

RESEARCH ARTICLE

An Oligomeric Additive Bridges Inner and Outer Helmholtz Planes to Enable Reversible Zn Anodes via Spatial and Functional Decoupling

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ABSTRACT

Precise molecular engineering of the electrode/electrolyte interface remains a key bottleneck for aqueous Zn-ion batteries (ZIBs). Here, we report an oxidative polymerization strategy to synthesize oligomeric chromotropic acid disodium salt (OCAD) as a multifunctional additive. The oligomeric architecture bridges the inner and outer Helmholtz planes (IHP and OHP), shifting regulation from IHP-localized adsorption to full IHP/OHP coverage. The expanded dimeric framework (1.51 vs. 0.65 nm) displaces water molecules and promotes Zn²⁺ desolvation at the OHP via steric hindrance and hydrophobic effects, while sulfonic and phenolic hydroxyl groups repel SO₄²⁻ and buffer pH at the IHP through electrostatic repulsion and proton donation. This functional decoupling overcomes the consumption-driven failure of conventional small-molecule additives, suppressing side reactions and guiding uniform Zn deposition. Consequently, symmetric cells with OCAD-modified Zn anodes achieve exceptional cycling stability exceeding 4300 h at 1 mA cm⁻²/1 mAh cm⁻² and operate at an 85.6% depth of discharge. A full battery paired with a Na₂V₆O₁₆ cathode retains 81.6% capacity after 4700 cycles at 20 A g⁻¹. The performance translates effectively to high-mass-loading cathodes and pouch cells, underscoring practical viability. This work establishes molecular oligomerization as a versatile paradigm for long-range interface regulation in durable aqueous ZIBs.

1 | Introduction

The growing need for grid integration and peak load management is accelerating the search for inherently safe, cost-effective, and long-duration post-lithium energy storage solutions. In this context, Zn-based electrochemistry has emerged as a prominent candidate [1, 2]. Zn's terrestrial abundance and compatibility with highly conductive aqueous electrolytes offer several system-level advantages, such as rapid kinetics, straightforward manufactur-

ing, environmental sustainability, and inherent non-flammability [3–5]. Accordingly, aqueous Zn-ion batteries (ZIBs) are increasingly regarded as promising candidates for grid-scale energy storage. Nevertheless, their cycling stability and Coulombic efficiency (CE) are severely compromised by interfacial instability at the Zn anode. This instability leads to detrimental dendrite growth, parasitic hydrogen evolution reactions (HER), and the formation of passivating by-products, which together hinder the practical adoption of ZIBs [6].

Yanjing Wang and Le Zhou contributed equally to this work.

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The structure of the electrical double layer (EDL) at the Zn/electrolyte interface fundamentally governs the ion transport, charge accumulation, and reaction kinetics responsible for these failures [7, 8]. Comprising a compact inner Helmholtz plane (IHP) of desolvated Zn^{2+} and adsorbed water and a diffuse outer Helmholtz plane (OHP) of solvated ions, the EDL precisely controls each stage of Zn electrodeposition from initial desolvation and surface diffusion to the final charge transfer and nucleation [9, 10]. Ineffective EDL regulation concentrates the local electric field and creates an uneven Zn^{2+} flux, promoting tip-preferential deposition and dendritic growth [11]. Furthermore, the high concentration of H_2O molecules at both the IHP and OHP hinders the desolvation of hydrated Zn^{2+} ions and exacerbates parasitic HER. The resulting local pH shift then accelerates corrosion and passivation processes [12].

Electrolyte engineering, especially the addition of organic compounds, has become a promising approach to suppress Zn dendrite formation and associated side reactions. Various organics, including alcohols, amides, ethers, and sulfonates, have been utilized to orchestrate Zn^{2+} solvation, mitigate HER, and modulate deposition [13–17]. Their functionality typically arises from polar groups (e.g., $-\text{OH}$, $\text{C}=\text{O}$, $-\text{NH}_2$, $-\text{SO}_3\text{H}$), which facilitate hydrogen bonding or electrostatic attraction at the interface [18, 19], leading to selective adsorption and partial control over interfacial processes [20]. However, most contemporary additive strategies employ a single molecular species, which is often limited by a narrow functional scope and small molecular size. This limitation hinders comprehensive, multifaceted addressing of the complex challenges within the EDL environment. Conventional small-molecule additives can adsorb onto the IHP to displace water and inhibit HER, yet their influence remains largely confined to this immediate region. As a result, they exert limited control over ion distribution and the water network in the OHP and diffuse layer, where persistent issues, such as sluggish desolvation and unstable ion fluxes continue to drive dendritic growth [21]. Furthermore, the limited availability of polar functional groups also means that most additive molecules lose their mass-transport-regulating sites upon adsorption on the electrode surface. To address these challenges, a molecular-level design strategy that fine-tunes additive structures to achieve long-range regulation across the EDL is essential for optimizing the interfacial chemistry of the Zn anode [22, 23]. Given the considerable thickness of the OHP, engineering larger additive molecules while preserving oriented functional sites is particularly promising. Beyond IHP modulation, such molecules could adsorb and spatially extend their influence across the OHP, governing key processes such as Zn^{2+} desolvation and diffusion [24]. This strategic approach offers a promising pathway to holistically optimize the interfacial environment and enhance Zn anode durability.

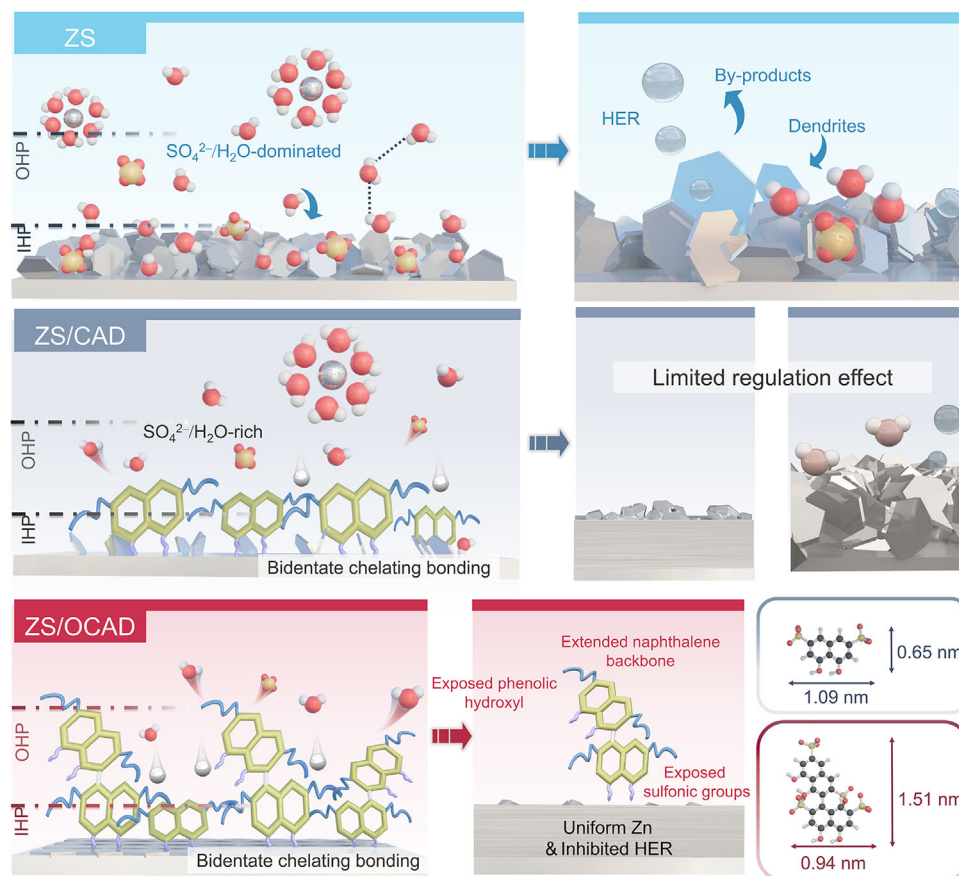
Herein, we report a molecular oligomerization strategy to engineer the EDL for highly reversible Zn anodes. Chromotropic acid disodium (CAD) is oxidatively polymerized to create an oligomeric additive system (OCAD) for a 1 M ZnSO_4 electrolyte (denoted as ZS/OCAD). The oligomer's extended hydrophobic naphthalene backbone modulates the OHP by displacing water molecules to create a dehydration interface. Simultaneously, OCAD anchors to the surface via bidentate chelation of its phenolic hydroxyl groups, while its exposed sulfonic and additional phenolic hydroxyl groups modulate the IHP through anion

repulsion and local pH buffering, thereby collectively suppressing side reactions. By integrating size-dominant control of the OHP with functional-group-driven management of the IHP, this stratified regulation accomplishes spatial scale bridging and interface functional decoupling within the EDL, thus optimizing Zn^{2+} kinetics and enabling reversible electrodeposition. Validating this approach, the ZS/OCAD electrolyte enables dendrite-free Zn plating/stripping in Zn//Zn symmetric cells, achieving an impressive cyclability of over 4300 h at $1 \text{ mA cm}^{-2}/1 \text{ mAh cm}^{-2}$, along with a high cumulative plating capacity and a Zn utilization rate of 85.6%. Furthermore, full batteries employing this additive maintain high-capacity retention rates of 88.8% with a high-mass-loading cathode (10.8 mg cm^{-2}) and 96.5% in a practical pouch cell configuration. This work demonstrates that molecularly tailored additives for stratified interfacial control offer a critical pathway toward practical aqueous ZIBs.

2 | Results and Discussion

The nanoscale architecture of the EDL fundamentally governs the stability of the Zn anode. Designed with this in mind, larger molecular or polymeric additives can extend their sphere of influence, enabling the simultaneous modulation of both the IHP and OHP. Therefore, moving beyond small molecules to strategically engineer additives with expanded dimensions is imperative for constructing a robust, multifunctional EDL, paving the way for highly durable Zn metal anodes. CAD, featuring a 1,8-dihydroxynaphthalene core structure can serve as a precursor for the oxidative polymerization process with the aid of hydrogen peroxide, ammonium persulfate (APS), and other related compounds [25, 26]. The generated radicals couple at the ortho-positions of the hydroxyl groups, facilitating the formation of extended dimers to yield an oligomeric system with a large molecular size. This structural evolution is crucial for achieving multiscale EDL regulation (Scheme 1). The adsorption of a monomeric CAD molecule with a width of 0.65 nm primarily modulates the IHP's local chemistry, but fails to substantially influence ion diffusion and desolvation dynamics. In contrast, the oxidatively formed dimer with a molecular size of 1.51 nm, creates a sprawling polymeric scaffold across the electrode surface. Moreover, due to its exposed phenolic hydroxyl groups, the oligomeric additive effectively repels anions and buffers interfacial pH. This functionality is absent in monomers, as these groups are consumed during interfacial adsorption. By simultaneously concentrating Zn^{2+} at the IHP and expanding the water-poor region across the IHP/OHP, OCAD forges an interfacial environment conducive to efficient desolvation and rapid Zn^{2+} diffusion, thereby markedly enhancing ion transport kinetics across the EDL.

The OCAD additive was synthesized by polymerizing CAD in an aqueous solution using APS as the initiator at 80°C . Liquid chromatography time-of-flight mass spectrometry (LC-TOF-MS) confirms the formation of oligomeric species, as evidenced by characteristic peaks at $m/z = 638.92$ (Figure 1a), indicating the presence of a mixture containing dimers, in contrast to the CAD monomer (Figure S1) [27]. The observed redshift of the characteristic peaks at around 239 and 356 nm in the ultraviolet-visible (UV-vis) absorption spectra also indicates an extended conjugated system in the products (Figure S2) [28]. This



SCHEME 1 | The oligomerization of CAD extends its hydrophobic naphthalene framework, creating a dehydrated interface that promotes Zn^{2+} desolvation and diffusion, while simultaneously exposing phenolic hydroxyl groups that buffer the interfacial pH environment.

spectroscopic change aligns with the pronounced color shift of the solution from light to dark after polymerization (Figure S3). To further clarify the oligomer composition, dynamic light scattering (DLS) was used to measure the hydrodynamic diameters of the CAD monomer and OCAD in aqueous solution (Figure 1b). The CAD monomer shows an average diameter of 1.11 nm, in good agreement with its theoretical molecular size of 1.09 nm. Following oxidative polymerization, OCAD exhibits a markedly increased average diameter of 1.50 nm, which closely matches the calculated size of the CAD dimer (1.51 nm) [29]. Collectively, these DLS results, along with the LC-TOF-MS and UV-vis data, confirm that OCAD consists primarily of dimeric species. In addition, comparisons across different polymerization temperatures and monomer-to-initiator ratios also suggest that the oligomeric products are consistently dominated by dimers (Figure S4). This is likely attributable to the rapid consumption of monomers or deactivation of active centers after the initial coupling step, which limits further extension of the polymerization degree. It is also worth noting that after dialysis of the polymerization products, the ultraviolet colorimetric test indicates that the initiator APS could be effectively removed (Figure S5) [30].

The solvation environment of different electrolytes was analyzed by nuclear magnetic resonance (NMR) and attenuated total reflectance Fourier transform infrared (ATR-FTIR) measurements. As shown in Figure S6, the ^2H NMR signals for both ZS/CAD and ZS/OCAD are centered at around 4.716 ppm

with no measurable shift, indicating that the additive molecules have a negligible influence on the solvation structures in the bulk electrolyte [31]. The corresponding ATR-FTIR spectra show that the characteristic vibrational stretches of both SO_4^{2-} and O–H remain unaltered with the introduction of CAD or OCAD additives (Figure S7), further corroborating that these molecules do not perturb the native solvation structure [32]. The specific role of each additive in stabilizing the Zn anode required further clarification, prompting a systematic study of their interfacial electrochemical behaviors. In particular, density functional theory (DFT) calculations were performed to unravel the molecular-level mechanism governing the interfacial behavior of the CAD dimer. As shown in Figure 1c, the CAD dimer achieves a significantly stronger adsorption energy (-3.65 eV) via bidentate chelation of its phenolic hydroxyl groups, compared to CAD (-2.55 eV) and H_2O (-0.83 eV), demonstrating its preferential adsorption and enhanced ability to displace interfacial water molecules. Furthermore, charge density difference analysis was employed to compare these interfacial interactions (Figure 1d–f). The distinct regions of charge accumulation and depletion confirm that adsorption occurs primarily via the phenolic bonding sites. Notably, the most substantial charge transfer corresponds to the bidentate chelation of a CAD dimer molecule on the Zn slab [33]. A further noteworthy point is that OCAD, generated through the oligomerization of CAD, bears supplementary phenolic hydroxyl groups relative to the monomer. This design circumvents the typical loss of mass transport regulation functionality

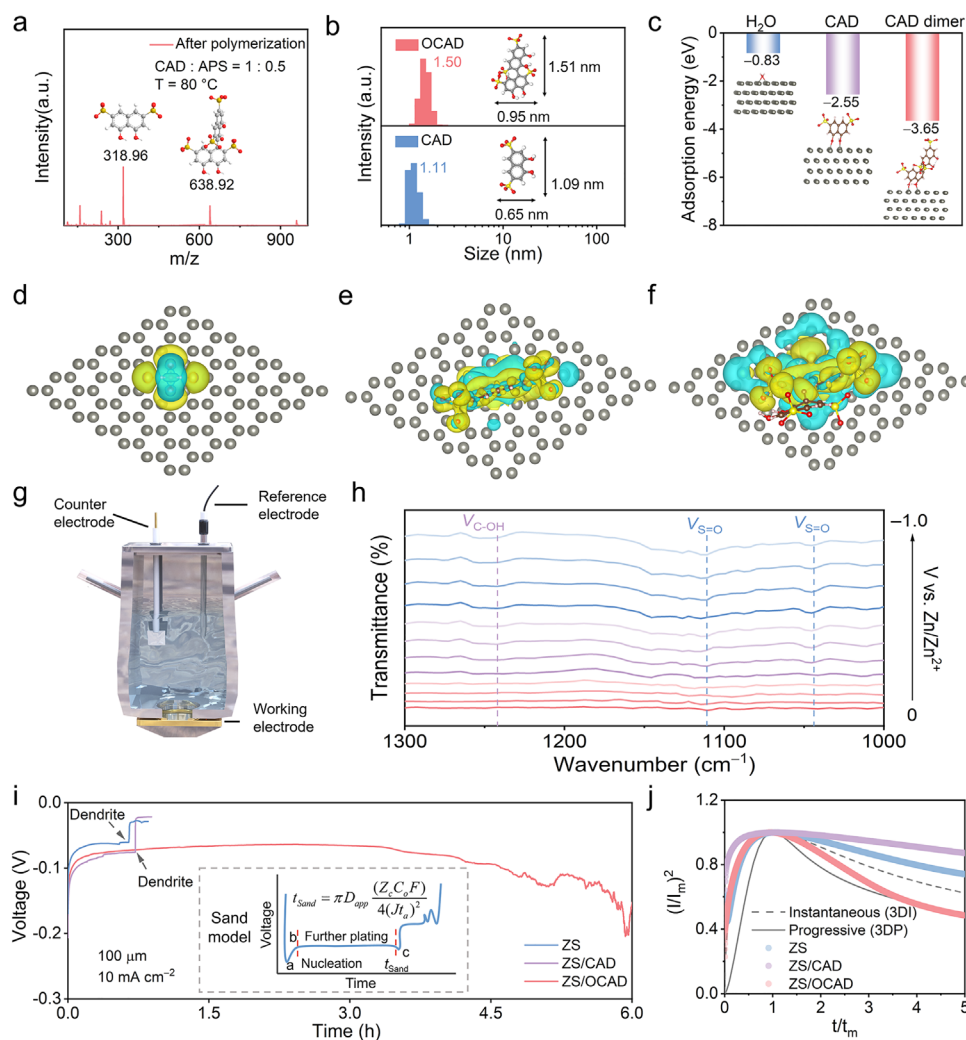


FIGURE 1 | (a) LC-TOF-MS of the OCAD-containing solution. (b) DLS size distribution of the solution before and after oxidative polymerization. (c) Adsorption energies of H_2O , CAD, and CAD dimer on Zn slab. Charge density difference of Zn slab with the adsorbed (d) H_2O , (e) CAD, and (f) CAD dimer molecule (yellow and cyan isosurfaces represent electron accumulation and depletion, respectively). (g) Schematic diagram of the in situ ATR-SEIRAS setup. (h) In situ ATR-SEIRAS spectra under various potentials for the OCAD-containing electrolyte in the range of 1000–1300 cm^{-1} . (i) Voltage-time curves of symmetric cells under 10 mA cm^{-2} for different electrolytes. (j) Modeling of 3D nucleation: normalized $(I^2/I_m^2 \text{ vs. } t/t_m)$ plots for different electrolyte systems.

following adsorption of polar molecules, thereby allowing for the modulation of interfacial pH and electrochemical reactions.

The molecular size of the interfacial adsorbate dictates the material composition and EDL structure at the Zn anode interface, which is decisive for the ensuing electrochemical reactions [34]. Compared to CAD, OCAD features an extended hydrophobic naphthalene ring structure of larger dimensions, complemented by exposed sulfonic acid and hydroxyl groups. This unique combination confers both hydrophobicity and zincophilic properties, creating favorable conditions for modulating the EDL structure. Contact angle measurements were performed to assess the ability of the additives to regulate water molecules at the interface (Figure S8). Zn foils were immersed in different electrolytes, and the water contact angles on the treated surfaces were measured. It is observed that the Zn foil immersed in the ZS/OCAD electrolyte exhibits the largest contact angle of 100° , which is greater than those obtained with ZS (52°) and ZS/CAD

(60°). This may be attributed to the adsorption of OCAD on the surface of the Zn electrode. The OCAD solution system provides larger naphthalene ring structures, which significantly enhance hydrophobicity and help establish a superior hydrophobic microenvironment. To elucidate the influence of additives on the EDL structure, differential capacitance (C_d) curves reveal that the ZS/OCAD electrolyte delivers higher capacitance over the 0–0.8 V voltage range than ZS and ZS/CAD (Figure S9). Moreover, we measured the interfacial capacitance across different electrolyte systems using cyclic voltammetry (CV) at various scan rates (Figure S10). The electric double-layer capacitance (EDLC) increases progressively and is well correlated with the molecular structure of the additive. This trend suggests that the enlarged hydrophobic naphthalene ring, synergizing with the exposed sulfonate and hydroxyl groups, promotes the formation of a more compact EDL by excluding H_2O molecules and SO_4^{2-} anions from the interface. The superior capacitance of ZS/OCAD directly corroborates this mechanism, as its oligomeric structures

provide a larger hydrophobic domain and optimized adsorption configurations, which collectively refine the ion distribution and enhance interfacial charge storage [35]. To quantitatively characterize the interfacial potential, zeta potential measurements were performed on Zn powders dispersed in different electrolyte solutions (Figure S11). The ZS/OCAD electrolyte exhibits the most negative zeta potential (-11.8 mV), compared to ZS/CAD (-10.6 mV) and the additive-free ZS electrolyte (-4.7 mV). This more negative surface potential arises from the adsorption of OCAD oligomers, which create an electron-rich interface. Such a negatively charged interface electrostatically attracts Zn^{2+} ions while repelling SO_4^{2-} anions, thereby promoting cation enrichment and suppressing anion-induced side reactions. In situ attenuated total reflection surface enhanced infrared absorption spectroscopy (ATR-SEIRAS) was employed to dynamically track the evolution of interfacial species during Zn electrodeposition. This measurement was conducted in a spectral electrochemical liquid cell, which comprised a Pt counter electrode, an Ag/AgCl reference electrode, a chemically deposited ultrathin Au film as the working electrode, and the ZS/OCAD electrolyte (Figure 1g). The Au film electrode was selected owing to the plasmonic resonance effect on its surface, which enhances the infrared signals of molecules in close proximity [17]. For the ZS/OCAD electrolyte, distinct characteristic peaks corresponding to sulfonate groups appear at approximately 1040 and 1110 cm^{-1} , attributed respectively to the asymmetric and symmetric stretching vibrations of the S=O bond (Figure 1h). As deposition progresses, these peaks become increasingly pronounced, revealing time-dependent exposure and interfacial enrichment of sulfonate groups. Additionally, a persistent absorption band at ~ 1240 cm^{-1} can be observed, assigned to the C–OH stretching of phenolic hydroxyl groups. This indicates that one pair of phenolic hydroxyl groups adsorbs onto the Zn surface via bidentate chelation, while the other pair remains exposed. This observation directly illustrates the functional decoupling enabled by OCAD. The sulfonate groups operate at the OHP to exclude SO_4^{2-} anions and mitigate side reactions, while the phenolic hydroxyl groups anchor the molecule to the Zn surface at the IHP and contribute to pH buffering.

Furthermore, the impact of additive concentration on interfacial electrochemistry was analyzed. During dissolution of the CAD monomer, it can be found that a maximum dissolution of 0.016 g is achieved in 40 mL of solution. Thus, the effect of lower precursor dosages on performance was then investigated. However, as the CAD monomer content is reduced to 0.004 g, the Zn//Zn symmetric cell exhibits a decreased differential capacitance, with an EDLC value of only 159 $\mu\text{F cm}^{-2}$, indicating insufficient adsorption density and poor EDL reconstruction (Figure S12). The long-term cycling performance of symmetric Zn//Zn cells using the oligomeric additive derived from different amounts of CAD precursor is shown in Figure S13. As the CAD monomer content decreases, the weakened interfacial regulation leads to a marked decline in the durability of Zn plating/stripping cycling. Specifically, when the monomer content is reduced from 0.016 g (which enables 400 h of stable cycling) to 0.004 g, the Zn//Zn symmetric cell failed to operate normally at 10 $\text{mA cm}^{-2}/10$ mAh cm^{-2} . These results confirm that at very low monomer concentrations, the oxidative polymerization generates insufficient amount of oligomeric OCAD species, rendering the additive incapable of providing effective interfacial regulation. The optimal OCAD

concentration used in this study (derived from 0.016 g of CAD precursor) ensures sufficient surface coverage, enabling stable interfacial electrochemical reactions. Accordingly, the maximum additive concentration was adopted for deep studies in this work. The reconfigured EDL structure is intimately linked to enhanced Zn^{2+} transfer kinetics and desolvation. This is corroborated by current-time (I - t) and electrochemical impedance spectroscopy (EIS) measurements (Equation S1 and Figure S14), which reveal a higher Zn^{2+} transference number in the ZS/OCAD electrolyte (0.71) than in ZS (0.57) and ZS/CAD (0.63) electrolytes. The elevated transference number likely stems from the specific adsorption of the OCAD additive, which excludes $\text{H}_2\text{O}/\text{SO}_4^{2-}$ and coordinates with Zn^{2+} ions at the interface. This process promotes cation desolvation and orders the EDL, thus preferentially facilitating Zn^{2+} transport over anion mobility. To further investigate the mass-transport properties, we examined polarization behavior in symmetric cells. As shown in Figure S15, the ZS/OCAD electrolyte not only delays the diffusion-controlled current peak, but also achieves the highest limiting current, indicating enhanced ion transport and suppressed concentration polarization. The operational timeline in Figure 1i quantitatively demonstrates this superior performance [36]. Specifically, at a current density of 10 mA cm^{-2} , symmetric cells employing ZS and ZS/CAD electrolytes undergo dendritic failure following 0.5 and 0.6 h of deposition, respectively. Conversely, the ZS/OCAD electrolyte enables a continuously stable deposition process until the Zn source in the counter electrode is completely depleted (up to 55 mAh cm^{-2}). This delayed Sand's time confirms that the OCAD additive facilitates a more robust interfacial environment for Zn^{2+} replenishment, which is critical for stable high-capacity plating and superior Zn utilization [36].

In situ optical microscopy was employed to directly observe the nucleation and growth mechanisms across the different electrolytes (Figure S16). As plating proceeds in the blank electrolyte, the surface of the Zn anode develops an irregular, convex morphology. In contrast, the addition of OCAD yields a smooth Zn surface. According to the Scharifker-Hills model [37], three-dimensional (3D) nucleation occurs via two distinct modes: Instantaneous (3DI) and progressive (3DP), which are differentiated by the timescale of nucleus formation (Equations S2 and S3) [38]. To differentiate between these modes experimentally, we conducted chronoamperometry (CA) at a fixed overpotential (Figure S17). The resulting current-time profiles were normalized by dividing the current (I) and time (t) by their corresponding maximum values (I_m and t_m), yielding I^2/I_m^2 versus t/t_m plots for comparison with the theoretical models. As shown in Figure 1j, the dimensionless transients for the ZS and ZS/CAD electrolytes align closely with the 3DI model, indicating the rapid exhaustion of nucleation sites at the early deposition stage. In contrast, the ZS/OCAD system exhibits a hybrid nucleation mode, with part of its transient curve lying between the 3DI and 3DP pathways. This suggests that nucleation sites are progressively activated during the growth process.

To further probe the interfacial chemistry, ab initio molecular dynamics (AIMD) simulations were conducted to compare the EDL structures across different electrolytes. Figure 2a–c present the simulated atomic-scale distribution of H_2O , SO_4^{2-} , Zn^{2+} , and additive molecules near the electrode surface, revealing distinct interfacial compositions for each electrolyte. CAD or

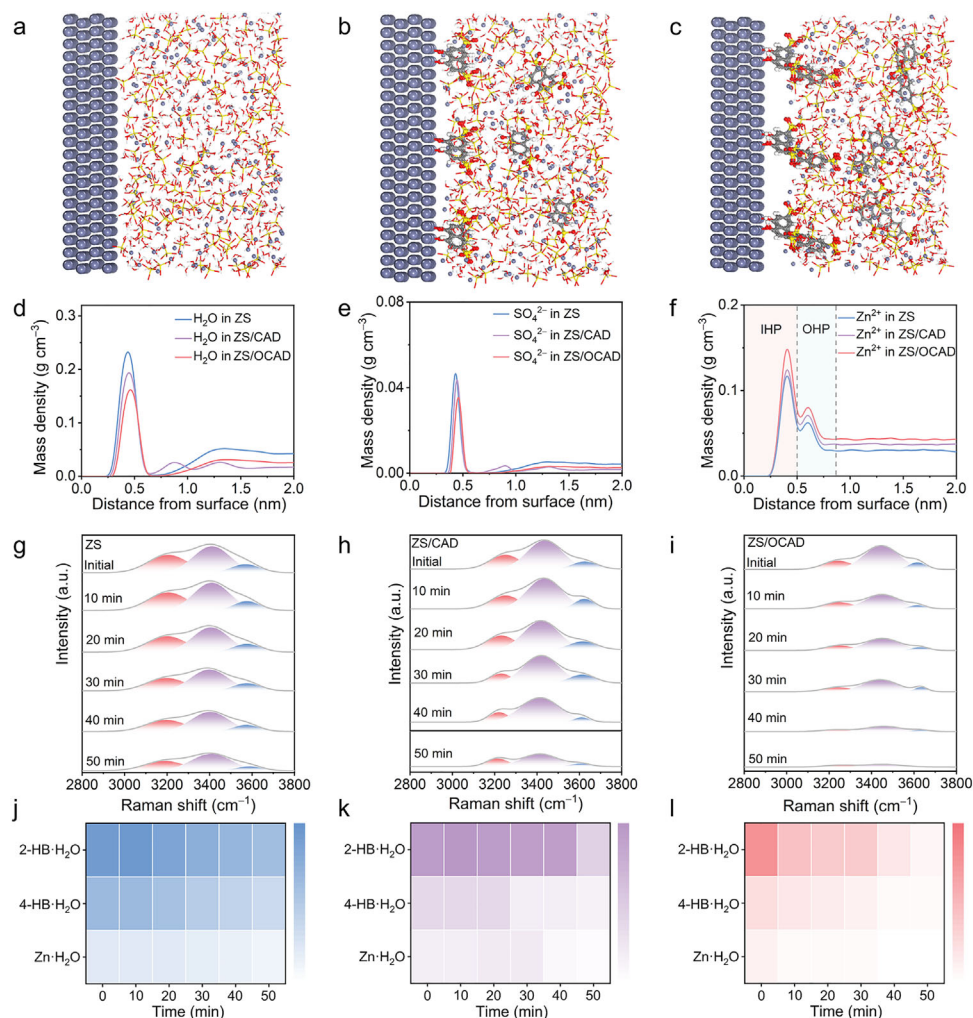


FIGURE 2 | Atomic-scale interface structures from AIMD simulations for (a) ZS, (b) ZS/CAD, and (c) ZS/OCAD electrolytes. Density distribution profiles of interfacial (d) H_2O molecules, (e) SO_4^{2-} ions, and (f) Zn^{2+} ions. In situ Raman spectra of interfacial water in (g) ZS, (h) ZS/CAD, and (i) ZS/OCAD electrolytes. The calculated ratios of the integral area of the three O—H stretching modes in (j) ZS, (k) ZS/CAD, and (l) ZS/OCAD electrolytes.

its dimer utilizes the phenolic hydroxyl group, leveraging its high electron affinity to compete with active water molecules and SO_4^{2-} anions for adsorption onto the Zn anode surface. This competitive adsorption behavior effectively prevents direct contact between $\text{H}_2\text{O}/\text{SO}_4^{2-}$ and the active sites of the Zn anode, thereby inhibiting HER and significantly improving interfacial stability. It can be observed that the enhanced efficacy of the CAD dimer in displacing H_2O molecules and SO_4^{2-} anions over CAD is attributed to the extended conjugated naphthalene rings in the oligomeric system, leading to more effective regulation of the EDL structure. Quantificationally, the statistical number density profiles and trajectory analyses of H_2O and SO_4^{2-} were extracted along the surface normal direction from the AIMD results. The distribution profiles of interfacial water molecules reveal their respective positions at 0.43, 0.45, and 0.47 nm from the Zn anode in ZS, ZS/CAD, and ZS/OCAD electrolytes, accompanied by a progressive decline in density (Figure 2d). An analogous shift is seen in the SO_4^{2-} anion distribution (Figure 2e). These findings collectively demonstrate that the bulky OCAD additive enables the construction of a hydrophobic and anion-repelling EDL, thereby accelerating interfacial Zn^{2+} transport. The extension of the conjugated naphthalene ring system introduces additional

molecular planes that serve as abundant functional sites for regulating molecular/ionic transfer, thus promoting efficient Zn^{2+} transport. AIMD simulations were conducted to analyze the distribution of Zn^{2+} ions within the interfacial layer, from which the IHP and OHP thicknesses, along with the corresponding Zn^{2+} charge densities, were extracted. According to the Zn^{2+} distribution profiles, the IHP thickness is 0.50 nm and the OHP thickness is 0.36 nm (Figure 2f) [39]. This EDL dimension aligns well with the molecular size of the OCAD dimer (1.51 nm). By contrast, the CAD monomer, following adsorption through bidentate chelation, exhibits a molecular width of only ~ 0.65 nm, which restricts its regulatory influence predominantly to the IHP. Moreover, the Zn^{2+} density in ZS/OCAD reaches 0.15 g cm^{-3} within the IHP and 0.080 g cm^{-3} within the OHP, substantially higher than those in ZS/CAD and ZS, thereby providing further evidence that OCAD facilitates interfacial Zn^{2+} enrichment (Figure S18). With the aim of gaining deeper insight into surface charge regulation by the OCAD additive, Kelvin probe force microscopy (KPFM) was employed to visualize the surface potential distribution (Figure S19). The results reveal distinct potential variations across the electrode surface in the ZS system, manifesting as a heterogeneous potential distribution

due to localized electron density fluctuations. In contrast, OCAD facilitates charge redistribution at the interface, leading to a more uniform potential distribution [40]. To further verify the efficacy of this molecular oligomerization strategy in enhancing mass transfer, AIMD simulations were analyzed to determine the mean square displacements (MSDs) at the electrode/electrolyte interface (Figure S20). The Zn^{2+} diffusion coefficient is highest in ZS/OCAD ($4.47 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$), compared to ZS/CAD ($3.60 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$) and ZS ($2.25 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$), again indicating its superior cation transport capability.

Electrochemical in situ spectroscopy techniques are powerful tools for studying the structure and spatial distribution of interfacial components. In situ Raman spectroscopy was employed to examine the content of interfacial water in different electrolytes under a current density of 1 mA cm^{-2} at various charging time intervals [41]. The Gaussian fitting resolved the broad O—H stretching band ($3000\text{--}3800 \text{ cm}^{-1}$) into three components, which correspond to three distinct O—H stretching environments. From low to high wavenumbers, these are designated as 4-coordinated hydrogen-bonded water (4-HB- H_2O), 2-coordinated hydrogen-bonded water (2-HB- H_2O), and Zn^{2+} -hydrated water ($\text{Zn}\cdot\text{H}_2\text{O}$) [42]. In situ Raman spectra shows a pronounced decline of the interfacial water signal during plating in ZS/OCAD (Figure 2g–i), as the adsorbed oligomeric molecules displace water from the anode. Quantitative area analysis of the O—H stretching modes further elucidates that this molecular configuration effectively reduces the abundance of interfacial water (Figure 2j–l), thereby mitigating its interference with Zn deposition in the EDL. Raman spectra also reveal that OCAD addition effectively depletes interfacial SO_4^{2-} anions (Figure S21), thereby contributing to an anion-depleted interface, a structural feature that was also verified by our AIMD simulations.

The impact of the additive molecular structure on the Zn^{2+} transport dynamics at the interface was further examined through EIS of Zn//Zn symmetric cells at multiple temperatures (Figure S22) [43, 44]. An equivalent circuit model was employed to fit the EIS data (Figure S23) [45]. The fitted Nyquist plot features two semicircles (Figure S24), indicating two distinct interfacial processes. These are modeled by R_1 and R_2 , representing the charge transfer resistance (R_{ct}) at high (1 Hz–100 kHz) and low (10 mHz–1 Hz) frequency ranges, respectively. Given the observed temperature dependence of the charge-transfer process, we quantified the associated activation energy (E_a) for Zn^{2+} transport by applying the Arrhenius equation to the fitted R_{ct} values (Figure 3a,b, and Equation S4). According to the atom model, the deposition mechanism comprises two consecutive steps [46]. The initial transition of Zn^{2+} ions from the OHP to the IHP involves partial desolvation, resulting in their adsorption. The subsequent step from the IHP to the electrode includes diffusion of the adsorbed ion along the surface, further desolvation, and culminates in its incorporation into the metal lattice. Accordingly, the R_1 and R_2 can be attributed to the charge transfer between the OHP and IHP, and between the IHP and the electrode, respectively. The presence of the OCAD additive at the OHP significantly reduces the E_{a1} for Zn^{2+} transfer across the OHP/IHP interface from 24.61 to 8.56 kJ mol^{-1} . This reduction suggests that the expanded modulation over the diffusion layer, resulting from the adsorption of the bulky hydrophobic naphthalene ring, facilitates Zn^{2+} desolvation and the subsequent formation

of adsorbed ions. Meanwhile, the E_{a2} for the IHP-to-electrode transfer step in the ZS/OCAD electrolyte (18.96 kJ mol^{-1}) is also lower than those in ZS (25.87 kJ mol^{-1}) and ZS/CAD (24.86 kJ mol^{-1}) electrolytes. This indicates that OCAD molecules adsorbed on the Zn surface promote the diffusion of adsorbed ions and enhance the final desolvation and lattice incorporation. OCAD adsorption effectively modulates the EDL structure, expands the hydrophobic domain, reduces the energy barrier for Zn^{2+} desolvation (Figure 3c), and thereby promotes uniform Zn deposition. In situ Raman spectroscopy was performed to directly probe the desolvation behavior of hydrated Zn^{2+} ions during electrodeposition by monitoring the Zn—O(H_2O) stretching vibration at $\sim 390 \text{ cm}^{-1}$, a characteristic peak corresponding to the primary solvation shell of $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ (Figure S25) [47]. In the ZS/OCAD electrolyte, the intensity of this peak progressively decreases upon the initiation of deposition at 5 mA cm^{-2} , indicating an efficient and rapid desolvation process at the electrode interface under the modulation of OCAD. Under identical conditions, however, the ZS electrolyte maintains a persistent peak corresponding to the solvation structure, indicating sluggish desolvation kinetics.

To further validate the enhanced charge transfer kinetics at the anode interface, in situ EIS was measured on cells employing different electrolytes (Figure 3d–f). The evolution of the impedance spectra during cycling reveals a consistent trend: the system incorporating the OCAD additive maintains the smallest and most stable values for both the R_{ct} and the diffusion resistance (R_{diff}). This notable reduction and stabilization of interfacial resistances strongly indicate that the macromolecular OCAD effectively modulates the electrode/electrolyte interface. By facilitating the transport and promoting the desolvation of Zn^{2+} ions, OCAD creates a more favorable microenvironment, which is instrumental in achieving uniform and stable Zn deposition. Given that Zn^{2+} and SO_4^{2-} ions migrate in opposite directions during Zn plating under an electric field, the concentration of SO_4^{2-} at the counter electrode interface, as measured by Raman spectroscopy, can be used to probe the state and distribution of Zn^{2+} ions at the Zn anode. The bare ZS electrolyte shows a significant drop in peak intensity after just 20 min of plating (Figure 3g), indicating unstable mass transfer and heightened concentration polarization, which can exacerbate dendrite growth. While the ZS/CAD electrolyte achieves a more stable Zn^{2+} concentration profile, it still experiences notable decay by 30 min (Figure 3h). Remarkably, the OCAD-containing system exhibits a consistent and stable signal throughout the plating process (Figure 3i). This sustained stability is a direct indicator of regulated ionic flux and homogeneous deposition morphology, underscoring the interfacial-stabilizing role of OCAD.

In situ pH monitoring was employed to elucidate how oligomeric additives enhance Zn reversibility through EDL modulation. Measurements were performed on Zn//Zn symmetric cells cycled at 20 mA cm^{-2} and 2 mAh cm^{-2} , with the experimental setup illustrated in Figure S26. As shown in Figure 3j,k, the ZS and ZS/CAD electrolytes exhibit comparable initial pH values. Upon cycling for 11 cycles; however, both experience considerable pH increases of 0.58 and 0.26, respectively. In contrast, the ZS/OCAD electrolyte presents a strikingly lower initial pH (Figure 3l). It demonstrates exceptional interfacial stability, with a minimal pH shift of merely 0.17 throughout the entire cycling test, in marked contrast to the significant drift observed in control

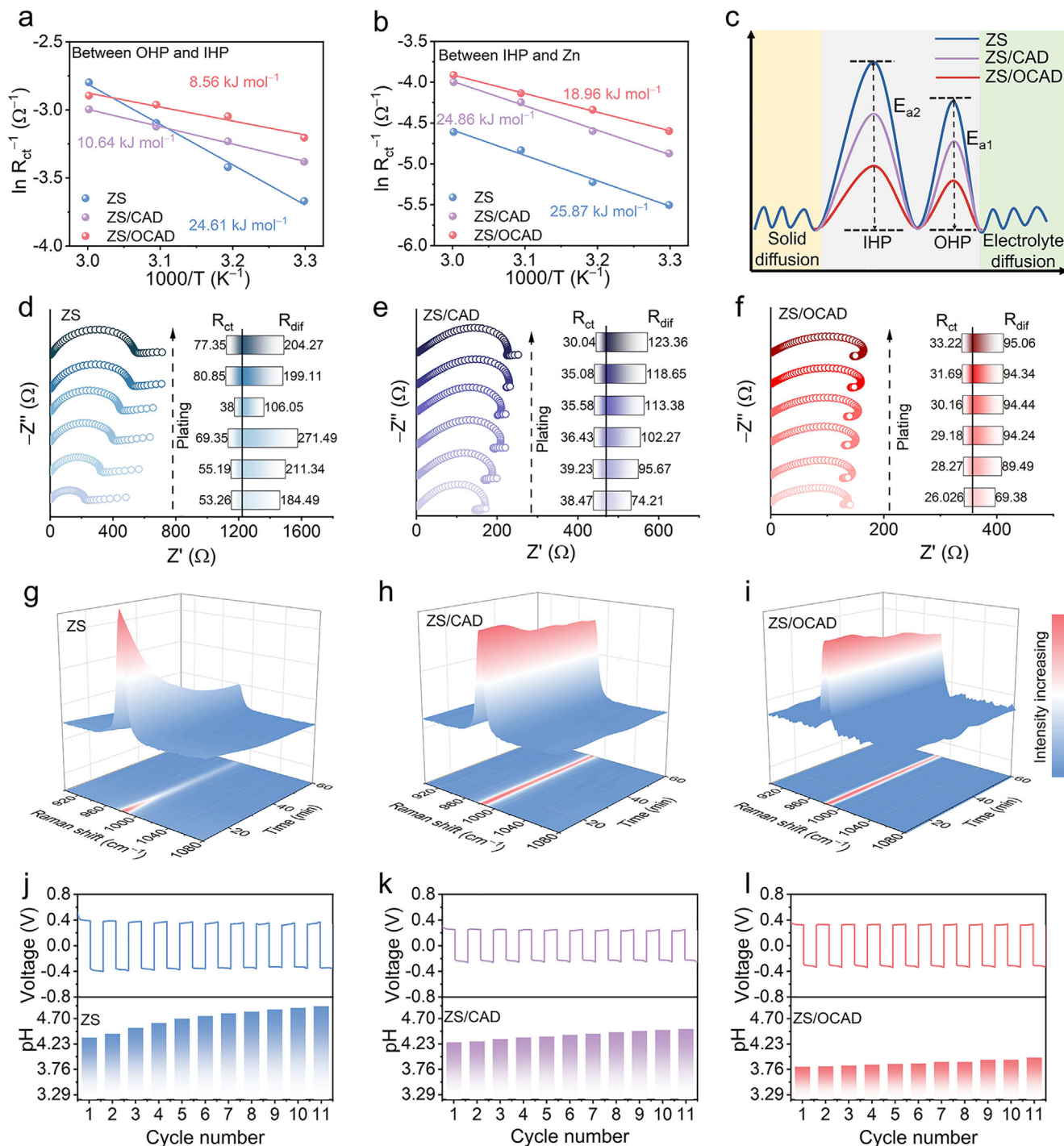


FIGURE 3 | The activation energies for (a) R_1 and (b) R_2 were derived from the Nyquist plots of Zn//Zn cells tested in different electrolytes. (c) Relationship between the desolvation energy barriers of Zn^{2+} ions in the IHP and OHP. In situ EIS tests of Zn//Zn cells using (d) ZS, (e) ZS/CAD, and (f) ZS/OCAD electrolytes. In situ Raman characterization during the Zn plating process for (g) ZS, (h) ZS/CAD, and (i) ZS/OCAD electrolytes. In situ pH monitoring of (j) ZS, (k) ZS/CAD, and (l) ZS/OCAD electrolytes within Zn//Zn cells upon cycling.

electrolytes. This superior stability is explained by the OCAD molecule's retention of an exposed pair of phenolic hydroxyl groups even after the other pair chelates with the Zn substrate. These remaining groups function as a molecular pH buffer through reversible H^+ release. In CAD, the phenolic hydroxyl groups are fully occupied in coordinating with the Zn substrate, thus rendering them unavailable for interfacial pH regulation. This intrinsic buffering capability effectively mitigates local pH

fluctuations and robustly suppresses the generation of basic by-products at the interface. Beyond that, linear sweep voltammetry (LSV) was employed to assess the effect of additives on the parasitic HER. The OCAD-containing electrolyte demonstrates the most negative onset potential (Figure S27), indicating significantly suppressed HER activity. This suppression is attributed to a hydrophobic interfacial layer constituted by large-sized naphthalene rings, which effectively limits water accessibility

at the electrode surface. The influence of the OCAD-created hydrophobic microenvironment on the electrochemical stability potential window (ESPW) of different electrolytes was evaluated by LSV using a Zn//Ti cell (Figure S28). The OCAD-containing electrolyte exhibits a markedly wider ESPW (2.93 V) compared to both the additive-free (2.72 V) and CAD-containing (2.83 V) counterparts. This enhancement arises from the water-depleted, hydrophobic interfacial layer formed by the adsorbed OCAD oligomers, which inhibits water decomposition and extends the electrolyte's operational voltage range.

The effect of the OCAD additive on the reversibility and stability of the Zn anode was evaluated through galvanostatic plating/stripping measurements. CE, a critical indicator of process reversibility, was measured using Zn//Cu coin cells at 1 mA cm^{-2} and 1 mAh cm^{-2} . The Zn//Cu cell employing the ZS/OCAD electrolyte exhibits a superior average CE of 99.1%, outperforming the ZS/CAD (98.4%) and ZS (97.9%) electrolytes (Figure 4a). The corresponding voltage profiles confirm this stability, showing a consistent overpotential of $\sim 49.6 \text{ mV}$ over 700 cycles without degradation, which manifests the exceptional reversibility enabled by the OCAD additive (Figure S29). This enhancement verifies that the additive enhances Zn plating/stripping reversibility by effectively inhibiting side reactions and preventing the formation of “dead Zn”.

The cycling stability of the Zn anode was further systematically evaluated using Zn//Zn symmetric cells under various conditions. When using the ZS and ZS/CAD electrolytes, the cells sustain stable operation for only 700 and 1100 h, respectively, at 1 mA cm^{-2} and 1 mAh cm^{-2} before failure due to short-circuiting. In stark contrast, the OCAD-modified electrolyte enables a dramatically extended cycle life of over 4300 h (Figure 4b). To understand the failure mechanism after ultra-long cycling, post-mortem scanning electron microscopy (SEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) analyses were performed on Zn anodes from symmetric cells cycled for 4300 h in ZS/OCAD. After we disassembled the failed cells, SEM revealed some protrusions on the Zn anode surface. These protrusions are attributed to byproduct accumulation after prolonged cycling (Figure S30). XRD clearly detects diffraction peaks corresponding to $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot 5\text{H}_2\text{O}$, confirming the formation of crystalline byproducts after cycling (Figure S31). XPS S spectrum further corroborates this observation, showing distinct sulfate/sulfite signals (Figure S32). These results demonstrate that, the eventual cell failure after $>4300 \text{ h}$ is primarily caused by the gradual accumulation of byproducts over prolonged cycling, which progressively increases interfacial resistance. This finding underscores the superior interfacial stabilization provided by the OCAD additive, which extends cell lifetime compared to the baseline ZS electrolyte, although trace byproduct accumulation ultimately limits the absolute lifespan. Such substantial performance improvement also extends to conditions involving a high depth of discharge (DOD). When operated at 6 mA cm^{-2} , but with a high DOD of 85.6%, the cell incorporating ZS/OCAD still achieves a lifespan exceeding 350 h (Figure 4c), outperforming those with ZS and ZS/CAD. To better simulate real-world battery operation, shelving-recovery tests were conducted. Specifically, Zn//Zn symmetric cells were cycled at 1 mA cm^{-2} and 1 mAh cm^{-2} , with a 10 h rest period introduced after every 10 cycles (Figure 4d). The ZS/OCAD-based cell exhibits exceptional long-

term stability, maintaining operation for over 700 h, whereas cells with ZS and ZS/CAD fail within 200 h. The improved Zn utilization and superior shelf-life recovery are attributed to oligomer-mediated suppression of side reactions and the resulting homogeneous Zn plating/stripping behavior. As indicated by the XRD patterns, the Zn electrode cycled in the ZS/OCAD electrolyte displays the diffraction peaks of hexagonal close-packed (hcp) Zn (Figure 4e). The markedly enhanced (002) peak intensity implies that the OCAD molecular layer promotes preferential electrodeposition along this crystal plane. Conversely, for the ZS electrolyte, the XRD pattern and Raman spectra reveal a distinct set of additional peaks (Figure 4f), identifying the formation of $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot 5\text{H}_2\text{O}$ byproducts. Post-cycling morphological analysis of the Zn anode surfaces reveals significant corrosion in the ZS electrolyte, as shown in optical images. Further SEM characterization indicates that the OCAD additive provides superior stabilization of the Zn anode compared to CAD, effectively suppressing dendrite formation and corrosive byproducts (Figure S33). Linear polarization measurements also corroborate these findings. The corresponding Tafel plots show that the ZS/OCAD electrolyte achieves both an increased corrosion potential and a decreased corrosion current density (Figure 4g), demonstrating the efficacy of OCAD in minimizing harmful side reactions on the Zn anode during electrochemical cycling. Validated by the excellent performance above, OCAD ranks favorably against other recently reported electrolyte additives. It demonstrates strong capabilities in essential parameters, like cycling durability, DOD, and cumulative plating capacity (Table S1), indicating considerable promise for practical implementation. Encouragingly, Fourier transform infrared (FTIR) spectra after different cycles show that the adsorbed OCAD molecule on the Zn electrode surface maintains its characteristic peaks, evidencing its structural stability (Figure S34). The enhanced reversibility of Zn plating/stripping in the Zn/OCAD electrolyte is ascribed to the in-situ adsorption of the bulky OCAD molecules. This process forms a unique EDL, that is, characteristically water-poor and anion-free. As depicted in Figure 4h, this engineered interface promotes Zn^{2+} desolvation and charge transfer for plating while enabling rapid dissolution and resolution during stripping. This efficient ion return to the electrolyte facilitates highly reversible Zn plating/stripping cycles.

Full batteries incorporating the $\text{Na}_2\text{V}_6\text{O}_{16} \cdot 3\text{H}_2\text{O}$ (NVO) cathode were assembled to further evaluate the practicability of the OCAD additive. The crystallographic characterization of the prepared NVO powder is shown in Figure S35. The SEM image also confirms that the high-purity rod-like NVO is obtained (Figure S36). The rate performance of Zn//NVO batteries employing different electrolytes was comprehensively evaluated within a current density range of $0.5\text{--}20 \text{ A g}^{-1}$. As illustrated in Figure 5a, the Zn//NVO battery using ZS/OCAD delivers highly reversible capacities of 324.2, 288.7, 243.3, 212.2, 186.0, 173.3, 152.5, and 139.7 mAh g^{-1} at 0.5, 1, 3, 5, 8, 10, 15, and 20 A g^{-1} , respectively (Equation S5). The obtained capacities are higher than those of the ZS-based counterpart under identical current densities (272.2, 236.8, 201.0, 180.6, 158.5, 147.8, 122.6, and 97.7 mAh g^{-1} at 0.5, 1, 3, 5, 8, 10, 15, and 20 A g^{-1}). Furthermore, galvanostatic charge-discharge (GCD) profiles (Figures 5b and S37) demonstrate comparable voltage plateaus across various current densities in both electrolyte systems, confirming that the introduction of the OCAD additive preserves the inherent

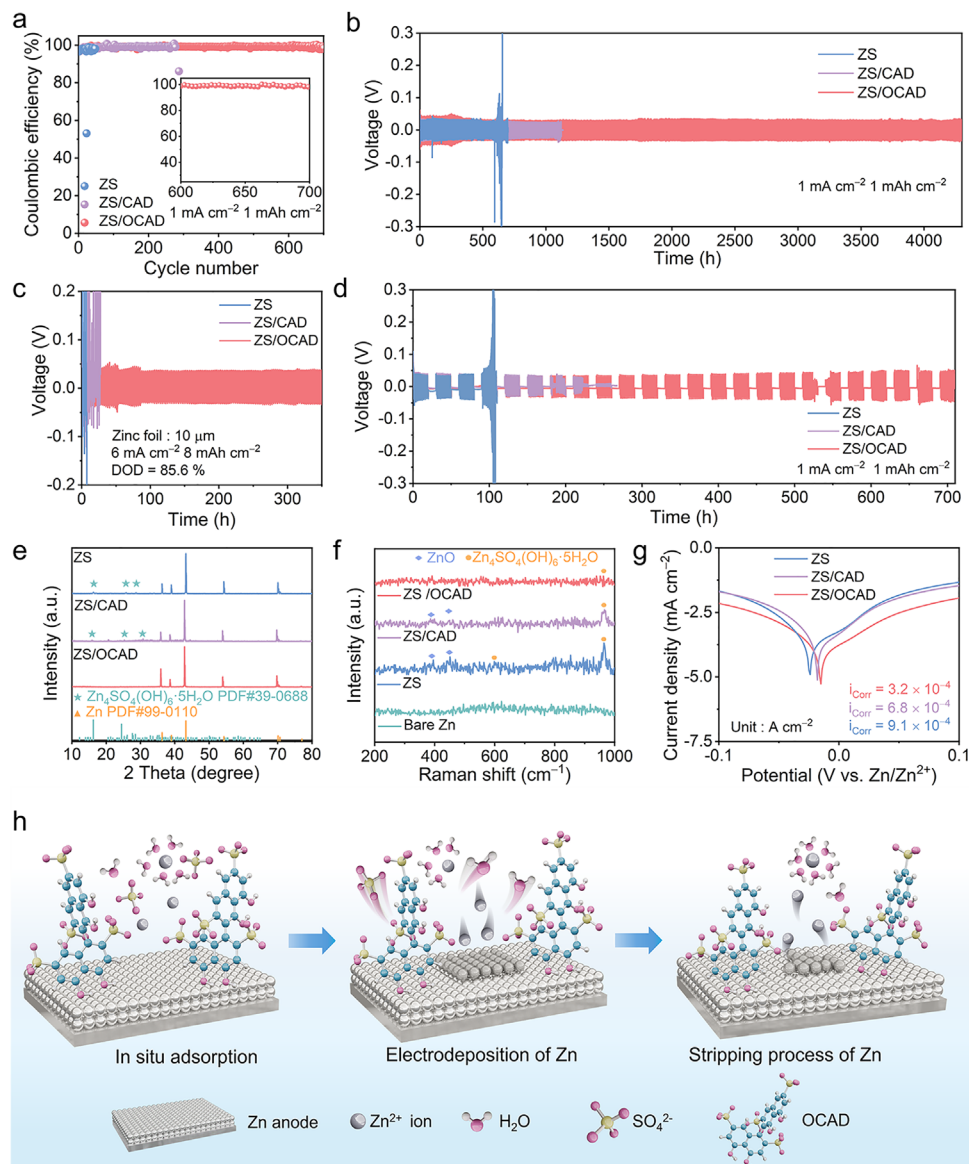


FIGURE 4 | (a) CE tests of Zn//Cu cells at $1 \text{ mA cm}^{-2}/1 \text{ mAh cm}^{-2}$. Voltage profiles of Zn//Zn cells using different electrolytes at (b) $1 \text{ mA cm}^{-2}/1 \text{ mAh cm}^{-2}$ and (c) $6 \text{ mA cm}^{-2}/8 \text{ mAh cm}^{-2}$. (d) The shelving-recovery performances at $1 \text{ mA cm}^{-2}/1 \text{ mAh cm}^{-2}$. (e) XRD and (f) Raman characterization of cycled Zn anodes. (g) Tafel plots in different electrolytes. (h) Mechanism illustration of the OCAD additive in stabilizing Zn plating/stripping cycling.

electrochemical characteristics of the Zn//NVO battery during operation while maintaining its fundamental redox mechanism. Self-discharge rate serves as a critical indicator for Zn battery durability. Encouragingly, the Zn//NVO battery with ZS/OCAD exhibits suppressed self-discharge behavior, as demonstrated by the lower capacitor decay compared to its ZS counterpart after 24 h of resting (Figure 5c). The Zn//NVO battery with ZS/OCAD delivers a capacity retention of 88.0%, while only a low capacity retention of 80.5% is observed in the battery with ZS, highlighting its enhanced stability during idle periods.

CV curves for both electrolytes show two pairs of distinct redox peaks, corresponding to the $\text{V}^{5+}/\text{V}^{4+}$ and $\text{V}^{4+}/\text{V}^{3+}$ redox couples at approximately 1.11/0.86 and 0.62/0.58 V, respectively. Additionally, a unique pair of small peaks at 1.42/1.30 V is significantly enhanced in the ZS/OCAD electrolyte. This enhancement

is likely associated with the ability of the OCAD additive to maintain a stable acidic environment, thereby facilitating H^+ insertion/extraction (Figure S38). Also, the Zn//NVO battery delivers better reversibility and redox kinetics in ZS/OCAD. As shown in Figure 5d,e, the Zn//NVO battery using ZS/OCAD displays a higher current response, indicating its stronger charge storage capability. Furthermore, as shown in Figure S39, CV curves at scan rates of 6–10 mV s^{-1} reveal linear relationships between the peak current densities (i_p) for the anodic and cathodic reactions and the square root of the scan rate ($v^{1/2}$) [48]. Compared to the ZS system, the ZS/OCAD electrolyte endows the Zn//NVO battery with significantly enhanced peak slopes in CV curves. The distinct behavior of the $\text{V}^{4+}/\text{V}^{5+}$ oxidation peak is attributed to improved H^+ kinetics. A comprehensive analysis of all CV redox peak currents demonstrates that OCAD effectively enhances the kinetics of the $\text{V}^{3+}/\text{V}^{4+}/\text{V}^{5+}$ redox couple. The

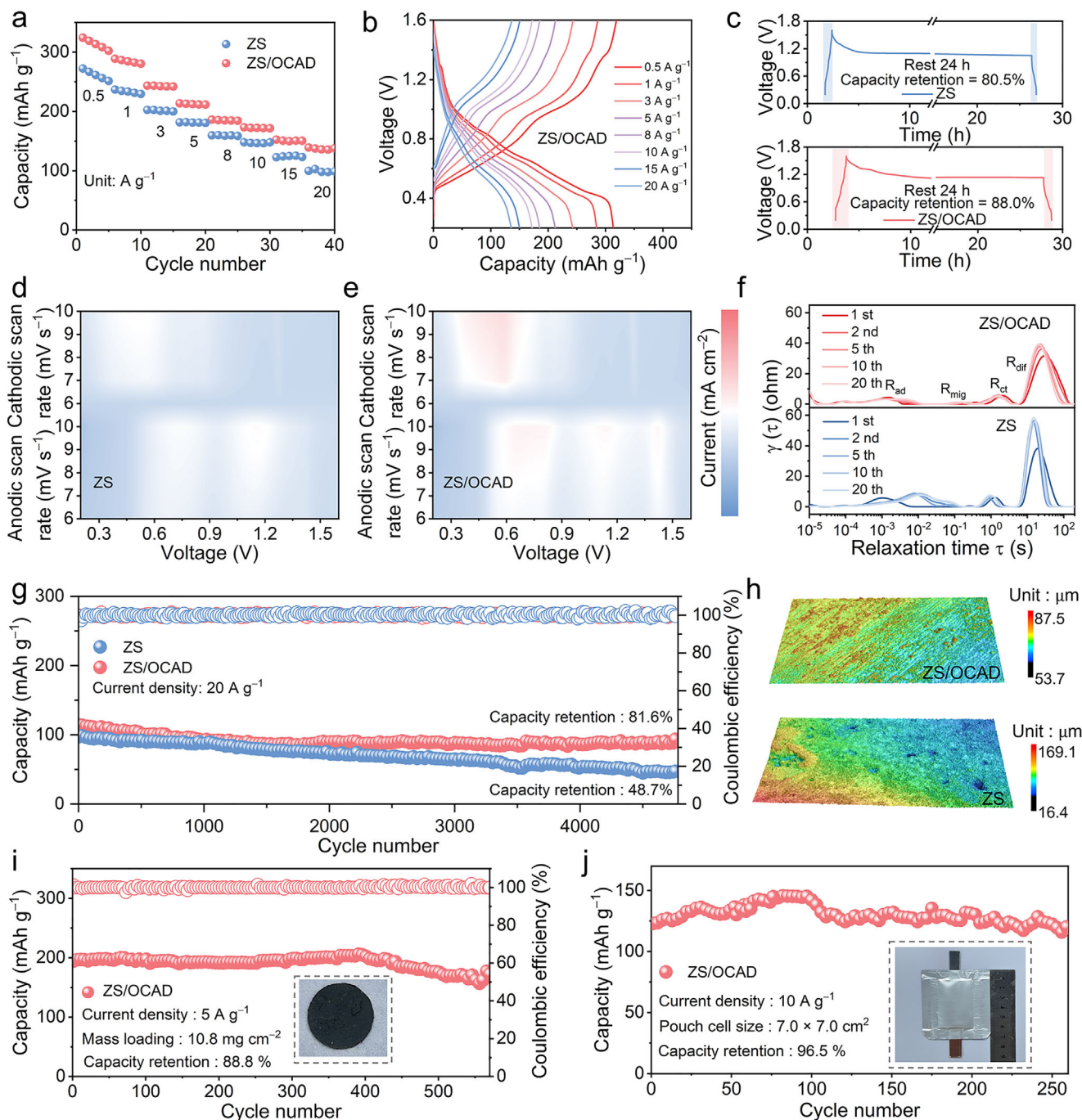


FIGURE 5 | (a) Rate capability of the Zn//NVO batteries with different electrolytes. (b) GCD profiles of the Zn//NVO battery with ZS/OCAD. (c) Self-discharge curves of Zn//NVO batteries with different electrolytes. CV contour plots at different scan rates in (d) ZS and (e) ZS/OCAD electrolytes. (f) DRT analysis of operando EIS measurements performed on full batteries with different electrolytes. (g) Cycling tests of Zn//NVO batteries in different electrolytes at 20 A g⁻¹. (h) CLSM images of cycled Zn anodes from Zn//NVO batteries with different electrolytes. (i) Cycling performances of Zn//NVO batteries with a high cathode mass loading. The inset shows the optical photograph of the NVO cathode. (j) Cycling performance of Zn//NVO pouch cells. The inset presents the optical photographs for the size of the Zn//NVO pouch cell.

distribution of relaxation times (DRT) of Zn//NVO full batteries was analyzed by operando EIS to unravel the interfacial reaction kinetics, where different electrochemical processes correspond to distinct relaxation times (τ). The ZS/OCAD-based battery maintains stable and low R_{diff} , R_{ct} , and migration resistance (R_{mig}) throughout prolonged cycling. Such low values imply efficient ion transport, fast charge transfer, and facile redox reactions at the cathode interface. The ZS-based battery shows a gradual

but continuous increase in resistance, indicating detrimental byproduct accumulation and progressive NVO cathode degradation (Figure 5f). These findings confirm that the OCAD additive enables superior redox kinetics.

Figure 5g displays the cycling performance of Zn//NVO batteries with different electrolytes at 20 A g⁻¹. In the ZS electrolyte, the battery suffers from pronounced capacity fading, retaining only

48.7% of its initial capacity after 4700 cycles. This rapid decay can be attributed to the continuous occurrence of detrimental processes, including HER, corrosion, dendrite growth, and vanadium (V) dissolution. In contrast, the battery employing the ZS/OCAD electrolyte demonstrates significantly improved cycling stability, retaining 81.6% of its initial capacity after the same number of cycles, along with a near-ideal CE of approximately 100%. To further validate the efficacy of the OCAD additive in a full cell under long-term cycling, the Zn//NVO battery after 4700 cycles was disassembled for post-mortem analysis. Confocal laser scanning microscopy (CLSM) was employed to examine the morphological details of the cycled Zn anodes. As shown in Figure 5h, the Zn anode from the ZS/OCAD electrolyte exhibits a strikingly uniform and smooth surface. In stark contrast, its counterpart from the ZS electrolyte shows severe surface non-uniformity and corrosion. This markedly improved morphology is attributed to the adsorption-induced reconstruction of the EDL by OCAD, which promotes uniform and dendrite-free Zn deposition. Inductively coupled plasma (ICP) measurements were employed to detect the V content in the electrolyte after full-cell cycling. The results show that the ZS/OCAD electrolyte exhibits a significantly lower concentration of dissolved V than the ZS electrolyte after cycling, suggesting effective suppression of V dissolution (Figure S40). To investigate the morphological evolution of the NVO cathode, post-cycling SEM characterization was also performed. As illustrated in Figure S41, the NVO cathode cycled in the ZS electrolyte suffers from severe structural degradation. The NVO cathode cycled in the ZS/OCAD electrolyte retains a well-preserved rod-like morphology. Post-cycling XRD analysis further indicates that the NVO cathode cycled in ZS/OCAD largely retains its well-defined characteristic peaks. In stark contrast, the NVO cathode cycled in ZS exhibits obvious structural degradation, with the characteristic NVO peaks completely disappearing and leaving only the peaks corresponding to the underlying carbon paper substrate (Figure S42).

Moreover, the merits of OCAD can enable stable long-term cycling over 560 cycles even at a practical mass loading of 10.8 mg cm^{-2} (Figure 5i). The battery utilizing the ZS/OCAD electrolyte still presents impressive capacity retention of 88.8% at 5 A g^{-1} . Then, the Zn//NVO pouch cell with an area of $7 \text{ cm} \times 7 \text{ cm}$ was assembled for the practicability evaluation. The pouch cell incorporating ZS/OCAD electrolyte achieves a high-capacity retention of 96.5% of over 260 cycles at 10 A g^{-1} (Figure 5j). The viability of the pouch-cell using the ZS/OCAD electrolyte was further confirmed by its ability to stably power an electronic timer (Figure S43), underscoring its potential for practical use. To rigorously assess the practical safety of the OCAD-based electrolyte system, Zn//NVO pouch cells were subjected to severe mechanical abuse tests (Figure S44), such as cutting, piercing, and puncturing. Remarkably, the pouch cells demonstrate exceptional resilience, maintaining stable open-circuit voltage even under these extreme conditions. This outstanding performance underscores the critical role of the electrolyte additive in stabilizing electrochemical reactions, thereby significantly enhancing the reliability and safety of the system for real-world applications. Therefore, the OCAD additive not only significantly enhances the cycling stability of the Zn metal anode, but also demonstrates great potential for advancing the development of high-performance and practical aqueous ZIBs.

3 | Conclusion

In summary, we tailored the interfacial environment to optimize Zn deposition through a molecular oligomerization strategy that precisely controls additive architecture. In the OCAD system, the extended hydrophobic backbone reduces water content across the IHP/OHP, creating a dehydration interface. Concurrently, strategically exposed sulfonic and phenolic hydroxyl groups repel SO_4^{2-} and stabilize pH at the IHP, which enriches Zn^{2+} and minimizes side reactions. Driven by cross-scale size control and functional group synergy, this deliberate molecular design delivers dual modulation of adsorption and mass transport, enabling highly reversible Zn plating/stripping. Consequently, OCAD-based symmetric cells deliver unprecedented cycling stability, exceeding 4300 h at $1 \text{ mA cm}^{-2}/1 \text{ mAh cm}^{-2}$ and 350 h at an 85.6% DOD. The Zn//NVO full battery exhibits outstanding durability, retaining 81.6% capacity after 4700 cycles at 20 A g^{-1} . Crucially, this additive system confers exceptional stability in practical full-cell scenarios, including high-loading cathodes and pouch-cell assemblies, validating its application potential. This work, therefore establishes a design principle for additive molecules that enables long-range regulation of anode interfacial chemistry toward high-performance ZIBs.

Author Contributions

Yanjing Wang: conceptualization, writing – original draft, data curation, and validation. **Le Zhou:** conceptualization, software, data curation, and validation. **Tianyu Zhang:** formal analysis and validation. **Wenzhuo Gao:** formal analysis and methodology. **Hongfei Wang:** conceptualization, funding acquisition, writing – original draft, supervision, and data curation. **Yong Hu:** conceptualization, writing – review and editing, project administration, supervision, and funding acquisition.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

Research data are not shared.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.

Supporting File: anie73637-sup-0001-SupMat.doc.