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**Toward High-Performance Hybrid Zn-Based Batteries via Deeply Understanding Their Mechanism and Using Electrolyte Additive**

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Abstract
Aqueous hybrid Zn-based batteries (ZIBs), as a highly promising alternative to lithium-ion batteries for grid application, have made considerable progress recently. However, few studies have been reported that investigate their working mechanism in detail. Here, the operando synchrotron X-ray diffraction is employed to thoroughly investigate the operational mechanism of a hybrid LiFePO$_4$(LFP)/Zn battery, which indicates only Li$^+$ extraction/insertion from/into cathode during cycling. Based on this system, a cheap electrolyte additive, sodium dodecyl benzene sulfonate, is proposed to effectively enhance its electrochemical properties. The influence of the additive on the Zn anode and LFP cathode is comprehensively studied, respectively. The results show that the additive modifies the intrinsic deposit pattern of Zn$^{2+}$ ions, rendering Zn plating/stripping highly reversible in an aqueous medium. On the other hand, the wettability of the LFP electrode is visibly a meliorated by introducing the surfactant additive, accelerating the Li-ion diffusion at the LFP electrode/electrolyte interface, as indicated by the overpotential measurements. Benefiting from these effects, the Zn/LFP batteries deliver high rate capability and cycling stability in both coin cells and pouch cells.

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Electrolyte additive enabled Zn dendrite-free and rapid ion diffusion in aqueous hybrid zinc-based batteries

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Abstract

Aqueous hybrid Zn-based batteries (ZIBs), as a highly promising alternative to lithium-ion batteries for the grid application, have gained a considerable achievement recently. However, few works were reported to study their working mechanism in detail. Here, the operando synchrotron X-ray diffraction was employed to thoroughly investigate the operational mechanism of hybrid LiFePO4(LFP)/Zn battery, which indicates only Li+ extraction/insertion from/into cathode during charge-discharge process. Based on this system, a cheap electrolyte additive, sodium dodecyl benzene sulfonate, was proposed to effectively enhance its electrochemical properties. The influence of the additive on the Zn anode and LFP cathode were comprehensively studied, respectively. The results show the additive modifies the intrinsic deposit pattern of Zn2+ ion, rendering Zn plating/stripping highly reversible in aqueous media. On the other hand, the wettability of LFP electrode was visibly meliorated by introducing the surfactant additive, accelerating the Li-ion diffusion at the LFP electrode/electrolyte interface, as convinced by the over-potential measurements. Benefiting from these effects, the LFP/Zn batteries deliver high rate capability and cycling stability in both coin-cell and pouch-cell. More importantly, this additive could also be extended to aqueous MnO2/Zn battery, assisting in its encouraging cycling stability.

Keywords: aqueous Zn battery, electrolyte additive, hybrid battery, Zn dendrite
Introduction

Lithium-ion batteries (LIBs) are the state-of-the-art secondary battery techniques in the market of portable electronics, and widely regards as a potential technology for electric vehicles due to their long cycle life and high energy density.[1-2] Unfortunately, the growing concerns about the safety issues as well as high cost limit their further developments. Moreover, the abandoned LIBs with the flammable organic electrolytes and toxic elements rise another huge environmental concern.[3] Therefore, seeking the safe, inexpensive and environmental-friendly alternatives to LIBs is of utmost urgency especially for smart-grid applicants.[4] Aqueous rechargeable batteries are particularly attractive for large-scale energy storage in terms of innate safety advantages, economy and environmental benignity, in which Zn-ion batteries (ZIBs) with zinc metal as anode have been investigated intensively due to its low potential (−0.76 V vs. standard hydrogen electrode (SHE)), high theoretical capacity (~820 mA h g⁻¹), and high over-potential for hydrogen evolution in aqueous media.[5-6]

Although ZIBs based on the mild aqueous electrolyte have gained some progress presently, their further development still faces the huge challenges due to the sluggish multivalent Zn-ion diffusion in host materials, which mainly caused by their strong electrostatic interaction with host lattice.[7] Recently, the hybrid Zn-based batteries were designed using the conventional cathode materials of LIBs or sodium ions batteries (e.g. LiFePO₄ or Na₀.₄₄MnO₂) and Zn foil anode.[8-9] Theoretically, this novel hybrid battery can not only avoid the sluggish Zn-ion diffusion kinetics in the cathode materials, but also broaden the research field of aqueous batteries by shifting from a single-ion to a double-ion mechanism.[10] Despite different hybrid Zn-based systems with advanced performance have been proposed in recent years,[11] their hybrid working mechanism is still confusing. As the radius of Li⁺ ion (0.76 Å) or Na⁺ ion (1.02 Å) is larger than that of Zn²⁺ ion (0.74 Å), indicating the higher energy barriers may encounter for the larger ions intercalation. Additionally, some polyanion based robust crystal architectures, such as LiV₂(PO₄)₃ and LiMn₀.₈Fe₀.₂PO₄, for the reversible intercalation/de-intercalation by Zn²⁺ ions have also been confirmed.[12] Thus, systematic exploring the working mechanism is needed.

Apart from the operational mechanism, the existing hybrid Zn-based techniques are still far from fulfilling the ambitions of excellent performances demanded by the ever-increasing energy consumption.[13] On one hand, the electroplating on the Zn metal anode with uneven morphology leads to the inhomogeneous distribution of Zn²⁺ ion near to its surface. The
protrusions with high curvature have a considerably higher electric field at the tips, which tends to attract more Zn$^{2+}$ ions, leading to further growth of the protrusions and finally evolving into Zn dendrites. The growth of Zn dendrites during plating/stripping process not only causes the “loss” of reversible capacity by formation of “dead” Zn, but also seriously fades the Coulombic efficiency and cycle life.$^{[14]}$ But even worse, Zn dendrites normally grow up in the direction perpendicular to the surface of Zn metal, which is a potential safety hazard for internal shorting failure of the battery after they pierce the separator.$^{[15-16]}$ On the other hand, the wetting property of electrode in aqueous media is limited, which severely impacts on ion diffusion at the interface of electrode and electrolyte.$^{[17-18]}$ Furthermore, insufficient electrolyte wetting on the cathode surface causes uneven electrochemical reactions and accelerates the degradation of cathode material, resulting in a poor rate capability and shortened cycle life.$^{[19]}$ Therefore, suppressing the Zn dendrite growth on Zn anode as well as improving the ion diffusion kinetics at the cathode/electrolyte interface are of top priority to enhance the electrochemical properties of hybrid Zn-based batteries.

Here, the working mechanism of hybrid LFP/Zn battery was studied by operando synchrotron X-ray diffraction (XRD) in detail, revealing only Li$^+$ ion involves in the reaction on the cathode during charge-discharge process. In addition, a cheap electrolyte additive, sodium dodecyl benzene sulfonate (SDBS), was reported to improve the electrochemical behaviors of a hybrid LFP/Zn battery. Based on the operating mechanism, the effects of the additive on this hybrid battery was investigated in detail. Specifically, the additive not only inhibits the Zn dendrite growth by manipulating the Zn plating pattern but also accelerates Li-ion diffusion at the LFP cathode/electrolyte interface at the same time. With the assistance of additive, Zn$^{2+}$ ions are deposited smoothly on the surface of Zn metal instead of vertical growth of Zn dendrite in the flake-shape. Simultaneously, the Li-ion diffusion coefficient was increased from $1.78 \times 10^{-11}$ cm$^2$s$^{-1}$ to $8.22 \times 10^{-11}$ cm$^2$s$^{-1}$ by improving the wettability of LFP electrode, which contributes to the rate capability of the battery. As a consequence, the hybrid LFP/Zn battery with the surfactant additive delivers a reversible capacity of 158.2 mA h g$^{-1}$ with a high initial Coulombic efficiency of 94.5% at 0.5 C and an excellent cycling stability over 500 cycles at 5 C. Additionally, the hybrid LFP/Zn pouch cell with electrolyte additive was assembled, which also shows an impressive electrochemical properties. To evaluate the broad feasibility of this additive, the electrochemical behaviours of the aqueous MnO$_2$/Zn batteries with/without additive were compared. The results confirmed that the battery with additive delivered a superior cycling stability to that without additive.
Results and discussion

The configuration and operational mechanism of this hybrid LFP/Zn battery were presented in Figure 1a, where LFP services as the cathode material, Zn foil functions as anode and current collector, and the hybrid 1 M Zn(SO₃CF₃)₂ and 1 M Li(SO₃CF₃) solution works as the electrolyte. The XRD (Figure S1 in supporting information) and Scanning electron microscope (SEM) techniques (Figure S2) were carried out to make sure that the LFP candidate has good crystalline structure and morphology. In this hybrid cell, Li⁺ ion will be extracted from LFP cathode and migrates into the electrolyte in the charging process. Meanwhile, the Zn²⁺ ion from the hybrid electrolyte will deposit on the surface of Zn anode as the potential of Zn²⁺/Zn (−0.76 V vs. SHE) is higher than that of Li⁺/Li (−3.04 V vs. SHE).[20] In the discharging process, it was proposed that Li⁺ ion from the hybrid electrolyte will inserted into the heterosite (FePO₄) by generating LFP. Simultaneously, Zn metal will lose electrons by forming Zn²⁺ ion and migrate back to the electrolyte. However, as the radius of Li⁺ ion (0.76 Å) is slightly larger than that of Zn²⁺ ion (0.74 Å), it is confusing whether the Zn²⁺ ion could co-insert into FePO₄ cathode or not.[21] Although the similar Zn-based batteries, including LiMn₂O₄/Zn, Li₃V₂(PO₄)₃/Zn and LiV₂(PO₄)₃/Zn batteries, have been reported before,[10, 12, 22] few work focus on exploring the operational mechanism of hybrid ions involving reaction was carried out. Therefore, to deeply understand the operational mechanism, in operando synchrotron XRD of the hybrid LFP/Zn battery first was conducted to study the LFP phase evolution during charge-discharge process. From the charge-discharge curves (Figure 1b), only one discharge plateau located at ~1.1 V can be observed, indicating the single phase transition. The uncycled LFP exhibits obvious some peaks at 7.7°, 9.2° and 11.4° that can be indexed to (020), (011), (021) and (121) planes, respectively.[23] During charging process, these peaks gradually disappeared along with new reflections at ~8.0°, 9.2°, 11.5° and 13.8° appear, which can be indexed to 200, 101, 201 and (211) planes, respectively.[23] Upon discharging, all of LFP peaks completely re-emerge with the crystalline phase of FePO₄ disappears, suggesting the excellent phase reversibility. More distinct changes can be observed in the contour maps (Figure 1c and Figure S3), which indicates that only Li⁺ ion instead of Zn²⁺ ion inserted into FePO₄ during discharge process although the size of Li⁺ ion is slightly larger than that of Zn²⁺ ion. The main reason could be ascribed to the nature of Zn²⁺ and Li⁺ ions: Zn²⁺ ion features a higher charge density (a double charge divided by a small radius of 0.74 Å) compared to Li⁺ ion, leading to reduced diffusivity within common polar crystalline hosts due to strong Coulomb interactions and
inhibited issues with respect to the electrolyte chemistry, such as the balancing of solvation/desolvation energies for efficient planting/stripping.[25] Overall, the working mechanism of LFP/Zn hybrid batteries can be expressed as the following equations.

Cathode: \( \text{LiFePO}_4 \leftrightarrow e^- + \text{Li}^+ + \text{FePO}_4 \)  
(1)

Anode: \( \text{Zn}^{2+} + 2e^- \leftrightarrow \text{Zn} \)  
(2)

Overall: \( 2\text{LiFePO}_4 + \text{Zn}^{2+} \leftrightarrow 2\text{Li}^+ + 2\text{FePO}_4 + \text{Zn} \)  
(3)

To explore the influence of SDSB additive concentration on the electrochemical performance of hybrid Zn/LFP batteries, the charge-discharge measurements were conducted at a current rate of 0.5 C (1 C = 170 mA h g\(^{-1}\)), as presented in Figure S4. The hybrid LFP/Zn battery with 1 mg mL\(^{-1}\) additive displays the highest capacity of \( \sim 158.2 \) mA h g\(^{-1}\) at 0.5 C with the highest initial Comlombic efficiency of 94.5% among these with different concentration (0.1, 2, and 5 mg ml\(^{-1}\)). In addition, the performance of battery with 1 mg mL\(^{-1}\) additive is also superior to that without additive (the capacity is \( 147.4 \) mA h g\(^{-1}\) with an initial Comlombic efficiency of 89.4%) (Figure 2a), which suggests that the electrolyte additive contributes to the improvement of reversible capacity. More importantly, the voltage difference of charge and discharge plateau in the battery with additive (1 mg mL\(^{-1}\)) is less than that without additive, demonstrating that the high reversibility of electrochemical reactions with additive, which was also confirmed by the cyclic voltammetry (CV) measurements (Figure 2b). The CV curve of the battery with additive collected at 0.1 mV s\(^{-1}\) displays a cathodic peak located at \( \sim 1.28 \) V, \( \sim 23 \) mV less than that without additive. Furthermore, CV shapes without additive were distorted with obvious redox peak shifts when the scan rate increases (Figure S5). In strong contrast, the CV shapes with additive could maintain well, which further supports that the surfactant additive contributes to the electrochemical reversibility. Based on the CV results, the Li\(^+\) diffusion coefficient (\( D_{\text{Li}^+} \)) of LFP electrode with additive was calculated to be \( 8.22 \times 10^{-11} \) cm\(^2\)s\(^{-1}\), much higher than that without additive (\( 1.78 \times 10^{-11} \) cm\(^2\)s\(^{-1}\)).[26] The high reversibility as well as the high Li-ion diffusion coefficient of LFP electrode will benefit to its rate capability and cycling stability. Figure 2d shows the rate capability of LFP/Zn batteries with/without additive. Only the capacity of 22.5 mA h g\(^{-1}\) was remained in LFP/Zn battery without additive when the current rate increase to 20 C, with a capacity retention of \( \sim 15.3\% \) compared to that obtained at 0.5 C. In comparison, a high capacity of 57.8 mA h g\(^{-1}\) was still obtained at the same current rate when the electrolyte additive was added. Additionally, the influence of the additive on cycling stability of LFP/Zn batteries was studies at 1 C, as shown in Figure 3e. The capacity
obtained from the battery without additive decayed obviously with only ~92.3 mA h g⁻¹ remaining after 100 cycles (75.1% capacity retention). In contrast, the battery with additive delivered a high capacity of 132.2 mA h g⁻¹ after 100 cycles at 1 C (the capacity retention of 88.6%). The impressive cycling stability was also convinced by the measurements at 5 C (Figure S6). The enhanced electrochemical properties render our LFP/Zn battery comparable to other aqueous hybrid systems, as summarized in Table S1.

In order to deeply understand working mechanism of electrolyte additive in hybrid LFP/Zn battery, the effect of additive on both Zn anode and LFP cathode were studied, respectively. It is well-known that Zn metal anode suffers from the irreversibility issues caused by the dendrite growth during plating/stripping process, rendering the cycle performance of aqueous Zn-based batteries highly unstable.[27-28] The Zn dendrite growth during cycling would eventually result in the internal shorting failure after the separator was pierced. Even before the battery failure, some Zn dendrites turn into “dead” part during the electrochemical reaction, leading to the loss of the capacities and electrolyte consumption.[14] Thus, it is of great importance to suppress the Zn dendrites growth for developing a high-performance Zn-based batteries. To study the influence of the surfactant additive on the Zn dendrite growth, the electrochemical deposition of Zn was performed in a two-electrode system (Figure S7), in which the hybrid solution of 1 M Zn(SO₃CF₃)₂ and 1 M Li(SO₃CF₃) with/without 1 mg ml⁻¹ additive services as the electrolyte and Pt foil functions as the counter electrode. Figures 3a-c illustrate the morphologies of commercialized Zn foil, and electrodeposited Zn electrodes with/without additive, respectively. Apparently, the surface of the fresh Zn foil is smooth and flat with some stripes produced possibly by its manufacturing process. The accumulated Zn nano-sheets were clearly found without additive (Figures 3b and S8a), indicating that the Zn dendrites were generated on the surface and further grew in the flake shape.[15, 29] Moreover, the similar morphology of the Zn dendrite was also observed on the Zn foil anode that stripped out from the LFP/Zn battery after 100 cycles (Figure S9). Serious corrosion occurred on the surface of Zn foil during charge-discharge process, which, in turn, leads to a poor Coulombic efficiency and unstable cycling performance of the battery.[30] Furthermore, the similar dendrite sheets perpendicular to the surface of Zn foil were observed, demonstrating that the Zn dendrites is a potential threat to battery safety by piercing the separator. On the contrary, the electrodeposited Zn electrode with surfactant additive displays a rough surface without Zn dendrite sheets (Figure 3c), which mainly due to a strong blocking effect of electrolyte additive. Specifically, the surfactant additive molecules are absorbed on the electrode surface and forming a surface
passivating film, which not only affects the kinetics of the electron transfer but also increases the competition between the nucleation and crystal growth.[31-32] Additionally, the additive also facilitates the wettability of Zn foil, the initial contact angle of 89.8° was reduced distinctly to 31.2°. (Figure S10). Thermodynamically, the good wettability changes the total Gibbs free energy of transformation of a spherical cap-shaped deposit from a liquid electrolyte,[33] which promotes the generation of electroplating nucleation on the electrically charged substrate, resulting in a uniformly plated surface. As a result, the pattern of Zn deposit was manipulated by the additive, suggesting strong suppression of Zn dendrite growth. Similarly, the Zn foil electrode, which was stripped out from the LFP/Zn battery within the additive electrolyte after 100 cycles, also show a rough surface without Zn dendrite flakes (Figure S11). No obvious corrosion was found on the surface of Zn foil, indicating that the additive relieves the Zn corrosion and restrains the growth of Zn dendrites, which assists in the high Coulombic efficiency and long cycling stability of battery.

XRD patterns of different Zn electrodes were collected to deeply study the Zn deposit with/without surfactant additive, as presented in Figure 3d. The bottom XRD pattern belongs to the commercial Zn foil, the peaks located at ~36.3°, 39.0°, and 43.2° are indexed to the (002), (100), and (101) planes of Zn (PDF#00- 004-0831).[34] The electrodeposited Zn without additive shows the similar XRD pattern with the highest intensity peak at 42° (middle), suggesting the Zn crystal growth mostly is in the orientation of (101). Although the dominant (101) peak is also found at the XRD pattern of electrodeposited Zn electrode with additive (top), the XRD pattern changes demonstrate that the growth of Zn crystal was modified by the additive via accelerating the zinc growth in the orientations of (100) and (110).[35] Furthermore, the polarization measurements of the Zn−Zn symmetric batteries in the hybrid electrolyte with/without additive were conducted at a constant current density of 0.5 mA cm$^{-2}$ to investigate the dynamical stability of the Zn/electrolyte interface. The over-potential of Zn stripping/plating in the symmetric cell without additive is approximately 50 mV at the beginning and almost keep this value in following cycles. After 900 h stripping/plating, a large and irreversible voltage drop was detected, indicating a battery failure of short circuit induced by the growth of Zn dendrite.[36] On a striking contrary, the Zn-Zn battery with additive displays an outstanding cycling stability under the same conditions, despite the relatively high-voltage polarization in the initial cycles for the electrode activation and formation of SEI layer. Figure S12 shows the over-potential of Zn stripping/plating with additive is only around 45.1 mV, lower that without additive (69.1 mV), which indicates a low energy barrier for generation of
Zn metal nucleation and then promotes a relatively uniform Zn plating process. More importantly, the Zn–Zn cell with additive still maintains an extremely low and stable polarization without short circuiting even after 1500 h cycling, demonstrating highly stable Zn plating/stripping cycling reversibility.

On the other hand, the wettability of electrode material is of great importance for the ion exchange at the electrolyte/electrode interface. To learn the impact of additive on wettability of the LFP cathode, the sessile drop contact angle technique was employed, as illustrated in Figures 4a and b. The contact angle of the LFP electrode with the pure electrolyte was measured to be 84.4°, demonstrating the limited hydrophilic of LFP electrode. Introducing electrolyte additive notably strengthens the absorbability of the LFP electrode surface with a small contact angle of 50.1°, as further supported by the insert images. According to S. Manne, the surfactant molecules will be adsorbed on the electrode surface, rendering the surface of LFP electrode more hydrophobic, which favours the electrochemical reaction at the interface of electrode/electrolyte. Based on the contact angle, the wetting free energy of electrode material was also evaluated. According to the simple model (Figure S13) built by Extrand, the change of the wetting free energy with/without additive media was calculated by the following equation:

\[
\Delta G = \frac{RT}{3} \ln \left(\frac{(1 - \cos \theta_A)^2}{4 \left(2 + \cos \theta_A\right)}\right)
\]

in which \( R \) is the ideal gas constant, \( T \) is absolute temperature and \( \theta_A \) is the contact angle.

Similar to surface energies, the absolute magnitude of \( \Delta G \) values was small for large contact angles. The calculation results show that the wetting free energy of LFP electrode surface without surfactant additive is \(-4.6 \text{ J mol}^{-1}\). The value of \(-\Delta G\) increases to \(7.33 \times 10^3 \text{ J mol}^{-1}\) in the additive media, indicating that the surfactant additive increases the hydrophilicity of LFP electrode and facilitates the \( \text{Li}^+ \) ion diffusion at the electrode/electrolyte interface. To further investigate the effects of additive on the LFP electrode at atomic scale, the ab into MD calculations was also performed on the interface of LFP (010) and aqueous electrolyte. The simulation snapshots (Figure 4c) illustrates the migration of \( \text{Li}^+ \) ion at the LFP(010)/electrolyte interface without surfactant additive. Initially, the migrating Li ion is located at the top of LFP [010] channel. As the simulation proceeds, the \( \text{Li}^+ \) coordinates to water molecules, then water molecules lift the \( \text{Li}^+ \) ion from its original position, and carry the \( \text{Li}^+ \) ion to migrate into the bulk of electrolyte. Thus, water molecules are involved into the \( \text{Li}^+ \) ion migration process rather than acting as the simple adsorbent. When the additive was added into electrolyte, the
LFP surface adsorbs tail group of the surfactants molecules (Figure 4d), which helps to reduce the wetting free energy. Therefore, more water molecules adhered to the LFP (010) surface, assisting in the Li$^+$ migration across the solid/liquid interface.

Additionally, to verify the additive accelerating the Li$^+$ ion transfer, the electrochemical reaction kinetics of both systems were compared using the galvanostatic intermittent titration technique (GITT) During GITT measurements, the LFP electrodes with/without surfactant additive were intermittently charged/discharged using the current pulses at 0.1 C with the equal duration of 0.5 h. Following each pulse, the batteries were left on open circuit for 1 h to reach equilibrium potentials, as illustrated in Figure 4e. Two potential plateaus can be observed on the curves, corresponding to the Li$^+$ ion extraction and insertion process.\cite{42} The insert of Figure 4e shows the LFP electrode without additive suffers from a large over-potential of \textasciitilde153 mV, almost twice larger than that with additive (\textasciitilde68 mV), demonstrating that the electrochemical reaction resistant is lower in the additive media.

The encouraging performance of LFP/Zn coin-cells with additive has motivated us to further assess the performance in soft-packed full-cells, which could be facilely assembled in ambient air without complicated procedures. The galvanostatic discharge-charge measurements of the pouch-cell were carried out at a current rate of 0.5 C, as illustrated in Figure 5a. One pair of redox plateaus was found, in good agreement with the CV (Figure S14), with a reversible capacity of 136.2 mA h g$^{-1}$. The full-cell delivers an energy density of \textasciitilde113.2 Wh kg$^{-1}$ based on the total weight of the active materials (including both cathode and anode), which far exceeds that of other aqueous batteries, such as aqueous LIBs (\textasciitilde50–90 Wh kg$^{-1}$)\cite{43} and aqueous Na-ion batteries (\textasciitilde30–40 Wh kg$^{-1}$)\cite{44,45}. The insert of Figure 5a shows the pouch cells light the five LED lights with different colours (two yellows, 2.0 V; two red, 2.0 V and one green, 3.0 V). The cycle life of the aqueous pouch-cell was evaluated at 1 C, as shown in Figure 5b. It exhibited an encouraging cycling stability, showing a discharge capacity of 102.1 mA h g$^{-1}$ after 150 cycles at 1 C for \textasciitilde80% capacity retention and a Coulombic efficiency of about 100%.

In order to assess the feasibility of SDBS additive in other aqueous batteries, the MnO$_2$/Zn battery was assembled, where the electro-deposited MnO$_2$, Zn foil, and 1 M Zn(SO$_3$CF$_3$)$_2$ + 0.5 M Mn(SO$_3$CF$_3$)$_2$ solution service as cathode, anode, and electrolyte, respectively. The typical charge-discharge curves were performed at the current rate of 0.5 C (1 C=327 mA h g$^{-1}$), as shown in Figure S15. The discharge curve show a flat plateau at approximately 1.4 V
followed with small plateaus at about 1.2 V, similar to previous reports.[46-47] The MnO₂/Zn battery can achieve a discharge capacity of 262.5 mA h g⁻¹ within the voltage window of 1.1–1.8 V. To study the influence of the surfactant additive on the MnO₂/Zn battery, the cycling stability of the MnO₂/Zn batteries with/without additive (1 mg ml⁻¹) was measured at 5 C, as presented in Figure S16. After 600 cycles, the battery with additive still displays a high capacity of 131.5 mA h g⁻¹ with the capacity retention of 95.8%, which is superior to the battery without additive (the capacity of 69.0 mA h g⁻¹ remaining after 600 cycles), indicating that the additive could be extend to aqueous MnO₂/Zn system to enhance its cycling performance. The Zn foils were stripped out from the MnO₂/Zn batteries after cycles, the photos suggest the Zn foil suffers from the serious corrosion on its surface without additive (Figure S17). In contrast, the corrosion on the Zn surface was alleviated with the assistance of additive.

Conclusion

In this work, the hybrid working mechanism of aqueous LFP/Zn battery was confirmed by operando synchrotron tests. Based on this hybrid system, a surfactant additive was developed and comprehensively studied. By modifying the intrinsic pattern of Zn electro-deposited, the formation and growth of Zn dendrites were effectively suppressed, which in turns enhanced the Coulombic efficiency and eliminated the potential safety hazard. Moreover, this surfactant additive accelerated the surface wettability of the electrode, facilitating the Li-ion diffusion at the interface of LFP electrode/electrolyte. Consequently, the Li-ion diffusion coefficient of LFP cathode was increased from 1.78 × 10⁻¹¹ cm²s⁻¹ to 8.22 × 10⁻¹¹ cm²s⁻¹. The rapid Li-ion diffusion at the solid/liquid interface was also confirmed by the MD calculation. Benefiting from the Zn dendrite-free anode and the rapid Li-ion diffusion kinetics of cathode, the hybrid LFP/Zn coin-cell with additive displays an high initial Coulombic efficiency of 94.5% at 0.5 C, a high rate capability with a capacity of 57.8 mA h g⁻¹ remaining at even 20 C. An encouraging cycling stability over 150 cycles was still achieved even in a LFP/Zn pouch-cell. Importantly, this additive was also applied in MnO₂/Zn battery, assisting in enhancing its cycling stability. The obtained promising electrochemical results and scientific understanding suggest that developing additive could be a viable strategy for advanced aqueous systems and encourage more relevant research on new additives for high-performance Zn-based batteries towards practical applications.

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References


Figure 1. a) The scheme of the hybrid aqueous Zn-LFP battery. b) The in-operando synchrotron patterns of the hybrid Zn-LFP (left) and the corresponding charge-discharge curve (right). c) The contour plots of the operando synchrotron XRPD data: 15.5°–16.5°, in which the (131) peak of LFP is converted to the (311) peak of FePO₄ during the initial charge process.
Figure 2. The electrochemical properties of LFP/Zn coin-cells with/without additive (1 mg mL⁻¹). a) The charge-discharge profiles at 0.5 C. b) The CV curves at 0.1 mV s⁻¹. c) The Li-ion diffusion coefficient in both systems, calculated based on the CV data at various scan rates. d) The rate capability tested from 0.5 to 20 C. e) the long cycling stability with the responding Coulombic efficiency measured at 5 C.
Figure 3. The influence of additive on the Zn anode. a, b and c) The morphologies of fresh Zn foil, and electrodeposited Zn electrodes with/without additive. d) XRD patterns of commercial Zn foil and electrodeposited Zn electrodes with/without additive. e) Polarization curves of Zn-Zn symmetric cells with/without additive at a constant current density of 0.5 mA cm$^{-2}$. 
**Figure 4.** The effect of surfactant additive on LFP cathode. a, b) The contact angle measurements at the LFP electrode/electrolyte interface with/without additive. c, d) The molecular dynamics calculations conducted at the LFP (010)/electrolyte interface with/without additive to study the Li-ion migration. Note: H in H\(_2\)O and SDBS (white); C in SDBS (brown); O ions in H\(_2\)O (red) and LiFePO\(_4\) (red); Li ions (green); Na in SDBS (yellow); PO\(_4\) (purple); FeO\(_6\) (brown). e) GITT measurements of LFP/Zn batteries with/without additive.
Figure 5. The electrochemical performance of LFP/Zn pouch-cell with additive. a) The charge-discharge profiles at 0.5 C, insert shows the LFP/Zn cells provide the power for 5 LEDs with different colours. b) The cycling stability.