

Article

Interface Stabilization of Aqueous Aluminum Batteries via Non-Flammable Co-Solvent

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Abstract

Aqueous aluminum-ion batteries (AAIBs) face significant challenges due to interfacial instability and parasitic side reactions during the reversible deposition of aluminum. Here, we introduce a hybrid electrolyte incorporating triethyl phosphate (TEP), a non-flammable co-solvent that reconstructs the Al^{3+} solvation environment by suppressing water activity. This design extends the electrochemical stability window and enables uniform Al–Zn alloy formation at the anode interface. As a result, symmetric Al–Zn cells achieve over 4000 h of stable cycling. In full-cell configurations with $\text{V}_2\text{O}_5/\text{C}$ cathodes, the system demonstrates high capacity retention ($\sim 96\%$ over 450 cycles at 2 A g^{-1}) and coulombic efficiency. This work underscores the potential of solvation structure engineering via functional, flame-retarding co-solvent to advance the development of safe and durable aqueous electrolytes.

Keywords: aqueous batteries; aqueous aluminum-ion batteries; electrolytes; aluminum anode; alloy



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1. Introduction

Aqueous aluminum-ion batteries (AIBs) have emerged as a highly promising candidate for next-generation grid-scale energy storage systems [1–5]. Unlike alkali-metal elements, e.g., lithium, sodium, etc., which face concerns regarding safety issues, scarcity and geographical concentration, aluminum (Al) is one of the most abundant metallic elements in the Earth’s crust, ensuring a virtually limitless and inexpensive resource for large-scale battery production with secured safety in aqueous medium [5,6]. Furthermore, aluminum’s trivalent charge carrier boasts significantly higher theoretical capacity (2980 mAh g^{-1} and 8046 mAh cm^{-3}) than that of monovalent lithium, translating into its potential for energy-dense devices.

Early Al batteries adapted ionic liquids as electrolytes [7–10], which, despite the advantage of non-flammability, are unsuitable for large-scale energy storage applications due to their high cost and sensitivity to ambient moisture, necessitating complex fabrication processes. The use of aqueous electrolytes simultaneously mitigates risks associated with thermal runaway and fire hazards, while providing cost-effective alternatives for grid-scale energy storage systems [11–14]. Despite these compelling advantages, the widespread practical application of aqueous AIBs remains constrained by several fundamental challenges.

Unlike ionic-liquid electrolytes—in which the redox-active species are chloroaluminate anionic complexes (e.g., $[\text{AlCl}_4]^-$ / $[\text{Al}_2\text{Cl}_7]^-$) [15–17] rather than Al^{3+} —aqueous electrolytes contain trivalent Al^{3+} predominantly as the hexa-aqua complex, $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$. The strong primary hydration thus imposes a substantial desolvation energy barrier [18,19].

Moreover, given the substantially negative standard reduction potential of Al (-1.67 vs. Standard Hydrogen Electrode, SHE), the hydrogen evolution reaction (HER) is thermodynamically more favorable in aqueous solutions. Perpetual decomposition of water drives the accumulation of an electrochemically inert passivation layer, mainly composed of Al_2O_3 , on the surface of the Al anode. The formation of this detrimental layer is directly responsible for the poor cyclability that hinders the practical application of Al-metal anodes in aqueous electrolytes [20,21]. To bypass such issues, recent research has focused on employing metal anodes capable of alloying with Al, e.g., Zn [22–24], Cu [25], Sn [26,27], etc. Rather than acting as a mere passive electron conduit, the current collector is envisioned to actively participate in the electrochemical process through a reversible alloying/de-alloying reaction with Al ions provided by the electrolyte.

In the pursuit of stabilization of aqueous electrolytes, another research trajectory has been the introduction of organic co-solvents like acetonitrile (ACN) [24,28–31], carbonates [32–34], and dimethyl sulfoxide (DMSO) [35–37]. The primary objective is to widen the electrochemical stability window (ESW) of water-based electrolytes and to alter the solvation structure around the active charge carriers. While effective in enhancing electrochemical performance, these solvents carry substantial risks of flammability and toxicity, which are antithetical to the core safety advantage of aqueous systems.

Herein, we propose a strategy to stabilize the Al–Zn alloy anode surface by incorporating non-flammable triethyl phosphate (TEP) as a co-solvent in 1 m aluminum trifluoromethanesulfonate ($\text{Al}(\text{Otf})_3$) aqueous electrolyte. Among its homologues, TEP's molecular structure offers a distinct advantage. Shorter alkyl chains, as in trimethyl phosphate (TMP), are less effective at displacing coordinated water molecules, while longer chains, as in tributyl phosphate (TBP), result in excessive viscosity that impedes ionic conductivity. TEP's ethyl groups thus represent an optimal balance, enabling effective solvation engineering without compromising the essential transport properties of the electrolyte.

The TEP-modified hybrid electrolyte reconfigures the Al^{3+} solvation sheath, effectively suppressing water activity and expanding the electrochemical stability window. This restructured solvation environment enables uniform and reversible aluminum plating/stripping via alloying while mitigating interfacial degradation and mechanical instability. As a result, symmetric Al–Zn cells exhibit exceptional cycling stability exceeding 4000 h without signs of dendritic growth or electrode pulverization. Surface and structural characterizations reveal the formation of a homogeneous, planar Al–Zn layer, supported by alloy-specific chemical signatures and crystallographic shifts. The practical viability of the hybrid electrolyte was further validated in a full cell paired with a $\text{V}_2\text{O}_5/\text{C}$ cathode, delivering a capacity of 133 mAh g^{-1} with $\sim 99\%$ coulombic efficiency over 450 cycles at 2 A g^{-1} . This work offers a robust electrolyte design platform for safe, low-cost, and long-lasting aqueous multivalent-ion batteries by leveraging solvation structure engineering and interfacial alloy stabilization.

2. Materials and Methods

2.1. Materials Preparation

Electrolytes were prepared by dissolving 1 m (mol kg^{-1}) aluminum trifluoromethanesulfonate ($\text{Al}(\text{Otf})_3$) ($(\text{CF}_3\text{SO}_3)_3\text{Al}$, 99.9%, Sigma-Aldrich, Inc., St. Louis, MO, USA) with a designated combination of solvents by volume ratio between de-ionized water and triethyl phosphate (TEP) ($(\text{C}_2\text{H}_5\text{O})_3\text{PO}$, $\geq 99.8\%$, Sigma-Aldrich, Inc.). The baseline aqueous electrolyte (AE) consisted of 1 m $\text{Al}(\text{Otf})_3$ in de-ionized (DI) water, while a specified portion in volume of DI water was replaced by TEP for the hybrid electrolytes. Upon mixing, the electrolytes were kept under magnetic stirring at 60°C overnight.

V₂O₅/C composite electrodes were prepared by mixing 70:30 wt.% vanadium (V) oxide (V₂O₅, 99.9% trace metals basis, Sigma-Aldrich, Inc.):multi-walled carbon nanotubes (MWCNTs, >98% carbon basis, Sigma-Aldrich, Inc.) by ball-milling (TMAX-QM-04.A, Tmax, Xiamen, Fujian province, China) at 300 rpm for 30 h. The electrode slurry was prepared by mixing 8:1:1 wt.% V₂O₅/C:Super P (battery grade, Sigma-Aldrich, Inc., St. Louis, MO, U.S.A.):polyvinylidene fluoride (PVDF) ((CH₂CF₂)_n, Sigma-Aldrich, Inc., St. Louis, MO, U.S.A.), which was casted on carbon paper (Wizmac, Seo-Gu, Daejeon, Republic of Korea) before being punched in a diameter of 14 mm. The average mass loading of V₂O₅ for each electrode was ~2 mg.

2.2. Material Characterization

The solvation environment of the electrolytes was examined by Raman spectroscopy (LabRam Soleil, Horiba Ltd., Minami-Ku, Kyoto, Japan) and Fourier-transform infrared spectroscopy (FT-IR) (IR Tracer-100, Shimadzu, Nakagyo-Ku, Kyoto, Japan). Structural and morphological evolution of the surface survey was conducted using a scanning electron microscope (SEM) (S-4700, Hitachi, Chiyoda-Ku, Tokyo, Japan), a high-resolution field-emission scanning electron microscope (HR FE-SEM) (MIRA3-LMH, Tescan, Brno, Czech Republic), X-ray photoelectron spectroscopy (XPS) (ESCALAB250, Thermo, Waltham, MA, USA), and X-ray diffraction (XRD) (D8 Advance, Bruker, Billerica, MA, USA). Electrodes were taken out after 10 cycles and rinsed with pure ethanol (anhydrous, Sigma-Aldrich, Inc.) for the analysis. Viscosity of the electrolytes was measured with Ametek Brookfield DV-1 (Ametek, Berwyn, PA, USA).

2.3. Electrochemical Measurements

Linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) were performed using the electrochemical work station (Bio-Logic Science Instrument-VSP, Seyssinet-Pariset, France). LSV was conducted in a three-electrode configuration with stainless foil electrodes with Ag/AgCl (5 M KCl) as a reference electrode.

Plating/stripping performance and galvanostatic charge–discharge (GCD) tests were evaluated using an automated battery cycler (CT-4008T, Neware, Shenzhen, Guangdong, China) in CR-2032 coin cells.

3. Results and Discussion

Electrochemical impedance spectroscopy (EIS) was employed to identify the optimal solvent composition by probing the interfacial kinetics (Figure 1a). Note that the concentration of Al(OTf)₃ was fixed at 1 m throughout the study. The charge transfer resistance (R_{ct}) exhibits a distinct minimum at a 50:50 (v/v) H₂O:TEP ratio, decreasing from the aqueous electrolyte (AE) and then sharply increasing at 70% TEP.

To rationalize this trend, we correlated the R_{ct} with the electrolyte's bulk properties (Figure S1). The addition of TEP introduces competing effects on the electrolyte's bulk transport properties. While the viscosity steadily increases with higher TEP content, the ionic conductivity also increases, reaching a maximum value of 1.05 mS/cm at 50% TEP. This suggests that up to this point, any positive effects from the modified Al³⁺ solvation environment—which enhance the effective mobility of charge carrier—outweigh the negative impact of the rising viscosity. Beyond the 50% TEP threshold, however, the sharply increasing viscosity becomes the dominant, rate-limiting factor, causing a steep drop in ionic conductivity and thus impairing bulk ion transport.

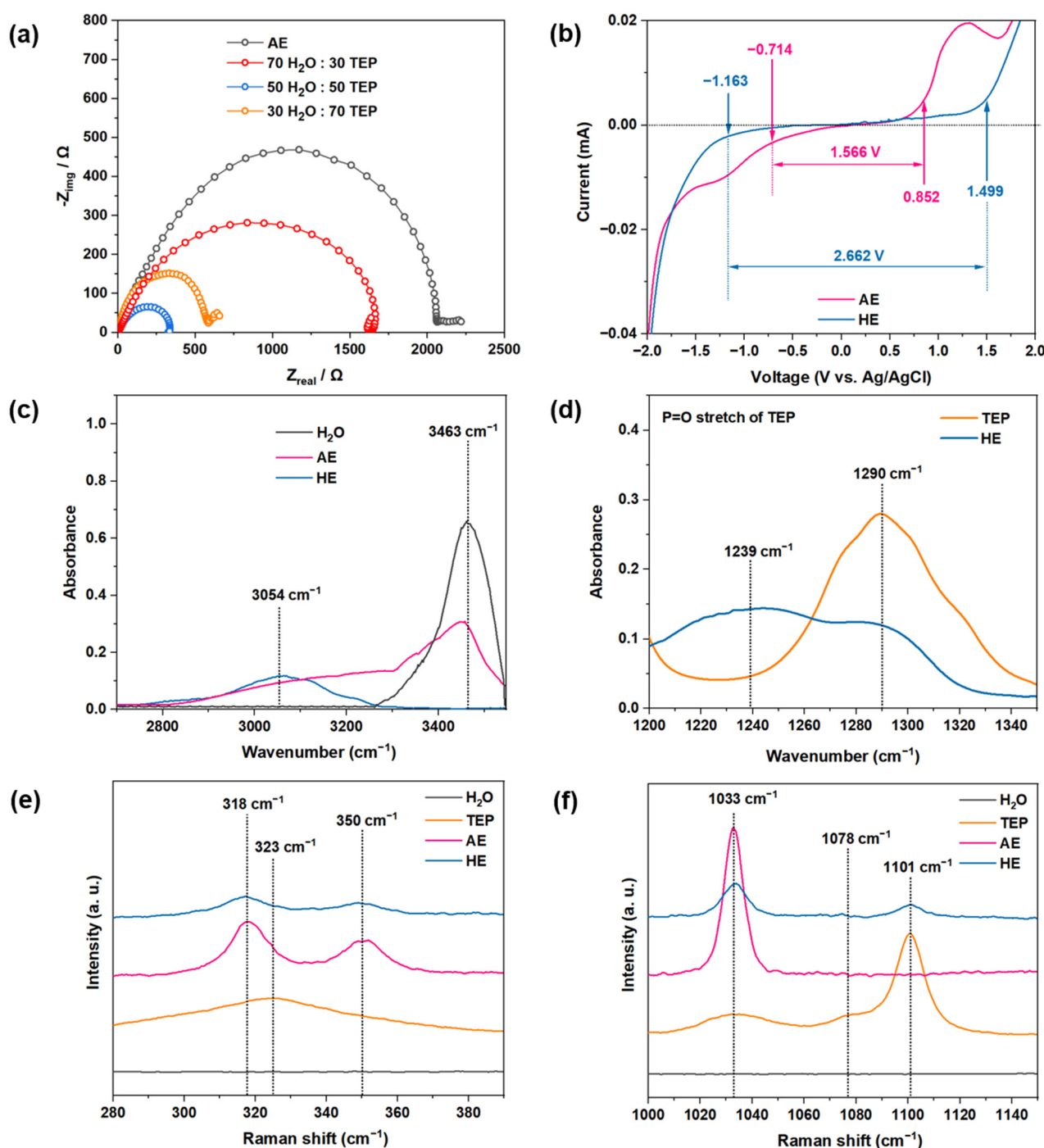


Figure 1. Electrochemical and spectroscopic characterization of electrolytes. (a) Nyquist plots of the electrolytes with varying H₂O:TEP volumetric ratios. (b) LSV curves of the AE and HE. FT-IR spectra from (c) 2700–3500 cm^{−1} and (d) 1200–1350 cm^{−1}. Raman spectra from (e) 280–390 cm^{−1} and (f) 1000–1150 cm^{−1}.

Therefore, the 50:50 H₂O:TEP mixture, which represents the optimal balance between favorable interfacial kinetics and sufficient bulk transport, was selected as the optimal solvent for the hybrid electrolyte (HE) for the subsequent investigations.

In addition to these kinetic and transport properties, the electrochemical stability was assessed using Linear Sweep Voltammetry (LSV) to complete the evaluation of the electrolytes (Figures 1b and S2). The LSV profiles reveal that the ESW systematically widens with increasing TEP content, expanding from 1.566 V in the AE to a maximum for the 70%

TEP electrolyte (Figure S2). Although the 70% TEP electrolyte offers the widest ESW, the HE (50:50) provides a substantial $\sim 70\%$ expansion to 2.662 V (Figure 1b). This significant gain in stability, combined with the superior interfacial kinetics (lowest R_{ct}) established, confirms that the HE composition represents the most effective overall compromise. This enhancement is attributed to the formation of a TEP-rich solvation sheath around Al^{3+} ions, which reduces the activity of free water molecules at the electrode interface [38,39].

To elucidate the molecular-level mechanisms underlying the improved ESW, the coordination environment of the electrolytes was systematically examined. In the Fourier-transform infrared (FT-IR) spectrum of the AE, a prominent and broad absorption band appears at approximately 3463 cm^{-1} , which corresponds to the O–H stretching vibrations associated with the extensive hydrogen-bonding network of bulk water (Figure 1c). In contrast, this band is significantly suppressed in the HE, indicating disruption of the hydrogen-bond network and the reduced free water content. Instead, a new broad band emerges at a lower wavenumber ($\sim 3054\text{ cm}^{-1}$), attributed to water molecules strongly coordinated to Al^{3+} in the TEP dominant solvation sheath [24,31]. The marked redshift and broadening of this bound water peak relative to that of bulk water confirms a strengthened Al^{3+} – H_2O interaction, confirming a restructured solvation environment dominated by TEP coordination.

Figure 1d provides the complementary spectral evidence of the coordination between Al^{3+} ions and TEP in the HE. Bare TEP displays a characteristic band at 1290 cm^{-1} , assigned to the non-coordinating phosphoryl group [40–42]. Upon the complexation in the HE, this peak shifts significantly to 1239 cm^{-1} and exhibits notable broadening with reduced intensity. This redshift is indicative of strong coordination between the phosphoryl oxygen and Al^{3+} , which weakens the P=O bond and results in a broader distribution of vibrational environments. The declined peak intensity further supports the conversion of free TEP molecules into Al^{3+} -bound species in the solvation sheath.

To further clarify the coordination environment of Al^{3+} ions in the HE, Raman spectroscopy was conducted (Figure 1e,f). In the low-frequency range (Figure 1e), the AE exhibits two distinct features: a sharp peak at $\sim 318\text{ cm}^{-1}$ and a broader band at $\sim 350\text{ cm}^{-1}$. The 318 cm^{-1} peak is associated with Al–O interactions involving either coordinated water or triflate anions [43–45], while the latter is indicative of Al–O stretching from $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ complexes [43,46,47]. The HE spectrum shows a broad shoulder spanning $315\text{--}325\text{ cm}^{-1}$, which is also observed in neat TEP. This feature is therefore attributed to P–O–C bending modes within the phosphate structure [48–51]. Although a comparable band appears in the AE spectrum, it is narrower and more intense, consistent with a well-defined Al–O coordination environment involving water. In contrast, the broader and less-defined feature observed in the HE reflects the involvement of TEP in Al^{3+} coordination, suggesting that TEP progressively replaces water and triflate anions.

The high-frequency region Raman spectra, shown in Figure 1f, offer further insight into the solvation structure. Pristine TEP exhibits bands at 1033 and 1101 cm^{-1} , corresponding to P–O–C and P=O stretching vibrations, respectively [48,52]. A shoulder band present near 1080 cm^{-1} originates from the combined band or overtone associated with P=O moiety [52]. Due to the overlapping contributions from the symmetric SO_3 stretching mode of $(\text{Otf})^-$, the intensity of 1033 cm^{-1} peak increases in the AE and the HE [53]. The 1101 cm^{-1} band remains weak in the AE, whereas it broadens in the HE. This broadening originates from the perturbation of the local P=O bonding due to the coordination between the phosphoryl oxygen of TEP and Al^{3+} [54]. Overall, the spectroscopic evidence confirms the formation of a distinct solvation structure in the HE, in which TEP plays a pivotal role. This reconfiguration of the Al^{3+} coordination environment underpins the improved electrochemical stability in the HE.

To investigate how reconfigured solvation environment practically translates into improved interfacial stability, the reversibility of plating/stripping was investigated using symmetric cells assembled with Al or Al–Zn electrodes in the AE at 0.2 mA cm^{-2} and 0.2 mAh cm^{-2} (Figure S3). The Al || Al cell displays a large initial overpotential, *ca.* 1.3 V, which gradually increases with cycling and leads to pronounced voltage instability beyond 130 h. This behavior is attributed to the accumulation of a native Al_2O_3 layer on the metallic Al surface, which hinders uniform Al deposition and dissolution. Even in the HE, the rapid failure of Al symmetric cells underscores the fundamental limitation of the inherently passivated Al metal anode (Figure S4).

Conversely, the Al–Zn symmetric cell shows markedly lower and more stable overpotentials of $\sim \pm 0.2 \text{ V}$ during early cycling period. This improvement is due to the formation of Al–Zn alloys, which facilitate nucleation of Al-ions by circumventing the insulating oxide layer [22–24]. The alloying interface provides a more favorable energetic landscape for charge transfer, enabling smoother plating/stripping during the initial operation. Despite the improved kinetics, the cycle life remains constrained in the AE; severe polarization leads to cell failure after $\sim 130 \text{ h}$, suggesting progressive interfacial degradation.

The Al–Zn symmetric cell in the HE upon the addition of TEP exhibits durable cycling stability, in stark contrast to the swift degradation observed in the AE (Figure 2a,b). The cell sustains highly reversible deposition of Al for over 4000 h with a markedly low and stable voltage hysteresis. The overpotential shows only a marginal increase of $\sim 10 \text{ mV}$ from 2500 h (Figure 2c) to 4000 h (Figure 2d), highlighting the favorable charge transfer with a stabilized electrode–electrolyte interface. To further probe the interfacial stability of the system, the rate capability was evaluated at current densities ranging from 0.2 to 3.2 mA cm^{-2} (Figure S5). The voltage hysteresis remained remarkably stable, showing only a modest increase at higher rates. This behavior is indicative of robust interfacial kinetics and the structural resilience of the Al–Zn electrode within the HE.

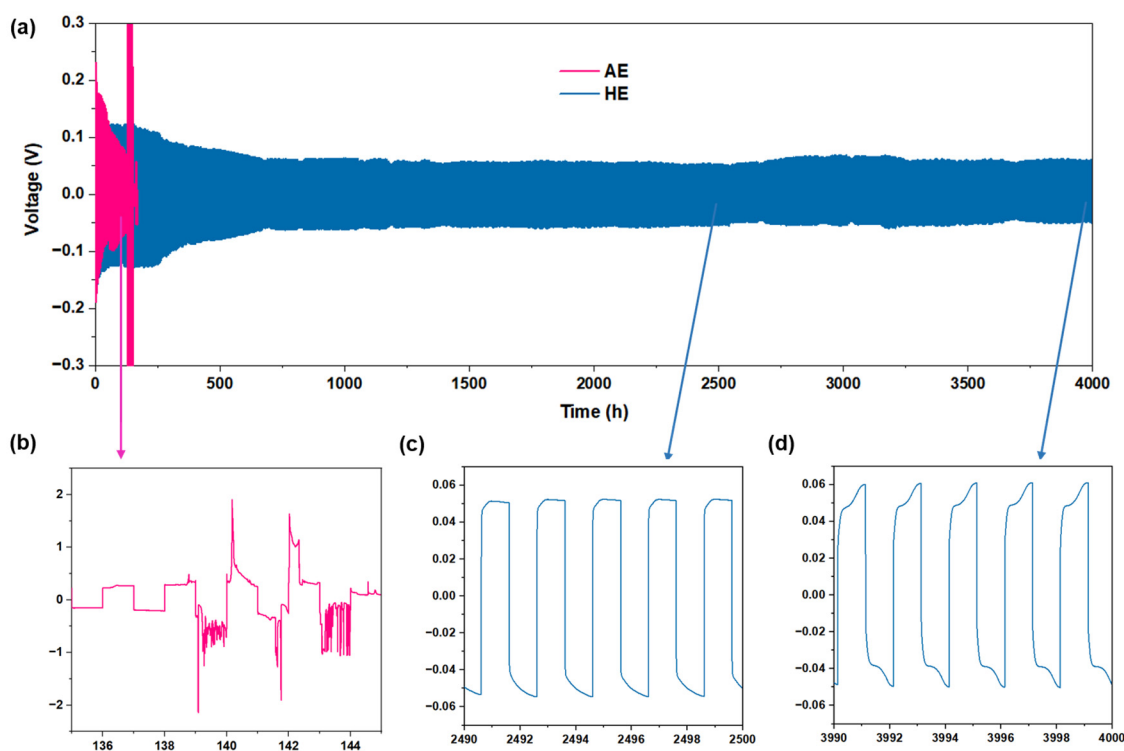


Figure 2. Electrochemical performance of Al–Zn symmetric cells (a) Long-term voltage profile. Enlarged voltage profiles from (b) 135–145 h of AE; (c) 2490–2500 h; and (d) 3990–4000 h in HE at 0.2 mA cm^{-2} and 0.2 mAh cm^{-2} .

A detailed post-mortem analysis was therefore conducted to characterize the morphology and composition of the anode interface responsible for the enhanced plating/stripping performance (Figure 3). The optical images of the cycled Al-Zn electrodes in Figure S6 visually contrast the deposition uniformity between the AE and HE systems after 10 plating/stripping cycles. While the AE-cycled electrode displays an uneven, patchy surface coverage, the HE-cycled electrode exhibits a smooth and homogeneously coated surface. To further investigate the surface morphology, scanning electron microscopy (SEM) was performed (Figure 3a,b).

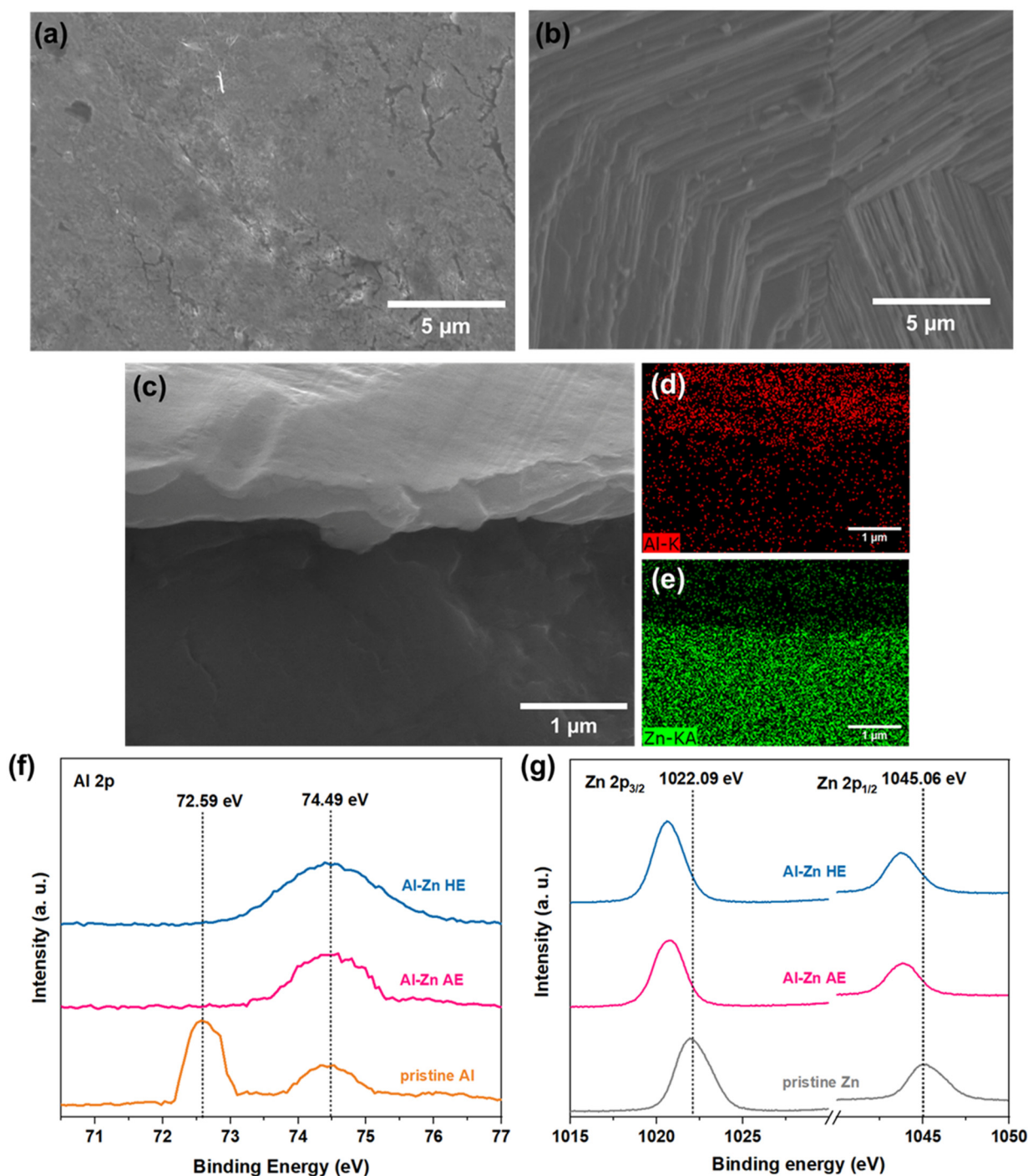


Figure 3. Structural analysis of electrodes after 10 cycles at 0.2 mA cm^{-2} and 0.2 mAh cm^{-2} . SEM images for Al-Zn cycled in (a) AE and (b) HE. (c) Cross-section HR FE-SEM image for Al-Zn cycled in HE with EDS mapping of (d) Al and (e) Zn. XPS spectra of (f) Al 2p and (g) Zn2p.

In the AE (Figure 3a), the anode surface consists of coarse, nodular deposits interspersed with pervasive microcracks. Such features are consistent with non-uniform local current density and parasitic side reactions, such as HER, that disrupt ion flux during the early cycles, producing a mechanically fragile and poorly adherent alloy layer. By contrast, the surface after cycling in the HE (Figure 3b) appears compact and terraced, lacking the porous nodules and crack network. This ordered, plate-like morphology is consistent with more uniform interfacial current distribution, yielding a cohesive deposit that induces the enhanced surface integrity of the Al–Zn anode in the HE.

A cross-section image of an electrode cycled in the HE from high-resolution field-emission SEM (HR FE-SEM) (Figure 3c) reveals a uniform and compact Al–Zn deposition layer with a clearly defined interface against the underlying Zn substrate. Elemental mapping by energy-dispersive X-ray spectroscopy (EDS) further verifies the formation of an Al–Zn alloy layer (Figure 3d), with aluminum uniformly distributed along the electrode surface (Figure 3e).

X-ray photoelectron spectroscopy (XPS) was conducted on Al–Zn electrodes after cycling to examine the surface chemical states (Figure 3f,g). The Al 2p spectrum for both samples shows a primary peak at ~ 74.5 eV, corresponding to oxidized Al^{3+} species [55,56]. However, a detailed analysis of the peak shape reveals critical differences. The Al 2p peak for the electrode cycled in the HE exhibits a more pronounced asymmetry with a broader shoulder at a lower binding energy, suggesting a significant contribution from an Al–Zn alloyed state alongside the oxide [57]. In contrast, the peak from the AE sample is more symmetric, closely resembling that of a standard passivating aluminum oxide layer [22–24].

This observation is complemented by the Zn 2p spectra (Figure 3g). Both cycled electrodes exhibit the characteristic Zn $2p_{3/2}$ and Zn $2p_{1/2}$ doublets shifted to lower binding energies compared to pristine Zn, confirming Al–Zn alloy formation [58,59]. Notably, this downshift is subtly more significant in the HE, indicating a more intimate and uniform electronic interaction between Al and Zn atoms. Taken together, these detailed XPS features—the asymmetric Al 2p peak and more pronounced Zn 2p shift in the electrode cycled in the HE—provide strong evidence for the formation of a more robust and electronically distinct Al–Zn alloy interface. This well-formed alloy interface is critical, as it acts as a stable, conductive pathway, effectively preventing the formation of a passivating, electrically insulating Al_2O_3 layer. This interfacial stabilization is the direct cause of the dramatically improved cycling stability and lower overpotentials observed for the HE system.

X-ray diffraction (XRD) analysis was conducted to further confirm the formation of Al–Zn alloy after electrochemical cycling (Figure S7). The diffraction pattern of pristine Zn displays two characteristic peaks centered at 36.51° and 39.31° , corresponding to the (002) and (100) planes of hexagonal Zn. In comparison, both peaks of Al–Zn in the AE and HE exhibit a slight shift toward lower 2θ values, indicative of lattice expansion induced by Al incorporation [60]. The absence of metallic Al or Al_2O_3 diffraction (i.e., 2θ of 38.47° for (111), 44.74° for (200), 65.13° for (220), 78.13° for (311) for Al (FCC), or broad peaks for $\gamma\text{-Al}_2\text{O}_3$) features suggest that Al is fully incorporated into the Zn lattice without forming separate crystalline Al or oxide phases. This lattice distortion, consistent with the XPS results, further supports the deposition via Al–Zn alloying.

Figure 4 demonstrates the electrochemical performance of the $\text{V}_2\text{O}_5/\text{C} \parallel \text{Al–Zn}$ full cell. The galvanostatic charge–discharge (GCD) profile at various current densities in the HE (Figure 4a) confirms its robust charge transfer kinetics. The cell delivered high reversible capacities of 378, 337, 295, 248, and 182 mAh g^{-1} at 0.2, 0.5, 1, 2, and 5 A g^{-1} , respectively, showcasing excellent rate capability. Even at a high current of 5 A g^{-1} , a

well-defined voltage profile was retained, indicating stable and fast charge transfer within the unique solvation structure of the HE.

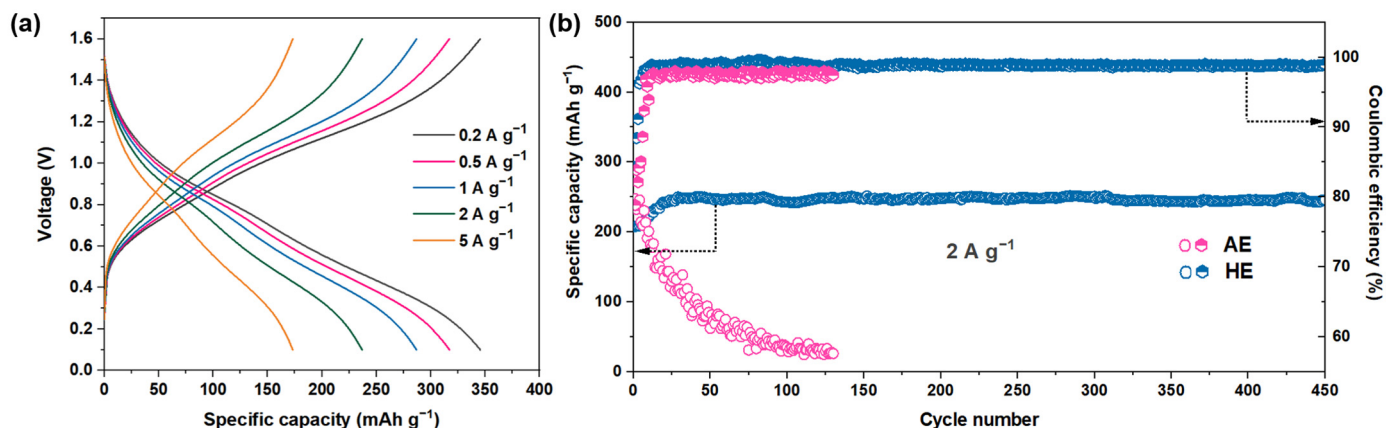


Figure 4. Electrochemical performance of $\text{V}_2\text{O}_5/\text{C} \parallel \text{Al-Zn}$. (a) GCD curves with varying current densities in HE. (b) Long-term cycling performance in AE and HE at 2 A g^{-1} .

A comparative long-term cycling performance was evaluated at 2 A g^{-1} to assess the enhanced interfacial stability by the HE. The AE cell exhibited rapid capacity fade, retaining <10% of its initial capacity after 130 cycles; whereas the HE cell maintained >96% of its post-formation capacity over 450 cycles with an average coulombic efficiency of 98.8%. Furthermore, post-mortem analysis confirmed that the Al-Zn anode maintained its structural integrity after 400 cycles, exhibiting a dense morphology without any signs of dendritic growth (Figure S8). Taken together, these results indicate that the TEP-modified hybrid electrolyte enhances interfacial stability at the Al-Zn alloy anode and mitigates surface degradation during extended cycling.

4. Conclusions

In summary, our findings demonstrate that the rational coordination environment design via TEP significantly reshapes Al^{3+} solvation, mitigates parasitic reactions, and stabilizes interfacial alloy formation. This approach not only resolves long-standing instability issues in aqueous Al batteries but also enables their integration into practical full cells with superior cycle life. The strategy opens avenues for electrolyte-driven stabilization in other multivalent-ion systems, offering a scalable path toward safe and sustainable energy storage.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/batteries11090324/s1>, Figure S1. Ionic conductivity (black) and viscosity (red) of the electrolytes with varying TEP composition; Figure S2. LSV curves of the electrolytes with varying TEP composition over (a) -2.0 – 2.0 V ; (b) -2.0 to 0.5 V ; and (c) 0.5 – 2.0 V ; Figure S3. Plating/stripping performance of $\text{Al} \parallel \text{AE} \parallel \text{Al}$ and (b) $\text{Al-Zn} \parallel \text{AE} \parallel \text{Al-Zn}$; Figure S4. Plating/stripping performance of $\text{Al} \parallel \text{HE} \parallel \text{Al}$; Figure S5. Voltage profile of $\text{Al-Zn} \parallel \text{HE} \parallel \text{Al-Zn}$ at varying current densities; Figure S6. Optical image of Al-Zn electrodes after 10 cycles in (a) AE and (b) HE; Figure S7. XRD pattern of pristine Zn and Al-Zn; Figure S8. SEM image for Al-Zn after 400 cycles in $\text{V}_2\text{O}_5/\text{C} \parallel \text{HE} \parallel \text{Al-Zn}$.

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Data Availability Statement: The data presented in this study are available upon request from the corresponding author to ensure integrity and prevent misunderstanding or misuse.

Conflicts of Interest: The author declares no conflicts of interest.

References

- Kim, K.-I. Progresses, Challenges and Prospects for Aluminum Anode in Aqueous Secondary Batteries. *J. Electrochem. Sci. Technol.* **2025**, *16*, 37–53. [\[CrossRef\]](#)
- Chao, D.; Zhou, W.; Xie, F.; Ye, C.; Li, H.; Jaroniec, M.; Qiao, S.Z. Roadmap for Advanced Aqueous Batteries: From Design of Materials to Applications. *Sci. Adv.* **2020**, *6*, eaba4098. [\[CrossRef\]](#)
- Blanc, L.E.; Kundu, D.; Nazar, L.F. Scientific Challenges for the Implementation of Zn-ion Batteries. *Joule* **2020**, *4*, 771–799. [\[CrossRef\]](#)
- Jia, H.; Wang, Z.; Tawiah, B.; Wang, Y.; Chan, C.Y.; Fei, B.; Pan, F. Recent Advances in Zinc Anodes for High-performance Aqueous Zn-ion Batteries. *Nano Energy* **2020**, *70*, 104523. [\[CrossRef\]](#)
- Ru, Y.; Zheng, S.; Xue, H.; Pang, H. Potassium Cobalt Hexacyanoferrate Nanocubic Assemblies for High-performance Aqueous Aluminum Ion Batteries. *Chem. Eng. J.* **2020**, *382*, 122853. [\[CrossRef\]](#)
- Butterwick, L.; Smith, G.D.W. Aluminum Recovery from Consumer Waste- I. Technology Review. *Resour. Conserv. Recycl.* **1986**, *9*, 281–292. [\[CrossRef\]](#)
- Kim, D.J.; Yoo, D.-J.; Otley, M.T.; Prokofjevs, A.; Pezzato, C.; Owczarek, M.; Lee, S.J.; Choi, J.W.; Stoddart, J.F. Rechargeable Aluminum Organic Batteries. *Nat. Energy* **2019**, *4*, 51–59. [\[CrossRef\]](#)
- Lin, Z.J.; Mao, M.L.; Yang, C.X.; Tong, Y.X.; Li, Q.H.; Yue, J.M.; Yang, G.J.; Zhang, Q.H.; Hong, L.; Yu, X.Q.; et al. Amorphous Anion-rich Titanium Polysulfides for Aluminum-ion Batteries. *Sci. Adv.* **2021**, *7*, eabg6314. [\[CrossRef\]](#)
- Pang, Q.; Meng, J.; Gupta, S.; Hong, X.; Kwok, C.Y.; Zhao, J.; Jin, Y.; Xu, L.; Karahan, O.; Wang, Z.; et al. Fast-charging Aluminum-chalcogen Batteries Resistant to Dendritic Shorting. *Nature* **2022**, *608*, 704–711. [\[CrossRef\]](#) [\[PubMed\]](#)
- Guo, Y.; Wang, W.; Lei, H.; Wang, M.; Jiao, S. Alternate Storage of Opposite Charges in Multisites for High-energy-density Al-MOF Batteries. *Adv. Mater.* **2022**, *34*, 2110109. [\[CrossRef\]](#)
- Ji, X. A Paradigm of Storage Batteries. *Energy Environ. Sci.* **2019**, *12*, 3203–3224. [\[CrossRef\]](#)
- Chen, Y.; Kang, Y.; Zhao, Y.; Wang, L.; Liu, J.; Li, Y.; Liang, Z.; He, X.; Li, X.; Tavajohi, N.; et al. A Review of Lithium-ion Battery Safety Concerns. *J. Energy Chem.* **2021**, *59*, 83–99. [\[CrossRef\]](#)
- Chayambuka, K.; Mulder, G.; Danilov, D.L.; Notten, P.H. From Li-ion Batteries toward Na-ion Chemistries: Challenges and Opportunities. *Adv. Energy Mater.* **2020**, *10*, 2001310. [\[CrossRef\]](#)
- Wang, Q.; Mao, B.; Stoliarov, S.I.; Sun, J. A Review of Lithium Ion Battery Failure Mechanisms and Fire Prevention Strategies. *Prog. Energy Combust. Sci.* **2019**, *73*, 95–131. [\[CrossRef\]](#)
- Angell, M.; Pan, C.-J.; Rong, Y.; Yuan, C.; Lin, M.-C.; Hwang, B.-J.; Dai, H. High Coulombic Efficiency Aluminum-ion Battery Using an AlCl₃-Urea Ionic Liquid Analog Electrolyte. *Proc. Natl. Acad. Sci. USA* **2017**, *114*, 834–839. [\[CrossRef\]](#)
- Lin, M.-C.; Gong, M.; Lu, B.; Wu, Y.; Wang, D.-Y.; Guan, M.; Angell, M.; Chen, C.; Yang, J.; Hwang, B.-J.; et al. An ultrafast rechargeable aluminium-ion battery. *Nature* **2015**, *520*, 324–328. [\[CrossRef\]](#)
- Garcia-Mendez, R.; Zheng, J.; Bock, D.C.; Jaye, C.; Fischer, D.A.; Marschilok, A.C.; Takeuchi, K.J.; Takeuchi, E.S.; Archer, L.A. Understanding the Reversible Electrodeposition of Aluminum in Low-cost Room-temperature Molten Salts. *Cell Rep. Phys. Sci.* **2023**, *4*, 101452. [\[CrossRef\]](#)
- Pastel, G.R.; Chen, Y.; Pollard, T.P.; Schroeder, M.A.; Bowden, M.E.; Zheng, A.; Hahn, N.T.; Ma, L.; Murugesan, V.; Ho, J.; et al. A Sobering Examination of the Feasibility of Aqueous Aluminum Batteries. *Energy Environ. Sci.* **2022**, *15*, 2460–2469. [\[CrossRef\]](#)
- Dong, T.; Ng, K.L.; Wang, Y.; Voznyy, O.; Azimi, G. An Aqueous Rechargeable Al-ion Battery Based on Cobalt Hexacyanoferrate and Al Metal. *Adv. Energy Mater.* **2021**, *11*, 2100077. [\[CrossRef\]](#)
- Zhao, Z.; Zhang, Z.; Xu, T.; Wang, W.; Wang, B.; Yu, X. Solvation Structure Regulation for Highly Reversible Aqueous Al Metal Batteries. *J. Am. Chem. Soc.* **2024**, *146*, 2257–2266. [\[CrossRef\]](#)
- Trachtman, M.; Markham, G.D.; Glusker, J.P.; George, P.; Bock, C.W. Interactions of Metal Ions with Water: Ab Initio Molecular Orbital Studies of Structure, Bonding Enthalpies, Vibrational Frequencies and Charge Distributions. 1. Monohydrates. *Inorg. Chem.* **1998**, *37*, 4421–4431. [\[CrossRef\]](#) [\[PubMed\]](#)
- Yan, C.; Lv, C.; Wang, L.; Cui, W.; Zhang, L.; Dinh, K.N.; Tan, H.; Wu, C.; Wu, T.; Ren, Y.; et al. Architecting a Stable High-energy Aqueous Al-ion Battery. *J. Am. Chem. Soc.* **2024**, *142*, 15295–15304. [\[CrossRef\]](#)
- Yang, X.; Zhang, C.; Chai, L.; Zhang, W.; Li, Z. Bimetallic Rechargeable Al/Zn Hybrid Aqueous Batteries Based on Al-Zn Alloys with Composite Electrolytes. *Adv. Mater.* **2022**, *34*, 2206099. [\[CrossRef\]](#)

24. Dou, Q.; Yao, N.; Pang, W.K.; Park, Y.; Xiong, P.; Han, X.; Rana, H.H.; Chen, X.; Fu, Z.-H.; Thomsen, L.; et al. Unveiling Solvation Structure and Desolvation Dynamics of Hybrid Electrolytes for Ultralong Cyclability and Facile Kinetics of Zn-Al Alloy Anodes. *Energy Environ. Sci.* **2022**, *15*, 4572–4583. [\[CrossRef\]](#)
25. Ran, Q.; Shi, H.; Meng, H.; Zeng, S.-P.; Wan, W.-B.; Zhang, W.; Lang, X.-Y.; Jiang, Q. Aluminum-copper Alloy Anode Materials for High-energy Aqueous Aluminum Batteries. *Nat. Commun.* **2022**, *13*, 576. [\[CrossRef\]](#)
26. Jia, B.E.; Hu, E.; Hu, Z.; Liew, J.J.; Hong, Z.; Guo, Y.; Srinivasan, M.; Zhu, Q.; Xu, J.; Chen, J.; et al. Laminated Tin-aluminum Anodes to Build Practical Aqueous Aluminum Batteries. *Energy Storage Mater.* **2024**, *65*, 103141. [\[CrossRef\]](#)
27. Wang, X.; Zhao, C.; Luo, P.; Xin, Y.; Ge, Y.; Tian, H. An Artificial Aluminum-tin Alloy Layer on Aluminum Metal Anodes for Ultra-stable Rechargeable Aluminum-ion Batteries. *Nanoscale* **2024**, *16*, 13171–13182. [\[CrossRef\]](#)
28. Chen, J.; Vatamanu, J.; Xing, L.; Borodin, O.; Chen, H.; Guan, X.; Liu, X.; Xu, K.; Li, W. Improving Electrochemical Stability and Low-temperature Performance with Water/acetonitrile Hybrid Electrolytes. *Adv. Energy Mater.* **2020**, *10*, 1902654. [\[CrossRef\]](#)
29. Shi, J.; Xia, K.; Liu, L.; Liu, C.; Zhang, Q.; Li, L.; Zhou, X.; Liang, J.; Tao, Z. Ultrahigh Coulombic Efficiency and long-life Aqueous Zn Anodes Enabled by Electrolyte Additive of Acetonitrile. *Electrochim. Acta* **2020**, *358*, 136937. [\[CrossRef\]](#)
30. Yang, D.; Watanabe, M.; Takagaki, A.; Ishihara, T. High Voltage and Capacity Dual-ion Battery Using Acetonitrile-aqueous Hybrid Electrolyte with Concentrated LiFSI-LiTFSI. *J. Electrochem. Soc.* **2022**, *169*, 120516. [\[CrossRef\]](#)
31. Dou, Q.; Lei, S.; Wang, D.-W.; Zhang, Q.; Xiao, D.; Guo, H.; Wang, A.; Yang, H.; Li, Y.; Shi, S.; et al. Safe and High-rate Supercapacitors Based on An “Acetonitrile/water in Salt” Hybrid Electrolyte. *Energy Environ. Sci.* **2018**, *11*, 3212–3219. [\[CrossRef\]](#)
32. Wang, F.; Borodin, O.; Ding, M.S.; Gobet, M.; Vatamanu, J.; Fan, X.; Gao, T.; Eidson, N.; Liang, Y.; Sun, W.; et al. Hybrid Aqueous/non-aqueous Electrolyte for Safe and High-energy Li-ion Batteries. *Joule* **2018**, *2*, 927–937. [\[CrossRef\]](#)
33. Miao, L.; Wang, R.; Di, S.; Qian, Z.; Zhang, L.; Xin, W.; Liu, M.; Zhu, Z.; Chu, S.; Du, Y.; et al. Aqueous Electrolytes with Hydrophobic Organic Cosolvents for Stabilizing Zinc Metal Anodes. *ACS Nano* **2022**, *16*, 9667–9678. [\[CrossRef\]](#)
34. Kakoty, B.; Vengarathody, R.; Mukherji, S.; Ahuja, V.; Joseph, A.; Narayana, C.; Balasubramanian, S.; Senguttuvan, P. Two for One: Propylene Carbonate Co-solvent for High Performance Aqueous Zinc-ion Batteries- Remedies for Persistent Issues at Both Electrodes. *J. Mater. Chem. A* **2022**, *10*, 12597–12607. [\[CrossRef\]](#)
35. Ren, H.; Li, S.; Xu, L.; Wang, L.; Liu, X.; Wang, L.; Liu, Y.; Zhang, L.; Zhang, H.; Gong, Y.; et al. Tailoring Water-in-DMSO Electrolyte for Ultra-Stable Rechargeable Zinc Batteries. *Angew. Chem.* **2025**, *137*, e202423302. [\[CrossRef\]](#)
36. Jia, H.; Jiang, X.; Wang, Y.; Lam, Y.; Shi, S.; Liu, G. Hybrid Co-solvent-induced High-entropy Electrolyte: Regulating of Hydrated Zn^{2+} Solvation Structures for Excellent Reversibility and Wide Temperature Adaptability. *Adv. Energy Mater.* **2024**, *14*, 2304285. [\[CrossRef\]](#)
37. Greenburg, L.C.; Holoubek, J.; Cui, Y.; Zhang, P.; Ai, H.; Zhang, E.; Liu, C.; Feng, G.; Cui, Y. Crowding Agent Stabilizes Aqueous Electrolyte for Reversible Iron Metal Anode. *ACS Energy Lett.* **2025**, *10*, 1022–1029. [\[CrossRef\]](#)
38. Wang, F.; Borodin, O.; Gao, T.; Fan, X.; Sun, W.; Han, F.; Faraone, A.; Dura, J.A.; Xu, K.; Wang, C. Highly Reversible Zinc Metal Anode for Aqueous Batteries. *Nat. Mater.* **2018**, *17*, 543–549. [\[CrossRef\]](#)
39. Naveed, A.; Yang, H.; Yang, J.; Nuli, Y.; Wang, J. Highly Reversible and Rechargeable Safe Zn Batteries Based on A Triethyl Phosphate Electrolyte. *Angew. Chem. Int. Ed.* **2019**, *58*, 2760–2764. [\[CrossRef\]](#)
40. Ali, A.F.; Mustarelli, P.; Magistris, A. Optimal Synthesis of Organo-phosphate Precursors for Sol-gel Preparations. *Mater. Res. Bull.* **1998**, *33*, 697–710. [\[CrossRef\]](#)
41. Rulmont, A.; Cahay, R.; Duyckaerts, M.L.; Tarte, P. Vibrational Spectroscopy of Phosphate: Some General Correlations between Structure and Spectra. *Eur. J. Solid State Inorg. Chem.* **1991**, *28*, 207–219.
42. Kim, D.J.; Hwang, H.Y.; Nam, S.Y. Characterization of Sulfonated Poly(Arylene Ether Sulfone) (SPAES)/Silica-phosphate Sol-gel Composite Membrane: Effects of the Sol-Gel Composition. *Macromol. Res. Up* **2013**, *21*, 1194–1200. [\[CrossRef\]](#)
43. Rudolph, W.W.; Mason, R.; Pye, C.C. Aluminum(III) Hydration in Aqueous Solution. A Raman Spectroscopic Investigation and an Ab Initio Molecular Orbital Study of Aluminum(III) Water Clusters. *Phys. Chem. Chem. Phys.* **2000**, *2*, 5030–5040. [\[CrossRef\]](#)
44. Rudolph, W.W.; Irmer, G. Hydration and Ion Pair Formation in Common Aqueous La(III) Salt Solutions- a Raman Scattering and DFT Study. *Dalton Trans.* **2015**, *44*, 295–305. [\[CrossRef\]](#)
45. Kumar, S.; Rama, P.; Yang, G.; Lieu, W.Y.; Chinnadurai, D.; Seh, Z.W. Additive-driven Interfacial Engineering of Aluminum Metal Anode for Ultralong Cycling Life. *Nanomicro Lett.* **2023**, *15*, 21. [\[CrossRef\]](#)
46. Latos, P.; Culkin, A.; Barteczko, N.; Boncel, S.; Jurczyk, S.; Brown, L.C.; Nockemann, P.; Chrobok, A.; Swadźba-Kwaśny, M. Water-tolerant Trifluoroaluminate Ionic Liquids: New and Unique Lewis Acidic Catalysts for the Synthesis of Chromane. *Front. Chem.* **2018**, *6*, 535. [\[CrossRef\]](#)
47. Ejigu, A.; Le Fevre, L.W.; Elgendy, A.; Spencer, B.F.; Bawn, C.; Dryfe, R.A. Optimization of Electrolytes for High-performance Aqueous Aluminum-ion Batteries. *ACS Appl. Mater. Interfaces* **2022**, *14*, 25232–25245. [\[CrossRef\]](#)
48. Czamara, K.; Majzner, K.; Pacia, M.Z.; Kochan, K.; Kaczor, A.; Baranska, E.M. Raman Spectroscopy of Lipids: A Review. *J. Raman Spectrosc.* **2015**, *46*, 4–20. [\[CrossRef\]](#)

49. Ta, K.M.; Cooke, D.J.; Gillie, L.J.; Parker, S.C.; Seal, S.; Wilson, P.B.; Phillips, R.M.; Skelton, J.M.; Molinari, M. Infrared and Raman Diagnostic Modeling of Phosphate Adsorption on Ceria Nanoparticles. *J. Phys. Chem. C* **2023**, *127*, 20183–20193. [\[CrossRef\]](#)
50. Latreche, M.; Willart, J.F.; Paccou, L.; Guinet, Y.; Danède, F.; Hédoux, A. Contribution of Low-frequency Raman Spectroscopy to Determine the Solubility Curves of Drugs in Polymers: The Case of Paracetamol/PVP. *Eur. J. Pharm. Biopharm.* **2020**, *154*, 222–227. [\[CrossRef\]](#)
51. Hadjiivanov, K.I.; Panayotov, D.A.; Mihaylov, M.Y.; Ivanova, E.Z.; Chakarova, K.K.; Andonova, S.M.; Drenchev, N.L. Power of Infrared and Raman Spectroscopies to Characterize Metal-organic Frameworks and Investigate Their Interaction with Guest Molecules. *Chem. Rev.* **2020**, *121*, 1286–1424. [\[CrossRef\]](#)
52. Fales, B.S.; Fujamade, N.O.; Nei, Y.W.; Oomens, J.; Rodgers, M.T. Infrared Multiple Photon Dissociation Action Spectroscopy and Theoretical Studies of Diethyl Phosphate Complexes: Effects of Protonation and Sodium Cationization on Structure. *J. Am. Soc. Mass Spectrom.* **2011**, *22*, 81–92. [\[CrossRef\]](#)
53. Horvath, A.; Anareddy, R.S.; Shaw, S.K. Solvents and Stabilization in Ionic Liquid Films. *Langmuir* **2022**, *38*, 9372–9381. [\[CrossRef\]](#)
54. Murugavel, R.; Choudhury, A.; Walawalkar, M.G.; Pothiraja, R.; Rao, C.N.R. Metal Complexes of Organophosphate Esters and Open-framework Metal Phosphates: Synthesis, Structure, Transformations, and Applications. *Chem. Rev.* **2008**, *108*, 3549–3655. [\[CrossRef\]](#)
55. Feliu, S., Jr.; Barranco, V. XPS Study of the Surface Chemistry of Conventional Hot-dip Galvanised Pure Zn, Galvanneal and Zn-Al Alloy Coatings on Steel. *Acta Mater.* **2003**, *51*, 5413–5424. [\[CrossRef\]](#)
56. Bonova, L.; Zahoranová, A.; Kováčik, D.; Zahoran, M.; Mičušík, M.; Černák, M. Atmospheric Pressure Plasma Treatment of Flat Aluminum Surface. *Appl. Surf. Sci.* **2015**, *331*, 79–86. [\[CrossRef\]](#)
57. Han, A.; Zhang, J.; Sun, W.; Chen, W.; Zhang, S.; Han, Y.; Feng, Q.; Zheng, L.; Gu, L.; Chen, C.; et al. Isolating Contiguous Pt Atoms and Forming Pt-Zn Intermetallic Nanoparticles to Regulate Selectivity in 4-Nitrophenylacetylene Hydrogenation. *Nat. Commun.* **2019**, *10*, 3787. [\[CrossRef\]](#) [\[PubMed\]](#)
58. Xu, Y.; Cui, X.; Wei, S.; Zhang, Q.; Gu, L.; Meng, F.; Fan, J.; Zheng, W. Highly Active Zigzag-like Pt-Zn Alloy Nanowires with High-index Facets for Alcohol Electrooxidation. *Nano Res.* **2019**, *12*, 1173–1179. [\[CrossRef\]](#)
59. Gong, M.; Deng, Z.; Xiao, D.; Han, L.; Hao, T.; Lu, Y.; Shen, T.; Liu, X.; Lin, R.; Huang, T.; et al. One-nanometer-thick Pt₃Ni Bimetallic Nanowires Advanced Oxygen Reduction Reaction: Integrating Multiple Advantages into One Catalyst. *Acs Catal.* **2019**, *9*, 4488–4494. [\[CrossRef\]](#)
60. Yang, C.; Wu, Z.; Zhang, G.; Sheng, H.; Tian, J.; Duan, Z.; Sohn, H.; Kropf, A.J.; Wu, T.; Krause, T.R.; et al. Promotion of Pd Nanoparticles by Fe and Formation of a Pd₃Fe Intermetallic Alloy for Propane Dehydrogenation. *Catal. Today* **2019**, *323*, 123–128. [\[CrossRef\]](#)

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