

COORDINATION AND FLUORINE-CONTROLLED REGULATOR Zn²⁺ FOR STABLE AQUEOUS ZINC-ION BATTERIES

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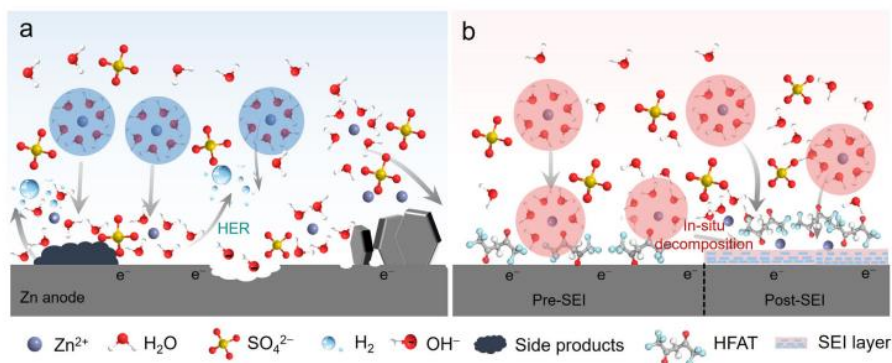
Electrolyte additives that simultaneously regulate Zn²⁺ solvation and induce the formation of a solid electrolyte interphase (SEI) offer an effective way to suppress dendrite growth, hydrogen evolution, and side reactions in aqueous zinc-ion batteries (AZIBs). Here, fluorinated acetylacetone derivatives are used to achieve these dual functions at low concentrations. Progressive fluorination enhances electron delocalization and lowers the lowest unoccupied molecular orbital (LUMO), which allows preferential accumulation on the Zn surface. In particular, hexafluoroacetylacetone (HFAT) forms stable [Zn(H₂O)₅HFAT]²⁺ solvation shells, which reduce the interfacial water activity and promote Zn²⁺ desolvation. The lower LUMO value of HFAT further enhances its preferential electrochemical reduction, leading to the formation of a gradient cement-brick-like ZnF₂-rich SEI that stabilizes Zn deposition and enhances Zn²⁺ transport. As a result, Zn||Zn symmetric cells exhibit a lifetime of over 4300 h at 1 mA cm⁻² / 1 mAh cm⁻², Zn||Cu cells achieve an average Coulomb efficiency of 99.62% over 1500 cycles, and Zn||I₂ full cells retain 125.8 mAh g⁻¹ after 10,000 cycles. This study highlights the potential of fluorine-guided electrolyte design to synergistically optimize solvation structure and interface stability for high-performance AZIBs.

Keywords: aqueous zinc-ion batteries, electrolyte additive, solid electrolyte interphase, solvation structure, zinc dendrites

1. Introduction:

The inherent safety and fast ionic conductivity of aqueous electrolytes, as well as the properties of the Zn metal anode, such as its resource-rich nature, high theoretical capacity (820 mAh g⁻¹, 5855 mAh cm⁻³), and low redox potential (-0.76 V vs. SHE), make aqueous zinc-ion batteries (AZIBs) an excellent choice for large-scale energy storage. Unfortunately, the instability exhibited by Zn anodes in aqueous electrolyte environments leads to rapid performance degradation, a phenomenon that has become a major obstacle to the commercialization of AZIBs. This instability mainly arises from two interrelated problems: dendrite growth and surface side reactions, both of which are fundamentally related to the solution structure of Zn²⁺ ions and the interface properties between the Zn anode and the electrolyte. In particular, a series of harmful side reactions, such as hydrogen evolution reaction (HER), Zn corrosion, and the formation of insulating byproducts such as Zn₄(OH)₆SO₄·4H₂O (ZHS) on the zinc surface, occur as a result of direct interaction with water molecules along the zinc anode in the unmodified electrolyte. In addition, the solvation shell of Zn²⁺ in the unmodified electrolyte is mainly coordinated by H₂O molecules, which have higher activity than ordinary water molecules and preferentially move towards the Zn anode surface. This creates a water-rich Zn anode/electrolyte interface environment, which enhances the anomalous distribution of Zn²⁺ ions and enhances the undesirable reactions associated with H₂O molecules, as shown in Scheme 1a. In addition, the heterogeneous Zn anode/electrolyte interface leads to an unbalanced Zn²⁺ deposition kinetic process, which promotes the formation of dendrites. It stands out as a particularly effective and simple method for stabilizing Zn metal anodes. In particular, electrolyte modulation offers the unique advantage of simultaneously tailoring the solvation structure of Zn²⁺ and modifying the state of the Zn electrode/electrolyte interface. For example, dimethyl sulfoxide (DMSO) can enter the inner solvation shell of Zn²⁺ due to its stronger binding ability to Zn²⁺ than water molecules, thereby suppressing

water reactivity. In addition, the preferential electro-reduction of DMSO molecules along the Zn surface led to the formation of a solid electrolyte interface (SEI), which protected Zn anodes from water molecules, smoothed Zn^{2+} diffusion, and controlled the Zn deposition process.



Scheme 1. Illustrations of the interfacial environment of the Zn electrode and interfacial solvation shells of Zn^{2+} cations a) in conventional aqueous electrolytes, b) with carbonyl-rich and F-rich HFAT additives.

Despite recent advances, the intrinsic correlation mechanism between the simultaneous regulation of solvation structure and in situ SEI formation by additives remains unclear. Therefore, future research should prioritize the development of multifunctional additives and fundamental investigation of their synergistic mechanisms at the molecular level to improve the longevity of Zn metal anodes and enhance the commercial viability of AZIBs. In this study, we present a fluorine-based electrolyte engineering strategy to modulate the electronic structure of a carbonyl-rich additive for AZIBs. Fluorination was found to enhance electron delocalization and significantly lower the lowest unoccupied molecular orbital (LUMO) energy. Among the additives tested, the highly fluorinated compound exhibited the lowest desolvation energy barrier and LUMO level and exerted a significant stabilizing effect on the Zn anode with a small concentration. As shown in **Scheme 1b**, the strong affinity of highly fluorinated hexafluoroacetylacetone (HFAT) for the Zn surface facilitates its accumulation at the electrode boundary. At the same time, the carbonyl groups interact strongly with Zn^{2+} and effectively replace the coordinated H_2O molecules in the Zn^{2+} solvation shell. This boundary solvation reconstruction mitigates water activity, suppresses dendrite growth and side reactions, and promotes faster insolubility of Zn^{2+} . Furthermore, the significantly reduced LUMO level facilitates the in situ formation of a ZnF_2 -rich SEI, which stabilizes the electrode interface, ensures uniform Zn^{2+} transport, and improves electrochemical performance. As a result, the dual-functional additive significantly extended the operating life of $\text{Zn}||\text{Zn}$ symmetric batteries to >4300 h at 1 mA cm^{-2} - 1 mAh cm^{-2} and maintained stable operation for >1120 h even under severe conditions (5 mA cm^{-2} - 5 mAh cm^{-2}). Furthermore, an excellent average Coulomb efficiency (CE) of 99.62% was achieved over 1500 cycles. The assembled full batteries with a realistic loading mass of $\approx 4.0 \text{ mg cm}^{-2}$ for the I_2 cathode exhibited excellent cycle stability, maintaining a high specific capacity of 125.8 mAh g^{-1} after 10,000 cycles.

2. Results and Discussion:

To systematically evaluate the effect of fluorine (F) substitution on the LUMO energy level in carbonyl-rich acetylacetone molecular orbital energy levels were calculated using density functional theory (DFT), as shown in **Figure 1a**. AT is an effective electrolyte additive to mitigate side reactions in AZIBs. The LUMO energy level of AT is -2.34 eV , while the highest occupied molecular orbital (HOMO) energy level is -5.95 eV . When one methyl group is replaced by a trifluoromethyl ($-\text{CF}_3$) group, the LUMO and HOMO energy levels (TFAT) of trifluoroacetylacetone decrease to -3.15 and -6.36 eV , respectively.

As in hexafluoroacetylacetone (HFAT), complete fluorination of both methyl groups lowers the LUMO and HOMO energy levels to -3.69 and -7.02 eV , respectively. This progressive decrease in orbital energies with increasing fluorination increases the reversibility of fluorinated additives, enhancing their degradation and facilitating SEI formation. The importance of fluorination strategies

in tuning electrochemical activity is highlighted. Electrostatic potential (ESP) analysis **Fig. 1b** shows that substitution of F on the carbonyl groups reduces the ESP, while electrons are localized around the F atoms due to their high electronegativity. Despite these changes, the carbonyl groups in the three additives retain significant electronegativity, thereby maintaining a strong coordination potential with Zn^{2+} within the valence shell. DFT calculations were performed to study the atomic-scale interactions between the additives and Zn electrolytes, focusing on the effect of fluorination on the Zn^{2+} solvation structures **Fig. 1c**. All carbonyl-rich additives exhibited higher binding energies with Zn^{2+} cations compared to pure water molecules. For example, the interaction energy between the —C=O groups of HFAT and Zn^{2+} was calculated to be -7.33 eV compared to -4.64 eV for water, indicating an increase in the stability of the solvation structure upon addition of the additive. Furthermore, these additives exhibited significantly lower binding energies with water molecules **Fig. 1d**, indicating a higher tendency to integrate into Zn^{2+} solvation shells.

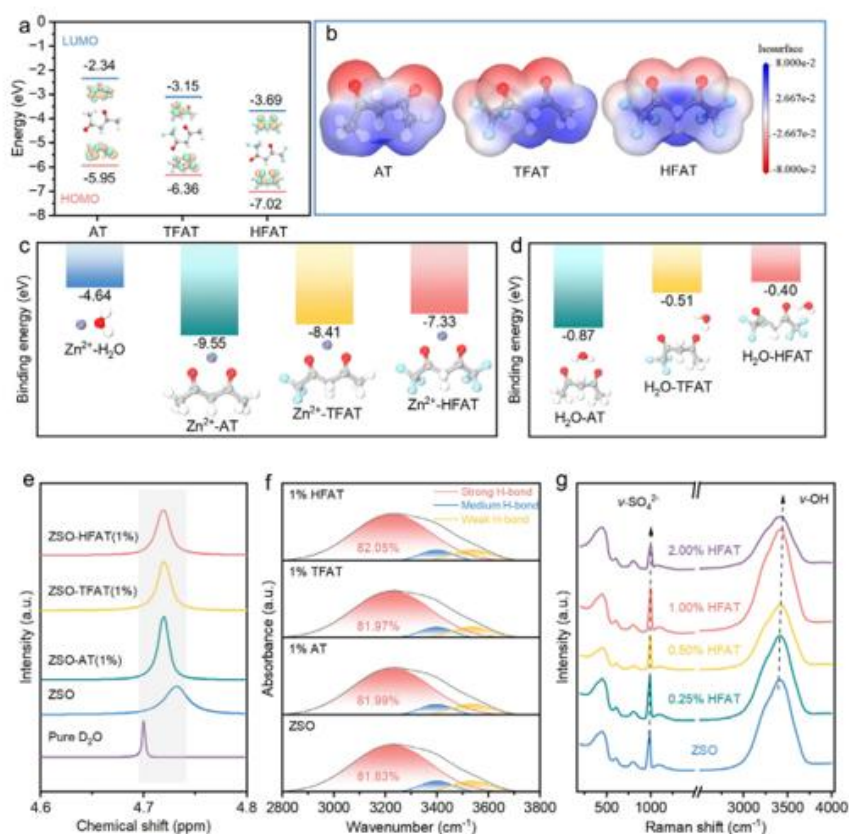


Figure 1. Electronic structure calculations of AT and the fluorinated TFAT, HFAT molecules, and their effect on water activity. a) The LUMO and HOMO energy values of different molecules. b) ESP diagrams for different molecules. c) Binding energies between the Zn^{2+} cations and the H_2O molecules or different additives. d) Binding energies between the H_2O molecules and different additives. e) ^1H NMR spectra of different solutions. f) FTIR spectra of different solutions. g) Raman spectra of different solutions.

It is noteworthy that this is due to the fact that ZnSO_4 has safer, more economical and chemically stable properties compared to other zinc salts. Nuclear magnetic resonance (NMR) spectroscopy was then used to study the interaction between the additives and Zn cations. As shown in **Fig. 1e**, the chemical shift caused by the addition of ZSO_4 reflects the decrease in electron density and the weakening of the screening of ^1H signals in water molecules, indicating a strong coordination between Zn^{2+} and H_2O . In contrast, the addition of additives (AT, TFAT to HFAT) causes an upward shift of water protons from 4.73 to ≈ 4.72 ppm, indicating a similar coordination between the additives and Zn^{2+} and transfers the bound water to the free state. Electrochemical tests confirm that this performance improvement is consistent with the lower LUMO energy level of HFAT and the moderate interactions between HFAT and Zn^{2+} ions. Further studies on the effect of fluorination on water activity were performed using Fourier transform infrared (FTIR) spectroscopy and Raman

spectroscopy. As shown in the figure, characteristic absorption signals corresponding to the carbonyl and trifluoromethyl functional groups in HFAT are clearly observed at ≈ 1750 and $\approx 1430/1360$ cm^{-1} , respectively. However, due to the relatively low concentration of HFAT in the electrolyte (1 vol%), these characteristic peaks are significantly attenuated and therefore difficult to detect in the FTIR spectrum of the complete electrolyte system. The O—H stretching bands of water are observed in the region of $2800\text{--}3800$ cm^{-1} **Fig. 1f**. strong H-bonding, medium H-bonding and weak H-bonding. It is noteworthy that the increase in strong H-bonding after the addition of AT, TFAT and HFAT indicates that the solvation structures are ordered, thereby converting the solvated water molecules into free states. Raman spectroscopy also confirms that as the amount of HFAT increases in ZSO₄ electrolyte, the $\nu(\text{O—H})$ peak exhibits a clear blue shift, indicating that HFAT is involved in the solvation shell of Zn^{2+} . Similarly, the $\nu(\text{O—H})$ band in the region from 2800 to 3800 cm^{-1} can be attributed to strong, medium and weak H-bonding. After the addition of HFAT, the proportion of strong H-bonds increased, while the proportion of medium-strength H-bonds decreased, further demonstrating that HFAT effectively liberated solvated water molecules and thereby modified the initial H-bond network in ZSO₄. The symmetric stretching vibration of SO_4^{2-} ($\nu\text{-SO}_4^{2-}$) witnessed a progressive blue shift with increasing electrolyte content, indicating that the addition of HFAT disrupts the electrostatic bonding between Zn^{2+} and SO_4^{2-} , further supporting the change in the solvation structure of Zn^{2+} by HFAT.

2.1 Regulation mechanism of Zn^{2+} solution structure:

As shown in **Figure 1b**, the negative ESP is mainly located at the carbonyl groups and to a lesser extent at the —CF_3 groups, indicating the presence of several potential anchoring sites for interaction with the metal surface. This distribution suggests that HFAT can preferentially adsorb onto the Zn surface, thereby providing modulation of the interface environment. To further investigate this behavior, theoretical calculations were performed to evaluate the adsorption properties. Specifically, the adsorption energies of H_2O and HFAT on the (002), (100), and (101) surfaces of Zn were calculated. The results shown in **Figure 2a** that HFAT exhibits significantly higher binding energies with the Zn anode than water molecules, indicating the preferential adsorption of HFAT on the Zn surface. In particular, HFAT selectively forms molecular layers on the Zn (002) surface, which is related to its relatively high adsorption energy on this surface. The decrease in contact angles with the addition of HFAT to the electrolyte can be a direct evidence of the change in the interfacial environment **Fig. 2b**. The gradual increase in wettability with increasing HFAT addition indicates the increased zincophilicity of HFAT. The electric double layer capacitance (EDLC) of the Zn electrode in Zn electrolyte and after the addition of 1 vol% HFAT is calculated. As shown in **Fig. 2c** the EDLC of the electrodes decreased significantly from 808 to 382 $\mu\text{F cm}^{-2}$ after the addition of HFAT. This decrease is due to the decrease in the effective electrochemical surface area at the HFAT-coated Zn/electrolyte interface. Due to the high interactions between the carbonyl groups of HAFT and Zn^{2+} , the diffusion and transport of Zn^{2+} across the interface is regulated. As observed from the chronoamperometry (CA) curves of the two electrolyte systems **Fig. 2d**, the current density in the pure ZSO electrolyte continuously decreases, which is consistent with the uncontrolled 2D diffusion behavior of Zn^{2+} on the electrode surface. This indicates that Zn^{2+} continuously diffuses to local high-activity nucleation sites, aggregates, and grows to form dendrites. In contrast, in the electrolyte containing HFAT, the current density gradually reaches equilibrium after 20 s. This is primarily due to the fact that the surface adsorption of HFAT onto metallic Zn regulates the Zn^{2+} transfer and homogenizes the Zn^{2+} flux. Meanwhile, the Zn^{2+} conduction number ($t_{\text{Zn}^{2+}}$), a key parameter reflecting the mobility of Zn^{2+} across the interface, increased from 0.38 in ZSO₄ to 0.61 in HFAT electrolyte **Fig. 2e**; indicating that HFAT electrolyte improves molecular dynamics, which may be related to the modulation of interface solvation. To confirm this, the activation energy (E_a) of the desolvation process of solvated Zn^{2+} was calculated to characterize the effect of HFAT on Zn^{2+} migration kinetics.

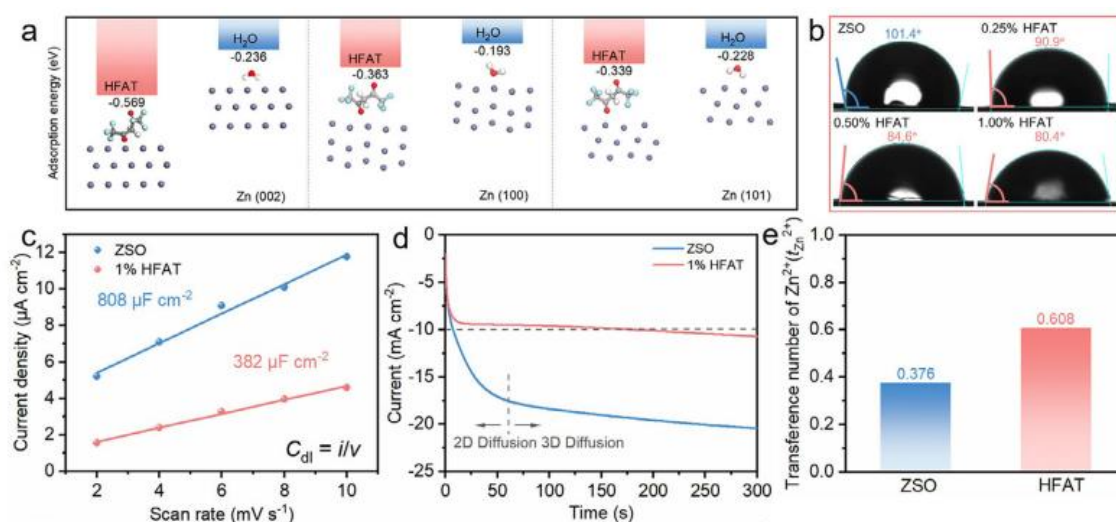


Figure 2. a) Adsorption energy of H₂O and HFAT molecules on the Zn surface. b) Contact angle measurements of different electrolytes on the Zn surfaces. c) EDLC of Zn||Zn symmetric cells. d) The Potentiostatic current-time transient curves of Zn foil tested in different electrolytes. e) $t_{Zn^{2+}}$ of two electrolyte systems.

2.2 Electrochemical performance of Zn anode:

We further assessed the enhanced effect of the HFAT additive on the zinc anodes, including the electrochemical stability and utilization rate. As shown in Figure 3a, the battery containing the HFAT additive exhibited remarkable reversibility and achieved a stable cycling for 4320 h, while the battery using the ZSO electrolyte only lasted for 103h, at 1 mA cm⁻²-1 mAh cm⁻². Impressively, at a higher current density of 5 mA cm⁻² Figure 3b, the battery with HFAT electrolyte had a cycling life as long as 1120 h, which was 24 times that of the ZSO battery. The latter suddenly failed after ≈ 46 h. The cycling stability was further evaluated at other current densities, all confirmed the positive effect of HFAT on the Zn electrode's stability. As shown in Figure 3c, when the current density was further increased to 20 mA cm⁻²-10 mAh cm⁻², the battery using the ZSO electrolyte would fail due to a short circuit within 79 h. In contrast, the HFAT battery could maintain a stable polarization voltage for as long as 410 h. Furthermore, the rate performance of the batteries was also evaluated within a current density range of 0.5–10 mA cm⁻². Notably, the symmetric batteries using the HFAT electrolyte exhibited superior rate performance with better stability and reversibility. Additionally, the cycling performance was further conducted at a higher depth of discharge (DOD). Under the condition of 5 mAh cm⁻²-3 mAh cm⁻², the DOD reached 51.3%.

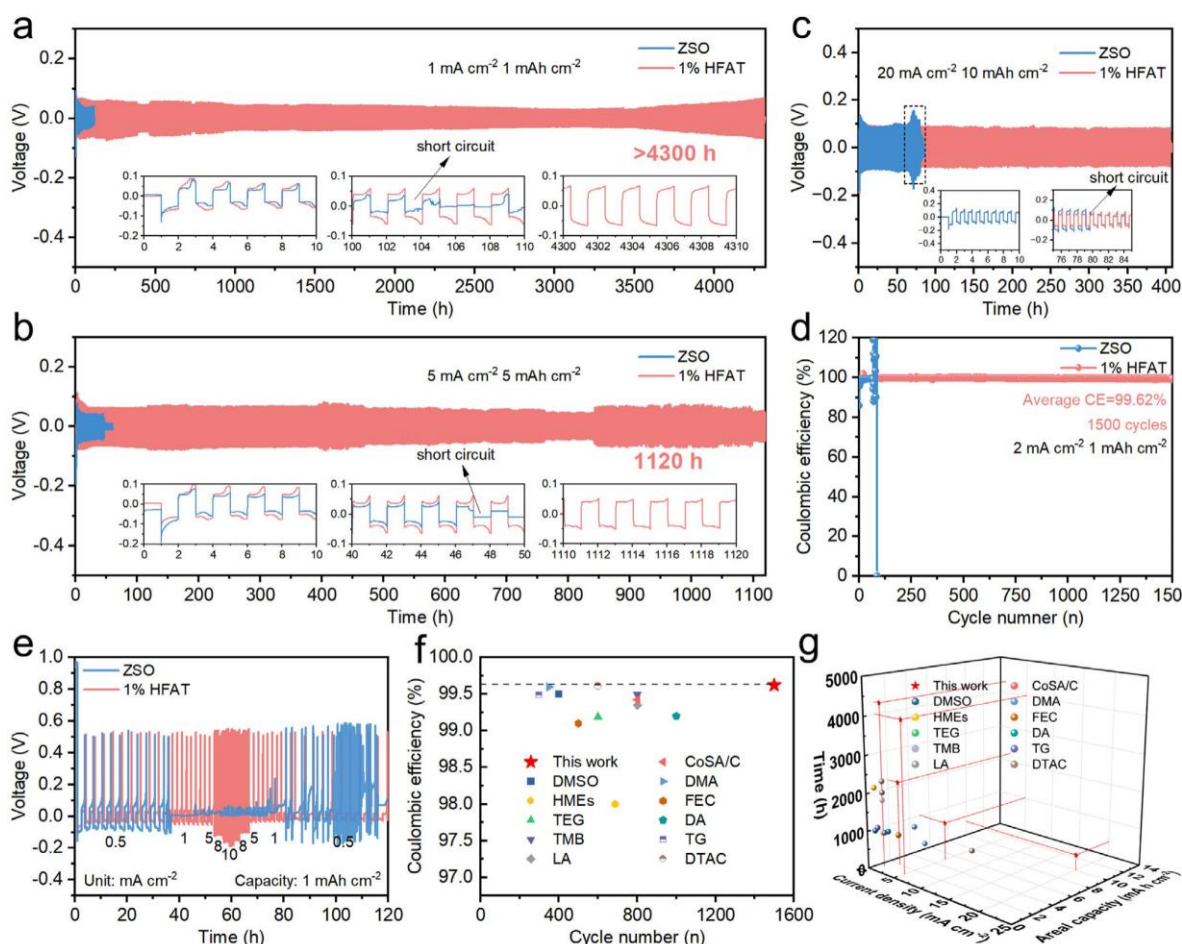


Figure 3. The stability evaluation and comparison of Zn anodes in different electrolytes. a–c) Cycling stability of Zn||Zn batteries at a) $1 \text{ mA cm}^{-2}/1 \text{ mAh cm}^{-2}$, b) $5 \text{ mA cm}^{-2}/5 \text{ mAh cm}^{-2}$, and c) $20 \text{ mA cm}^{-2}/10 \text{ mAh cm}^{-2}$. d) The CE of Zn plating/stripping on Zn||Cu asymmetric cells at $2 \text{ mA cm}^{-2}/1 \text{ mAh cm}^{-2}$. e) Rate performance. f) The comparison of the CE and cycle life enabled by HFAT with previously reported electrolytes. g) Comparison of the overall performance of the Zn anode with other reported symmetrical cells in modified electrolytes.

The Zn||Zn symmetric cell with HFAT achieved a lifetime of 286 h compared to 55 h for the cell with ZSO, which has contributed to the synergetic effect of SEI formation and solvation modulation of HFAT additive. The superiority of the gradient cementbrick-like SEI over other types of SEI films with F elements is also illustrated, whenever under a small capacity of 1 mAh cm^{-2} or a higher capacity of 5 mAh cm^{-2} , this work displayed notable extended cycling life. The CE was also evaluated based on Zn||Cu asymmetric cells to further evaluate the reversibility of the zinc anode. As depicted in **Figure 3d**, the HFAT electrolyte exhibited stable plating/stripping over 1500 cycles, with an average CE of 99.62%, which was significantly superior to that of the ZSO electrolyte. The ZSO electrolyte suffered from a short circuit after 66 cycles. Moreover, under the condition of 2 mA cm^{-2} - 1 mAh cm^{-2} , the initial CE of the HFAT electrolyte was evidently surpassed that of ZSO (97.05% vs 85.91%). Even after 1500 cycles, the HFAT electrolyte could still maintain 99.77%. Additionally, **Figure 3e** shows a plot of the multiplicative performance of the Zn||Cu asymmetric cells, which further highlights the excellent multiplicative performance of the HFAT electrolyte. The cells using ZSO electrolyte quickly failed at slightly higher current densities. In sharp contrast, the inclusion of HFAT in the electrolyte markedly promoted reversibility and facilitated uniform zinc deposition, thereby maintaining cell integrity and improving cycling stability. This remarkably prolonged cycling performance under high-rate and high-capacity conditions transcends that of other recently reported electrolyte systems **Figure 3f,g**; thus affirming HFAT as an effective additive with a synergistic effect of tuning solvation structure and in situ building SEI.

3. Conclusion:

This study demonstrates that fluorine-engineering can tailor the electronic structure of carbonyl-rich additives, thereby effectively addressing key challenges of Zn anodes in AZIBs by dual-regulation of solvation structure and SEI formation. The carbonyl-rich HFAT molecule can replace one H₂O molecule in the Zn²⁺ solvation shell along the interface due to the accumulated distribution of HFAT molecules and the high interactions between HFAT and Zn²⁺ cations, forming a stable [Zn(H₂O)₅HFAT]²⁺ structure with delocalized charge distribution. This reconfiguration facilitates charge decoupling and Zn²⁺ desolvation, reduces water reactivity, suppresses hydrogen evolution, and mitigates Zn corrosion. The relatively lowered LUMO energy level of HFAT from the fluorinated effect and its preferential adsorption on Zn surfaces guarantee the formation of a ZnF₂-rich SEI layer, by an in-situ electrochemical decomposition reaction. XPS and TEM analyses validate a gradient cement-brick-like ZnF₂-rich SEI layer, which isolates the anode from corrosive electrolytes, promotes the desolvation, accelerates the Zn²⁺ transfer, and homogenizes Zn²⁺ flux, enabling dendrite-free deposition and enhanced utilization ratio. Electrochemical tests highlight the superiority of HFAT: symmetric cells exhibit ultra-long cycling stability (>4300 h at 1 mA cm⁻²), while full cells retain high capacity (125.8 mAh g⁻¹ after 10 000 cycles). The enhanced performance stems from the synergistic effects of solvation regulation and SEI stabilization, which collectively suppress side reactions and ensure uniform Zn deposition. This work underscores the importance of fluorination engineering in tailoring the electronic structure of carbonyl-rich additives to simultaneously regulate the interfacial chemistry and solvation dynamics, offering a scalable pathway toward high-performance, durable AZIBs for grid-scale energy storage.

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