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Solid Electrolyte Interphase Design 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 hydrogen evolution reaction (HER). Here, we design a low-concentration aqueous Zn(O Tf)2-Zn(NO3)2 electrolyte to in situ form a robust inorganic ZnF-ZnIO2(OH)-organic bi-layer SEI where the inorganic inner layer promotes Zn-ion diffusion while the organic outer layer suppresses water penetration. Comprehensive characterization reveals that insulating Zn(OH)2(NO3)2-2H2O layer is first formed on Zn anode surface by self-terminated chemical reaction of NO3- with Zn2+ and OH- generated via HER, and then it transforms into Zn-ion conducting Zn(NO3)2(OH)2 which in-turn promotes ZnF2 formation as the inner layer. The organic dominated outer layer is formed by the reduction of OTF-. 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-1) with 96.5% retention for 700 cycles in Zn||MnO2 cells with a low Zn|MnO2 capacity ratio of 2:1.

Introduction

Aqueous Zn battery is promising for large-scale energy storage owing to its high theoretical capacity (820 mAh g-1), high abundance of Zn, and intrinsic safety[1]. Since the reduction potential of Zn (-0.762 V vs standard hydrogen electrode (SHE)) is negative than that of hydrogen evolution reaction (HER), water is reduced to H2 during Zn deposition (Fig. 1a), which changes the local pH to a strong alkaline[2]. The alkaline environment corrodes Zn anode surface by formation of porous Zn(OH)2 and ZnO[3]. The inhomogeneous morphology of the Zn(OH)2 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 electrolyte interphase (SEI) by coating inorganic[5] or polymer[6] on Zn surface that allow Zn2+ to transport but block water penetration to Zn surface. Unfortunately, these interphases suffer from crack and/or degradation during repeat volume changes of cycles[7]. Since these artificial SEI are not self-repairable 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-)[8] 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 H2 gas generation during Zn plating in low-concentration 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 H2 gas evolution cannot be completely inhibited by additives, which reduces the average CE.

Here, we prevented the H2 gas evolution during Zn plating/stripping by adding 20 mM Zn(NO3)2 additive into aqueous 3 M Zn(O Tf)2 electrolyte (denoted as Zn(O Tf)2-Zn(NO3)2) to chemically form a thin and dense Zn(OH)2(NO3)2-2H2O passivation layer upon the contact of Zn with electrolyte which blocks water penetration. Since the passivation layer is self-repairable, hydrogen evolution will be prevented even if the passivation layer cracks during Zn plating/stripping cycles. Upon contact of Zn with Zn(O Tf)2-Zn(NO3)2 electrolyte, water reduces on Zn surface generating a local alkaline environment, which triggers thermodynamically and kinetically favourable reaction between Zn and NO3-/OH- and forms an electrically and ionically resistive Zn(OH)2(NO3)2-2H2O passivation layer[9] before Zn electrodeposition. The Zn(OH)2(NO3)2-2H2O layer inhibits water penetration onto Zn surface, which allows reduction of OTF- anion to form SEI on Zn surface. As an intermediate template layer, Zn(OH)2(NO3)2-2H2O layer gradually transforms into a more stable Zn-ion conductive Zn(OH)2(NO3)2(OH)2 layer through metathesis reaction due to the lower solubility product (2.0×10^-15) of Zn(OH)2(OH)2 than that (7.4×10^-11) of Zn(OH)2(NO3)2-2H2O[10], when CO32- forms from the reduction of Zn(O Tf)2. At the same time, the organic components out-layer forms from the reaction between (CF3SO2-) and NO3- acting as flexible protection layer, and the zinc ion conducting ZnF2 forms in the inner part (Fig. 1b).

The highly flexible outer layer prevents SEI from crack due to volumetric change and facilitates solvated Zn ion to immigrate. The hydrophobic ZnF2 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 Zn2+ to transport through. This robust SEI enhanced the Zn plating/stripping CE to 99.8% in 200 h. The Zn||MnO2 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 a Zn plate in Zn(OTf)2-Zn(NO3)2 electrolyte (pH=3.8). After 4 h treatment in Zn(OTf)2-Zn(NO3)2 electrolyte at room temperature, the color of Zn metal surface changed from light silver to gray (Supplementary Fig. 1). X-ray powder diffraction (XRD) in Supplementary Fig. 2 demonstrated that Zn(OH)2(NO3)2·2H2O passivation layer was formed based on the chemical reaction\(^5\) in Fig. 1b. For comparison, Zn was also immersed in Zn(NO3)2 reference aqueous electrolyte (pH=3.6). However, well-defined peaks of ZnO/Zn(OH)2 (Supplementary Fig. 3) were observed. The Zn surface passivation layer morphologies were characterized using the scanning electron microscopy (SEM).

Supplementary Fig. 4 showed that Zn(OH)2(NO3)2·2H2O passivation layer presented 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(NO3)2 electrolyte (Fig. 2a), in the first cathodic scan, the in-situ formed Zn(OH)2(NO3)2·2H2O 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 reduced with charge/discharge cycles and showed a normal Zn plating peak at -0.15 V and Zn stripping peak at +0.15 V in the 10th charge/discharge cycle. Therefore, the Zn(OH)2(NO3)2·2H2O layer gradually became a 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(NO3)2 reference electrolyte (Supplementary Fig. 5) due to formation of porous ZnO/Zn(OH)2 layer on Zn.

The formation of Zn(OH)2(NO3)2·2H2O passivation layer is attributed to the unique Zn\(^{2+}\) solution sheath structure in bulk electrolyte. Nuclear Magnetic Resonance (NMR) demonstrated that only 20 mM NO\(_3\)\(^-\) additive can move the Zn\(^{65}\) chemical shift from 2.0 ppm in Zn(OTf)2 reference electrolyte to 0.7 ppm in Zn(NO3)2-Zn(OH)2 electrolyte (Supplementary Fig. 6a), indicating a shielding effect of the solvation sheath on Zn nucleus. This is because that NO\(_3\)\(^-\) is involved in solvation sheath and replaces some OTF- due to larger electron-donating ability of NO\(_3\)\(^-\) than that of OTF-. Additionally, the 10\(^{1}\) chemical shift of OTF- showed a downshift with the addition of NO\(_3\)\(^-\) (Supplementary Fig. 6b), confirming that NO\(_3\)\(^-\) anions entered the Zn\(^{2+}\) solvation sheath. Both Zn\(^{65}\) and NO\(_3\)\(^-\) NMR spectroscopy demonstrated that Zn\(^{2+}\) preferentially coordinates with NO\(_3\)\(^-\) instead of OTF-, which is beneficial for the generation of Zn(OH)2(NO3)2·2H2O.

During 10 activation cycles, the Zn50(OH)5(NO3)2·2H2O layer gradually converts into Zn-ion conducting Zn50(OH)5(CO3)2·2H2O SEI, as evidenced by XRD (Supplementary Fig. 2), which enables reversible Zn plating/stripping (Fig. 2a), but suppresses water reduction. The conversion of Zn50(OH)5(NO3)2·2H2O into Zn50(CO3)2·2H2O is attributed to the replacement of NO\(_3\)\(^-\) by CO\(_3\)\(^2-\), which are generated mainly from OTF- reduction with minor contribution from dissolved CO2, because the solubility product (2.0×10\(^{-15}\)) of Zn50(OH)5(NO3)2·2H2O in water is three order of magnitude lower than that (7.4×10\(^{-11}\)) of Zn50(OH)5(NO3)2·2H2O. To validate the conversion of Zn50(OH)5(NO3)2·2H2O into Zn50(CO3)2·2H2O through reduction of OTF- into CO\(_3\)\(^2-\), synthesized Zn50(OH)5(NO3)2·2H2O\(_{10}\)O\(_{10}\) powers were coated on inert Ti electrode and scanned using CV in an inert electrolyte, i.e. 1M NaCl aqueous electrolyte (Supplementary Fig. 7a-d). Since the insulating Zn50(OH)5(NO3)2·2H2O cannot transist into Zn-ion conductive Zn50(CO3)2·2H2O in 1M NaCl aqueous electrolyte, the Zn-ion insulating Zn50(OH)5(NO3)2·2H2O layer on Ti shifted the Zn plating and water reduction potential to -0.8 V vs Zn/Zn\(^2+\), while the Zn can be normally stripped at a low potential of 0.15 V due to formation of micro-cracks (Supplementary Fig. 7d). However, after 10 cycles, the Zn plating/stripping was completely inhibited on Zn50(OH)5(NO3)2·2H2O coated on Ti electrode because the formation of ZnO during charge/discharge sealed the cracks (Supplementary Fig. 7d). Therefore, the formation of insulating Zn50(OH)5(NO3)2·2H2O passivation layer on Zn after immersion in Zn(NO3)2-Zn(OH)2 electrolyte suppressed water decomposition while the OTF reduction during followed activation cycles converted the insulating Zn50(OH)5(NO3)2·2H2O layer into Zn-ion conducting Zn50(CO3)2·2H2O SEI without damaging from H\(_2\) evolution.
The effect of Zn(NO$_3$)$_2$ additive on the reversibility of Zn plating/stripping in Zn(OTF)$_2$ electrolyte was investigated using a Zn||Zn symmetric cell under galvanostatic condition (Fig. 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 (~77 mV) of Zn||Zn cells at 0.5 mA cm$^{-2}$ in the first cycle in Zn(OTF)$_2$-Zn(NO$_3$)$_2$ electrolyte than that (~30 mV) in Zn(OTF)$_2$ electrolyte (Fig. 2b) is attributed to the large Zn$^{2+}$ transport resistance in the Zn(NO$_3$)$_2$·2H$_2$O passivation layer than that in porous ZnO/Zn(OH)$_2$ layer. However, the overpotential of Zn plating/stripping in Zn(OTF)$_2$-Zn(NO$_3$)$_2$ electrolyte gradually decreased and eventually stabilized at ~20 mV due to the transformation of ionic-resistant Zn$_6$(OH)$_5$(NO$_3$)$_2$·2H$_2$O passivation layer into a high Zn$^{2+}$ transport SEI. Furthermore, the plating/stripping reversibility of Zn anode in two electrolytes were compared at a high current density of 10 mA cm$^{-2}$ and a high capacity of 10 mAh cm$^{-2}$. As shown in Supplementary Fig. 8, the cell using Zn(OTF)$_2$ 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 pre-formed Zn$_6$(OH)$_5$(NO$_3$)$_2$·2H$_2$O passivation layer promoted the formation of Zn$_6$(CO$_3$)$_2$(OH)$_6$ SEI by suppressing H$_2$ evolution. The hydrogen gas evolution during Zn plating/stripping in two electrolytes was investigated by operando monitoring evolved hydrogen using a home-built system (Fig. 2c). 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 carrier gas. The EIS of Zn(OTF)$_2$-Zn(NO$_3$)$_2$-Zn(OH)$_2$·2H$_2$O electrolyte during cycling (Fig. 2d) during Zn plating/stripping cycles, contrary to the reference electrolyte (Fig. 2e), confirmed the effective suppression of hydrogen evolution by pre-formed passivation layer.

The Zn-ion conduction increase during transition from Zn$_6$(OH)$_5$(NO$_3$)$_2$·2H$_2$O to Zn$_6$(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$^{-2}$ and 0.5 mAh cm$^{-2}$ 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.

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m Ah cm$^{-2}$ was recorded. In Fig. 2f and Supplementary Fig. 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$_2$(OH)$_2$(NO$_3$)$_2$·2H$_2$O passivation layer. However, the interface impedance quickly reduced to 114 ohm after 10 plating/stripping cycles because Zn plating/stripping triggered the transformation of ionic-insulating Zn$_2$(OH)$_2$(NO$_3$)$_2$·2H$_2$O layer into a fast-ion conducting Zn$_2$(CO$_3$)$_2$(OH)$_2$ layer. After 10 Zn plating/stripping cycles, the interface resistance of dense Zn$_2$(CO$_3$)$_2$(OH)$_2$ (Supplementary Fig. 4c-e) passivated Zn is slightly larger than that of passivated by porous undesirable byproducts (such as Zn(OH)$_2$; ZnCO$_3$; Zn(OH)$_2$·Zn$_2$O$_2$ and ZnO) formed on Zn surface with hydrogen evolution interference in Zn(OTF)$_2$ electrolyte (Supplementary Fig. 3, Supplementary Fig. 4f-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)$_2$ electrolyte is mainly attributed to activation process. Therefore, the presence of Zn$_2$(OH)$_2$(NO$_3$)$_2$·2H$_2$O passivation layer inhibited Zn corrosion and created a water/gas-free micro-environment on Zn surface, promoting the formation of a robust SEI.

The impact of NO$_3^-$ additive on Zn plating/stripping CE was investigated using Zn||Ti cells at 1 mA cm$^{-2}$ and 0.5 mA cm$^{-2}$ (Fig. 2g, Supplementary Fig. 10). Fig. 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 >98.8% 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 ~95% in the initial few cycles, but quickly drop to <90% after 10 cycles before short circuit at the 25th cycle. Therefore, the NO$_3^-$ additive effectively suppressed side reactions between Zn and water, increasing Zn plating/stripping CE. The activation process along with phase transition from Zn$_2$(OH)$_2$(NO$_3$)$_2$·2H$_2$O into Zn$_2$(CO$_3$)$_2$(OH)$_2$ based SEI in Zn(OTF)$_2$-Zn(NO$_3$)$_2$ electrolyte was also evidenced by quickly reduced overpotential from 205 mV at the beginning to 85 mV at 200th cycle (Supplementary Figs. 11a, b). Although the Zn plating/stripping behavior of Zn||Ti cells in Zn(OTF)$_2$ 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 Fig. 11c, d).

**Morphology and structure of SEI on Zn anodes**

The Zn deposition morphologies and cross-sectional views of Zn-metal anode in different electrolytes were observed by using SEM (Fig. 3). Zn surface after 100 cycles in Zn(OTF)$_2$ reference electrolyte showed mossy growth (Fig. 3a, b), where a cross-section of the 20 μm thick plated Zn reveals highly porous Zn deposition (Fig. 3c). This morphology was caused by continuous side reactions between Zn and electrolyte, as evidenced by a low CE (< 90%) (Fig. 2d) and poor cycling stability. In contrast, in Zn(OTF)$_2$-Zn(NO$_3$)$_2$ electrolyte, the Zn metal maintained a dense and smooth surface (Fig. 3d, e), evidenced by decreased thickness of cycled Zn from 20 μm in Zn(OTF)$_2$ reference electrolyte to 9.5 μm (Fig. 3c, f). Therefore, NO$_3^-$ induced hydrophobic SEI on Zn surface (Supplementary Fig. 12) effectively suppressed Zn dendrite growth and parasitic reactions between Zn anode and water, leading to compact and smooth Zn deposit. Furthermore, the surface passivation layer in different electrolytes were investigated using transmission electron microscopy (TEM) (Supplementary Fig. 13). A 3.5 nm SEI layer was observed on the surface of cycled Zn in Zn(OTF)$_2$-Zn(NO$_3$)$_2$ electrolyte, confirming the NO$_3^-$ induced formation of SEI layer.

![SEM images of surface and cross-section Zn electrodes recovered from Zn||Zn symmetrical cells after 100 plating/stripping cycles in (a-c) Zn(OTF)$_2$ and (d-f) Zn(OTF)$_2$-Zn(NO$_3$)$_2$ electrolytes.](image_url) (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.

The SEI composition on the Zn anode after 50 plating/stripping cycles was analyzed using X-ray photoelectron spectroscopy (XPS) facilitated by Ar$^+$ sputtering. On the surface (before sputtering) of SEI in Zn(OTF)$_2$-Zn(NO$_3$)$_2$ electrolyte, N exists as organic N-C at ~400 eV[11], rather than inorganic NO$_3^-$ from the N 1s spectrum (Fig. 4a), because Zn$_2$(OH)$_2$(NO$_3$)$_2$·2H$_2$O converts into Zn$_2$(CO$_3$)$_2$(OH)$_2$, consistent with XRD results (Supplementary Fig. 2). In addition, organic components (CF$_3$-C-O, C-S, C-N; 90.3%) with minor inorganic CO$_3^-$ species (9.7%) were also detected on the SEI surface, as evidenced by the C 1s spectra in Fig. 4b. The C-N and C-O species arise from reduction products of NO$_3^-$ and OTF. The CF$_3$ and C-S species arise from either of incomplete reduction products of OTF$^-$ or trace Zn(OTF)$_2^-$ residue on Zn surface. The decomposition of OTF$^-$ was further verified by ZnS and ZnSO$_3$ signals in S 2p spectrum (Supplementary Fig. 14). The inorganic CO$_3^-$ species, formed from either of decomposition of Zn(OTF)$_2^-$ or dissolved CO$_2$ in electrolytes, participated in the formation of Zn$_2$(CO$_3$)$_2$(OH)$_2$. The SEI surface also contains organic CF$_3$ (94.7%) with minor inorganic ZnF$_2$ (5.3%) (F 1s spectrum in Fig. 4c). The organic fluorine species arises from either of incomplete reduction products of Zn(OTF)$_2^-$ or trace Zn(OTF)$_2^-$ residue on Zn surface, while inorganic ZnF$_2$ is due to Zn(OTF)$_2^-$ reduction. Therefore, the topmost surface is mainly composed of organic components, including C-N and CF$_3$. 

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After 300 s sputtering, the organic N-C peak disappeared (Fig. 4a), in consistent with C 1s spectrum (Fig. 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$_2$ from the reduction of Zn(OTF)$_2$ decreased (C element in Fig. 4b), although the signal intensity of C element obviously decreased compared with that before sputtering. As for F element, the content of inorganic ZnF$_2$ increased from 79.3% at 300 s sputtering to 88.0% at 1500 s sputtering (Fig. 4c). Therefore, the SEI contacting with Zn is composed of ZnF$_2$-dominated inorganic components.

Fig. 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, trace amount of NO$_3^-$ additive promotes 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$_2$(CO$_3$)$_3$(OH)$_4$ 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 Fig. 4e revealed dense Zn plating, while a large amount of F element exists within the surface layer (Fig. 4f), implying the uniformity of the SEI. In contrast, no decomposed component, like ZnF$_2$, ZnS, or ZnSO$_4$, was found on a Zn electrode recovered from the Zn(OTF)$_2$ reference electrolyte (Supplementary Fig. 15).

**Electrochemical performance of Zn-metal full cells**

The Zn(OTF)$_2$-Zn(NO$_3$)$_2$ aqueous electrolyte enabled Zn|MnO$_2$ full cells to achieve high energy density and long cycle life. Tunnel-structured β-MnO$_2$ with a high theoretical capacity of 308 mAh/g (0.5 Zn per MnO$_2$) was used as a cathode. First, the electrochemical performance of MnO$_2$ cathode in two electrolytes was investigated using CV at 0.1 mV/s in Zn|MnO$_2$ cells with a high Zn-to-MnO$_2$ capacity ratio (N/P) of 3.0 to reflect MnO$_2$ behavior. MnO$_2$ in both electrolytes featured two redox peaks (Fig. 5a), consistent with the previous work[12]. The polarization voltage of the cell with NO$_3^-$ additive is slightly larger than that without NO$_3^-$ additive, which is apparently associated with the dense SEI-induced overpotential. Charge-discharge curves at various C-rates in Zn(OTF)$_2$-Zn(NO$_3$)$_2$ electrolyte are presented in Fig. 5b. When the rate was set as 0.5 C, the cell showed a reversible capacity of 268.1 mAh g$^{-1}$ (168 Wh kg$^{-1}$ based on the cathode and anode). At high current density of 5 C and 10 C, Zn||MnO$_2$ cells...
with Zn(OTF)$_2$-Zn(NO$_3$)$_2$ 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$^{2+}$ ions insertion/extraction for MnO$_2$ cathode and transfer kinetics through fluorinated SEI for Zn anode. In addition, the cell using Zn(OTF)$_2$ reference electrolyte showed similar rate performance, verifying the fast kinetics of aqueous electrolyte (Supplementary Fig. 16).

![Graph](image1.png)

**Fig. 5** Electrochemical performance of Zn||MnO$_2$ cells using Zn(OTF)$_2$-Zn(NO$_3$)$_2$ and Zn(NO$_3$)$_2$ electrolytes. a) CV of Zn|MnO$_2$ full cells at a scan rate of 0.1 mV/s. b) Charge-discharge profiles at various current density in Zn(OTF)$_2$-Zn(NO$_3$)$_2$ electrolytes. c) Long-term cycling performance of the Zn[MnO$_2$ cells in Zn(OTF)$_2$-Zn(NO$_3$)$_2$ and Zn(NO$_3$)$_2$ electrolytes with 0.1 M Mn$^{2+}$ to suppress Mn$^{4+}$ dissolution at 10 C.

The high Zn plating/stripping efficiency and long cycle life of MnO$_2$ cathode enable a high energy Zn[MnO$_2$ full cell with a low N/P (2.0). The cyclic stability of Zn[MnO$_2$ cells using Zn(OTF)$_2$-Zn(NO$_3$)$_2$ electrolyte outperformed their counterparts with Zn(NO$_3$)$_2$ electrolyte at a charge/discharge rate of 10 C (Fig. 5c). The cell with Zn(OTF)$_2$-Zn(NO$_3$)$_2$ electrolyte exhibit a 96.5% capacity retention after 700 cycles, whereas the cell with Zn(NO$_3$)$_2$ electrolyte only maintained <60% capacity (from 138.2 to 72.0 mAh g$^{-1}$) after 250 cycles at 10 C, indicating enhanced reversibility of Zn anode protected by NO$_3^-$ additive-induced SEI even during rapid plating/stripping at a high current density.

**Conclusion**

We introduced NO$_3^-$ additive into low-concentration 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$_3^-$ 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$_2$O(OH)(NO$_3$)$_2$·2H$_2$O passivation layer, effectively creating water-free environment on Zn surface and avoiding the flow away of SEI components; (2) During Zn plating/stripping, solvated NO$_3^-$ promotes the decomposition of OTF$^-$, contributing to the transformation of Zn$_2$O(OH)(NO$_3$)$_2$·2H$_2$O layer into an electrically insulating but ionically conductive SEI. The SEI features ZnF$_2$-Zn$_2$(CO$_3$)$_2$(OH)$_2$ SEI inner part coated by the organic outer part. The ZnF$_2$-Zn$_2$(CO$_3$)$_2$(OH)$_2$ inner part removes strongly solvated H$_2$O around Zn$^{2+}$ 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$_2$ cells with a low Zn-to-MnO$_2$ capacity ratio of 2.0 to achieved a high energy density of 168 Wh kg$^{-1}$ (based on cathode and anode) and remained 96.5% of initial capacity after 700 cycles at 10 C.

**Keywords:** aqueous zinc batteries • insulating passivation layer • conversion • reversibility

Benefiting from a sacrificial Zn$_2$(OH)$_6$(NO$_3$)$_2$·2H$_2$O insulating layer, Zn-ion conductive and water-proof fluorine solid electrolyte interphase (SEI) is in situ formed 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||Zn cells, and a high energy density (168 Wh kg$^{-1}$) with 96.5% retention for 700 cycles in Zn||MnO$_2$ cells.