to formation of microcracks (Supplementary Figure 7d). However, after 10 cycles, the Zn plating/stripping was completely inhibited on Zn<sub>5</sub>(OH)<sub>8</sub>(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O coated on Ti electrode because the formation of ZnO during charge/discharge sealed the cracks (Supplementary Figure 7d). Therefore, the formation of insulating  $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$  passivation layer on Zn after immersion in  $Zn(OTF)_2$ - $Zn(NO_3)_2$  electrolyte suppressed water decomposition while the OTF- reduction during followed activation cycles converted the insulating

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**Figure 4.** The composition of the SEI layer. X-ray photoelectron spectroscopy (XPS) of a) N 1s, b) C 1s, and c) F 1s, which are displayed in rows, with corresponding durations of  $Ar^+$  sputtering in columns. d) Atomic composition of the SEI on Zn after 50 plating/stripping cycles in Zn(OTF)<sub>2</sub>-Zn(NO<sub>3</sub>)<sub>2</sub> electrolyte. e,f) The time-of-flight secondary-ion mass spectrometry (TOF-SIMS) analysis of the SEI using a Ga<sup>+</sup> ion beam of 5  $\mu$ m x 5  $\mu$ m area. e) The crater sputtered by the Ga<sup>+</sup> ion beam. f) TOF-SIMS analysis for the F element.

 $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$  layer into Zn-ion conducting  $Zn_5 - (CO_3)_2(OH)_6$  SEI without damaging from  $H_2$  evolution, which has never been reported before.

The effect of  $Zn(NO_3)_2$  additive on the reversibility of Zn plating/stripping in Zn(OTF)<sub>2</sub> electrolyte was investigated using a Zn/Zn symmetric cell under galvanostatic condition (Figure 2b). After the initial activation, the symmetric Zn/Zn cell using  $Zn(OTF)_2$ - $Zn(NO_3)_2$  electrolyte exhibited steady charge/discharge process over 1200 h. In contrast, the Zn/Zn cell using  $Zn(OTF)_2$  reference electrolyte shorted after 480 h. The larger average overpotential ( $\approx$  77 mV) of Zn/Zn cells at  $0.5 \text{ mA cm}^{-2}$  in the first cycle in  $Zn(OTF)_2$ - $Zn(NO_3)_2$  electrolyte than that ( $\approx 30 \text{ mV}$ ) in Zn(OTF)<sub>2</sub> electrolyte (Figure 2b) is attributed to the large  $Zn^{2+}$  transport resistance in the  $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$  passivation layer than that in the porous  $ZnO/Zn(OH)_2$  layer. However, the overpotential of Zn plating/stripping in Zn(OTF)<sub>2</sub>-Zn(NO<sub>3</sub>)<sub>2</sub> electrolyte gradually decreased and eventually stabilized at  $\approx 20 \text{ mV}$  due to the transformation of ionic-resistant Zn<sub>5</sub>(OH)<sub>8</sub>(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O passivation layer into a high Zn<sup>2+</sup> transport SEI. Furthermore, the plating/stripping reversibility of Zn anode in two electrolytes were compared at a high current density of 10 mA cm<sup>-2</sup> and a high capacity of 10 mAh cm<sup>-2</sup>. As shown in Supplementary Figure 8, the cell using Zn(OTF)<sub>2</sub> electrolyte shorted after only 29 h, while the cell using  $Zn(OTF)_2$ - $Zn(NO_3)_2$ electrolyte operated steadily for >90 h, confirming the robustness of SEI even at a high current density and high area capacity. The chemical formation of water-proof passivation layer on Zn anodes, followed by gradual conversion into zinc-ion conductive SEI during Zn plating/stripping cycles, lays the foundation for designing high power, high energy and long cycle Zn batteries.

The chemically preformed  $Zn_5(OH)_8(NO_3)_2$ ·2H<sub>2</sub>O passivation layer promoted the formation of  $Zn_5(CO_3)_2(OH)_6$  SEI by suppressing H<sub>2</sub> evolution. The hydrogen gas evolution during Zn plating/stripping in two electrolytes was investigated by operando monitoring evolved hydrogen using a home-built system (Figure 2 c). The evolved hydrogen gas, released from meshed Zn/Zn cells, was transferred from a sealed container to an online gas chromatograph (GC) using nitrogen as a carrier gas. The low and also rapidly reduced hydrogen evolution in Zn(NO<sub>3</sub>)<sub>2</sub>-contained electrolyte (Figure 2 d) during Zn plating/stripping cycles, contrary to the reference electrolyte (Figure 2 e), confirmed the effective suppression of hydrogen evolution by preformed passivation layer.

The Zn-ion conduction increase during transition from  $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$  to  $Zn_5(CO_3)_2(OH)_6$  was confirmed by interfacial impedance spectroscopy (EIS). The EIS of Zn/Zn symmetric cells after charge/discharge at 0.5 mA cm<sup>-2</sup> and 0.5 mAh cm<sup>-2</sup> was recorded. In Figure 2 f and Supplementary Figure 9, the interface impedance (impedance of charge-

transfer plus passivation interphase resistance) of Zn/Zn cells in  $Zn(OTF)_2$ - $Zn(NO_3)_2$  electrolyte before cycle show ionic insulating nature with a large interface impedance of 11350 ohm due to the formation of  $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ passivation layer. However, the interface impedance quickly reduced to 114 ohm after 10 plating/stripping cycles because Zn plating/stripping triggered the transformation of ionicinsulating Zn<sub>5</sub>(OH)<sub>8</sub>(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O layer into a fast-ion conducting Zn<sub>5</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>6</sub> layer. After 10 Zn plating/stripping cycles, the interface resistance of dense  $Zn_5(CO_3)_2(OH)_6$ (Supplementary Figure 4c-e) passivated Zn is slightly larger than that of passivated by porous undesirable byproducts (such as  $Zn(OH)_2$ ,  $xZnCO_3 \cdot yZn(OH)_2 \cdot zH_2O$  and ZnO) formed on Zn surface with hydrogen evolution interference in Zn(OTF)<sub>2</sub> electrolyte (Supplementary Figure 3, Supplementary Figure 4 f-h). Different from phase-transition induced resistance-reduction of Zn/Zn cell in the initial 10 charge/discharge cycles in  $Zn(OTF)_2$ - $Zn(NO_3)_2$  electrolyte, the initial decrease in the interface resistance for Zn/Zn cell in Zn(OTF)<sub>2</sub> electrolytes is mainly attributed to activation process. Therefore, the presence of  $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ passivation layer inhibited Zn corrosion and created a water/ gas-free microenvironment on Zn surface, promoting the formation of a robust SEI.

The impact of NO<sub>3</sub><sup>-</sup> additive on Zn plating/stripping CE was investigated using Zn/Ti cells at 1 mA cm<sup>-2</sup> and  $0.5 \text{ mAh cm}^{-2}$  (Figure 2g, Supplementary Figure 10). Figure 2g showed that the CE in  $Zn(OTF)_2$ - $Zn(NO_3)_2$  electrolyte quickly increased from 63.3% at the first cycle to 99.8% within the initial 20 cycles with an average CE of 95.7%, and then stabilized at > 99.8 % for > 200 cycles, with an average CE of 99.4% for the entire 200 cycles. In contrast, the CE in the  $Zn(OTF)_2$  reference electrolyte reached  $\approx 95\%$  in the initial few cycles, but quickly drop to <90% after 10 cycles before short circuit at the 25<sup>th</sup> cycle. Therefore, the NO<sub>3</sub><sup>-</sup> additive effectively suppressed side reactions between Zn and water, increasing Zn plating/stripping CE. The activation process along with phase transition from Zn<sub>5</sub>(OH)<sub>8</sub>-(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O into Zn<sub>5</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>6</sub> based SEI in Zn(OTF)<sub>2</sub>- $Zn(NO_3)_2$  electrolyte was also evidenced by quickly reduced overpotential from 205 mV at the beginning to 85 mV at 200<sup>th</sup> cycle (Supplementary Figure 11 a, b). Although the Zn plating/stripping behavior of Zn || Ti cells in Zn(OTF)<sub>2</sub> electrolyte shows a low overpotential (71 mV to 40 mV) due to low diffusion resistance of porous passivation layer, the Zn stripping curves are not stable due to Zn dendrite growth (Supplementary Figure 11 c, d).

#### Morphology and Structure of SEI on Zn Anodes

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The Zn deposition morphologies and cross-sectional views of Zn-metal anode in different electrolytes were observed using SEM (Figure 3). Zn surface after 100 cycles in Zn(OTF)<sub>2</sub> reference electrolyte showed mossy growth (Figure 3a, b), where a cross-section of the 20  $\mu$ m thick plated Zn reveals highly porous Zn deposition (Figure 3c). This morphology was caused by continuous side reactions between Zn and electrolyte, as evidenced by a low CE (<90%)

(Figure 2d) and poor cycling stability. In contrast, in Zn-(OTF)<sub>2</sub>-Zn(NO<sub>3</sub>)<sub>2</sub> electrolyte, the Zn metal maintained a dense and smooth surface (Figure 3d, e), evidenced by decreased thickness of cycled Zn from 20  $\mu$ m in Zn(OTF)<sub>2</sub> reference electrolyte to 9.5  $\mu$ m (Figure 3c, f). Therefore, NO<sub>3</sub><sup>-</sup> induced hydrophobicity SEI on Zn surface (Supplementary Figure 12) effectively suppressed Zn dendrite growth and parasitic reactions between Zn anode and water, leading to compact and smooth Zn deposition. Furthermore, the surface passivation layer in different electrolytes were investigated using transmission electron microscopy (TEM) (Supplementary Figure 13). A 3.5 nm SEI layer was observed on the surface of cycled Zn in Zn(OTF)<sub>2</sub>-Zn(NO<sub>3</sub>)<sub>2</sub> electrolyte, confirming the NO<sub>3</sub><sup>-</sup> induced formation of SEI layer.

The SEI composition on the Zn anode after 50 plating/ stripping cycles was analyzed using X-ray photoelectron spectroscopy (XPS) facilitated by Ar<sup>+</sup> sputtering. On the surface (before sputtering) of SEI in  $Zn(OTF)_2$ - $Zn(NO_3)_2$ electrolyte, N exists as organic N-C at  $\approx 400 \text{ eV}$ ,<sup>[11]</sup> rather than inorganic NO<sub>3</sub><sup>-</sup>, from the N 1s spectrum (Figure 4a), because Zn<sub>5</sub>(OH)<sub>8</sub>(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O converts into Zn<sub>5</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>6</sub>, consistent with XRD results (Supplementary Figure 2). In addition, organic components (CF3, C-O, C-S, C-N; 90.3 %) with minor inorganic  $CO_3^{2-}$  species (9.7 %) were also detected on the SEI surface, as evidenced by the C 1s spectra in Figure 4b. The C-N and C-O species arise from reaction products of NO<sub>3</sub><sup>-</sup> and OTF<sup>-</sup>. The CF<sub>3</sub> and C-S species arise from either of incomplete reduction products of OTF- or trace Zn(OTF)<sub>2</sub> residue on Zn surface. The decomposition of OTF<sup>-</sup> was further verified by ZnS and ZnSO<sub>3</sub> signals in S 2p spectrum (Supplementary Figure 14). The inorganic  $CO_3^{2-}$ species, formed from either of decomposition of Zn(OTF)<sub>2</sub> or dissolved CO<sub>2</sub> in electrolytes, participated in the formation of  $Zn_5(CO_3)_2(OH)_6$ . The SEI surface also contains organic  $CF_3$ (94.7%) with minor inorganic  $ZnF_2$  (5.3%) (F 1s spectrum in Figure 4c). The organic fluorine species arises from either of incomplete reduction products of Zn(OTF)<sub>2</sub> or trace Zn- $(OTF)_2$  residue on Zn surface, while inorganic ZnF<sub>2</sub> is due to  $Zn(OTF)_2$  reduction. Therefore, the topmost surface is mainly composed of organic components, including C-N and CF<sub>3</sub>.

After 300 s of sputtering, the organic N-C peak disappeared (Figure 4a), in consistent with C 1s spectrum (Figure 4b). Upon further sputtering to 1500 s, no organic N-C peak was detected. However, the content of inorganic  $CO_3^{2-}$  species increased, while that of CF<sub>2</sub>, from the reduction of Zn(OTF)<sub>2</sub> decreased (C element in Figure 4b), although the signal intensity of C element obviously decreased compared with that before sputtering. As for F element, the content of inorganic ZnF<sub>2</sub> increased from 79.3% at 300 s sputtering to 88.0% at 1500 s sputtering, while that of organic CF<sub>2</sub> peak decreased from 20.7% at 300 s sputtering to 12.0% at 1500 s sputtering (Figure 4c). Therefore, the SEI contacting with Zn is composed of ZnF<sub>2</sub> dominated inorganic components.

Figure 4d summarized the element distribution across the SEI recovered from  $Zn(OTF)_2$ - $Zn(NO_3)_2$  electrolyte. From the SEI surface to the interface at SEI/Zn, the organic components gradually decreased, while the inorganic components increased, and ZnF is rich in SEI at the SEI/Zn

interface, confirming that the SEI consist of an organic-rich outer layer and inorganic  $ZnF_{2}$ -rich inner layer.

In summary, a trace amount of  $NO_3^-$  additive promotes the decomposition of  $Zn(OTF)_2$  salt and stabilizes the deposition product on the Zn surface in low-concentration aqueous electrolyte, facilitating the generation of a dense SEI where  $ZnF_2$ - $Zn_5(CO_3)_2(OH)_6$  inner part was coated by organic species outer part. Besides, F element distribution of the SEI was further investigated using time-of-flight secondary-ion mass spectrometry (TOF-SIMS) at various sputtering depths. The void-free crater in Figure 4e revealed dense Zn plating, while a large amount of F element exists within the surface layer (Figure 4 f), implying the uniformity of the SEI. In contrast, no decomposed component, like  $ZnF_2$ , ZnS, or ZnSO<sub>3</sub>, was found on a Zn electrode recovered from the Zn(OTF)<sub>2</sub> reference electrolyte (Supplementary Figure 15).

#### Electrochemical Performance of Zn-Metal Full Cells

The Zn(OTF)<sub>2</sub>-Zn(NO<sub>3</sub>)<sub>2</sub> aqueous electrolyte enabled Zn  $\parallel$  MnO<sub>2</sub> full cells to achieve high energy density and long cycle life. Tunnel-structured  $\beta$ -MnO<sub>2</sub> with a high theoretical capacity of 308 mAhg<sup>-1</sup> (0.5 Zn per MnO<sub>2</sub>) was used as a cathode. First, the electrochemical performance of MnO<sub>2</sub> cathode in two electrolytes was investigated using CV at 0.1 mV s<sup>-1</sup> in Zn  $\parallel$  MnO<sub>2</sub> cells with a high Zn-to-MnO<sub>2</sub> capacity ratio (N/P) of 3.0 to reflect MnO<sub>2</sub> behavior. MnO<sub>2</sub> in both electrolytes featured two redox peaks (Figure 5a), consistent with the previous work.<sup>[12]</sup> The polarization voltage of the cell with NO<sub>3</sub><sup>-</sup> additive is slightly larger than that without NO<sub>3</sub><sup>-</sup> additive, which is apparently associated with the dense SEI-induced overpotential. Charge-discharge curves at various C-rates in Zn(OTF)<sub>2</sub>-Zn(NO<sub>3</sub>)<sub>2</sub> electrolyte



**Figure 5.** Electrochemical performance of Zn || MnO<sub>2</sub> cells using Zn-(OTF)<sub>2</sub>-Zn(NO<sub>3</sub>)<sub>2</sub> and Zn(OTF)<sub>2</sub> electrolytes. a) CV of Zn || MnO<sub>2</sub> full cells at a scan rate of 0.1 mVs<sup>-1</sup>. b) Charge–discharge profiles at various current densities in Zn(OTF)<sub>2</sub>-Zn(NO<sub>3</sub>)<sub>2</sub> electrolytes. c) Long-term cycling performance of the Zn || MnO<sub>2</sub> cells in Zn(OTF)<sub>2</sub>-Zn(NO<sub>3</sub>)<sub>2</sub> and Zn(OTF)<sub>2</sub> electrolytes with 0.1 M Mn<sup>2+</sup> to suppress Mn<sup>2+</sup> dissolution at 10 C.

are presented in Figure 5b. When the rate was set as 0.5 C, the cell showed a reversible capacity of  $268.1 \text{ mAh g}^{-1}$  (168 Wh kg<sup>-1</sup> based on the cathode and anode). At high current density of 5 C and 10 C, Zn || MnO<sub>2</sub> cells with Zn-(OTF)<sub>2</sub>-Zn(NO<sub>3</sub>)<sub>2</sub> electrolyte showed high capacity retention of 58.0% and 49.3% of that at 0.5 C, respectively. This indicated a strong tolerance to the rapid Zn<sup>2+</sup> ions insertion/ extraction for MnO<sub>2</sub> cathode and transfer kinetics through fluorinated SEI for Zn anode. In addition, the cell using Zn(OTF)<sub>2</sub> reference electrolyte showed similar rate performance, verifying the fast kinetics of aqueous electrolyte (Supplementary Figure 16).

The high Zn plating/stripping efficiency and long cycle life of MnO<sub>2</sub> cathode enable a high energy Zn || MnO<sub>2</sub> full cell with a low N/P (2.0). The cyclic stability of Zn || MnO<sub>2</sub> cells using Zn(OTF)<sub>2</sub>-Zn(NO<sub>3</sub>)<sub>2</sub> electrolyte outperformed their counterparts with Zn(OTF)<sub>2</sub> electrolyte at a charge/discharge rate of 10 C (Figure 5 c). The cell with Zn(OTF)<sub>2</sub>-Zn(NO<sub>3</sub>)<sub>2</sub> electrolyte exhibit a 96.5% capacity retention after 700 cycles, whereas the cell with Zn(OTF)<sub>2</sub> electrolyte only maintained <60% capacity (from 138.2 to 72.0 mAhg<sup>-1</sup>) after 250 cycles at 10 C, indicating enhanced reversibility of Zn anode protected by NO<sub>3</sub><sup>-</sup> additive induced SEI even during rapid plating/stripping at a high current density.

#### Conclusion

For the first time, we introduced NO<sub>3</sub><sup>-</sup> additive in lowconcentration aqueous  $Zn(OTF)_2$  electrolyte to chemically form insulating passivation layer suppressing water decomposition. Then, the insulating passivation layer converted into Zn-ion conductive SEI during initial Zn plating/stripping activation cycles with inhibited hydrogen gas interference. NO<sub>3</sub><sup>-</sup> additive plays two key roles in promoting SEI formation and electrochemical stability over long-term operation: (1) Upon contact with Zn anode in aqueous electrolyte,  $NO_3^-$  forms electrically and ionically insulating  $Zn_5(OH)_{8^-}$ (NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O passivation laver, effectively creating waterfree environment on Zn surface and avoiding the flow away of SEI components; (2) During Zn plating/stripping, solvated NO<sub>3</sub><sup>-</sup> promotes the decomposition of OTF<sup>-</sup>, contributing to the transformation of  $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$  layer into an electrically insulating but ionically conductive SEI. The SEI features  $ZnF_2$ - $Zn_5(CO_3)_2(OH)_6$  SEI inner part coated by the organic outer part. The  $ZnF_2-Zn_5(CO_3)_2(OH)_6$  inner part removes strongly solvated H<sub>2</sub>O around Zn<sup>2+</sup> before reaching Zn surface, while the organic dominated outer part protects the inner part from significant volume change induced crack during Zn plating/stripping. The fluorinated SEI protected Zn anodes enabled a Zn anode to achieve a reversible and dendrite-free Zn plating/stripping CE of 99.8%, and Zn || MnO<sub>2</sub> cells with a low Zn-to-MnO<sub>2</sub> capacity ratio of 2.0 to achieve a high energy density of 168 Whkg<sup>-1</sup> (based on cathode and anode) and remained 96.5% of initial capacity after 700 cycles at 10 C.

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## Conflict of interest

The authors declare no conflict of interest.

**Keywords:** batteries · insulating passivation layer · solid electrolyte interphase · zinc batteries

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# **Research Articles**







Benefiting from a sacrificial  $Zn_5(OH)_{8}$ -( $NO_3$ )<sub>2</sub>·2 H<sub>2</sub>O insulating layer, a Zn-ion conductive and waterproof fluorine solid electrolyte interphase (SEI) is formed in situ for highly reversible Zn plating/ stripping in low-concentration aqueous electrolytes. The in situ formed SEI enables a high Coulombic efficiency of 99.8% for 200 h in Ti  $\parallel$  Zn cells, and a high energy density (168 Wh kg<sup>-1</sup>) with 96.5% retention for 700 cycles in Zn  $\parallel$  MnO<sub>2</sub> cells.