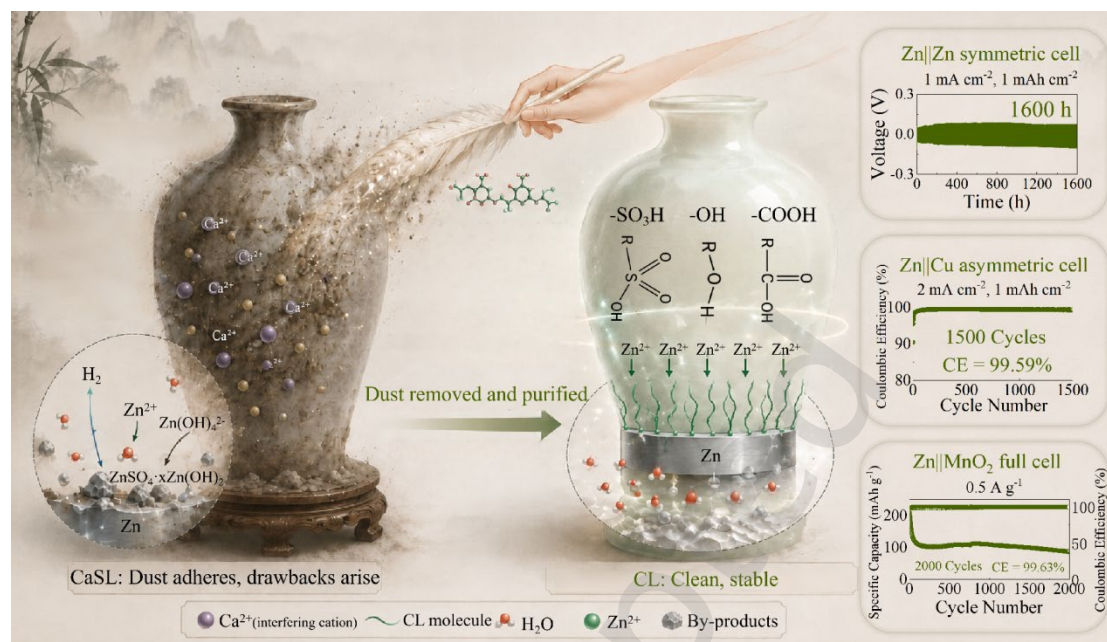


Graphical Abstract



Calcium lignosulfonate (CaSL) suffers from interfering Ca^{2+} counterions, triggering side-reactions including hydrogen evolution, Zn corrosion and by-product precipitation on zinc anode. After cation-exchange purification, the obtained lignosulfonic acid (CL) exposes abundant $-\text{SO}_3\text{H}$, $-\text{OH}$ and $-\text{COOH}$ groups, which adsorb preferentially on Zn surface and rebuild a water-poor interfacial layer. Such organic adsorption layer isolates active water from Zn metal and achieves highly stable zinc plating/stripping for both symmetric and full cells.

Research Article

Counterion-interference-free lignosulfonic acid additive stabilizes zinc anode interfacial behavior

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Abstract

Aqueous zinc-ion batteries (AZIBs) have attracted extensive attention owing to their high safety, low cost, and environmental benignity. However, water-induced parasitic reactions severely compromise the stability of Zn metal anodes, limiting their practical application. Electrolyte additives with functional anions provide an effective strategy to regulate the interfacial reaction microenvironment and construct a durable Zn/electrolyte interface. Nevertheless, conventional polyanionic additives contain counterions that can interact with their functional groups and influence interfacial Zn^{2+} transport. Herein, a biomass-derived lignosulfonic acid additive was prepared from calcium lignosulfonate via an H-type cation-exchange strategy. This process removes interfering Ca^{2+} counterions and releases abundant polar functional groups, including $-\text{SO}_3\text{H}$, $-\text{OH}$, and $-\text{COOH}$. The activated lignosulfonic acid preferentially adsorbs on the Zn surface and reconstructs the original water-rich electric double layer into a water-deficient inner Helmholtz layer dominated by organic molecular adsorption. This interfacial layer effectively blocks the direct contact between active water molecules and Zn metal, thereby suppressing hydrogen evolution, corrosion and the formation of basic zinc sulfate byproducts. As a result, the lignosulfonate additive enables the assembled $\text{Zn}||\text{Zn}$ symmetric cell to operate stably for 1600 h at 1 mA cm^{-2} and 1 mAh

cm^{-2} , and allows the Zn||Cu cell to sustain 1500 plating/stripping cycles at 2 mA cm^{-2} with an average Coulombic efficiency of 99.59%. Furthermore, the Zn||MnO₂ full cell delivers stable cycling performance over 2000 cycles at 0.5 A g^{-1} with an average Coulombic efficiency of 99.63%.

Keywords: aqueous zinc-ion batteries; lignosulfonic acid; water-deficient electric double layer; zn metal anode stabilization

1 Introduction

Aqueous zinc-ion batteries (AZIBs) have emerged as promising candidates for large-scale energy storage systems due to their intrinsic safety, low cost, environmental benignity, and high theoretical capacity [1-3]. In contrast to battery systems based on flammable organic electrolytes or highly reactive metal anodes, AZIBs operate with water-based electrolytes, which inherently avoid thermal runaway, fire, and explosion [4-6]. The typical electrolyte for AZIBs is a cost-effective, slightly acidic ZnSO₄ aqueous solution with favorable coordination properties, offering high ionic conductivity and intrinsic safety. However, the inherent reactivity of water renders the Zn metal anode thermodynamically unstable, making it prone to dissolution and corrosion, and inducing detrimental dendrite growth at the solid/liquid interface, thereby compromising the battery performance [7-10]. Electrolyte additive engineering provides a straightforward and cost-effective strategy to address these issues by reshaping the local reaction microenvironment, regulating Zn²⁺ solvation/desolvation behavior, and modulating interfacial Zn deposition without complicated electrode modification [11, 12].

Among various additive strategies, anion regulation has proven to be particularly effective in stabilizing the Zn/electrolyte interface. Functional anions can regulate Zn deposition and interfacial side reactions through multiple pathways, including coordination substitution in the Zn²⁺ solvation sheath, electrostatic adsorption on the Zn surface, steric modulation of ion flux, and disruption of the hydrogen-bond network of water molecules. For example, CF₃SO₃⁻ has been reported to compete with H₂O molecules in the Zn²⁺ solvation sheath due to its hydrophobicity and strong electron-withdrawing nature, thereby reducing the coordination number of Zn²⁺ and accelerating

the desolvation process ^[13, 14]. TFSI⁻ has been shown to partially replace water molecules surrounding Zn²⁺, decreasing the activity of free water and improving the reversibility of Zn plating/stripping ^[15, 16]. NTA³⁻ preferentially adsorbs at the inner Helmholtz plane, constructing a water-deficient and Zn-rich interfacial environment that homogenizes charge distribution and lowers interfacial decomposition energy ^[17-21]. In addition, adsorbed anions can anchor heterogeneous charge sites and mitigate uneven Zn²⁺ flux prior to Zn deposition ^[22, 23]. More importantly, the functional groups carried by these anions, such as carbonyl, sulfonate, and hydroxyl groups, can form dense interfacial adsorption layers or participate in hydrogen-bond interactions with water, thereby reducing the population of reactive H₂O species and suppressing hydrogen evolution and corrosion ^[24]. Therefore, an ideal electrolyte additive should provide interfacially active functional anions while avoiding unnecessary ionic interference.

Lignosulfonates, as natural biomass-derived polyanionic macromolecules rich in sulfonate (-SO₃⁻), hydroxyl (-OH), and aromatic functional groups, possess strong metal-ion coordination ability and excellent hydrophilicity. These characteristics make lignosulfonates promising candidates for regulating Zn²⁺ solvation behavior and interfacial deposition. In electrochemical energy-storage systems, lignosulfonate-based materials have been reported to modulate interfacial reactions through coordination interactions and structural stabilization. For instance, lignosulfonates have long been used as expanders in lead-acid batteries to inhibit the formation of dense passivating PbSO₄ layers and prolong cycling life ^[25]. In AZIBs, sodium lignosulfonate-chitosan gel polymer electrolytes have achieved Coulombic efficiencies exceeding 99.7% at 5000 μA cm⁻² ^[26]. Quaternized lignin (QL80), employed as an electrolyte additive, has been shown to alleviate zinc anode corrosion and increase the reversible capacity to 74.5% after 3000 cycles at 1.5 A g⁻¹ ^[27]. These studies indicate that lignosulfonate-derived functional groups can participate in interfacial regulation and suppress dendrite growth, which meets the requirements for effective anion additives in AZIBs.

Among various lignosulfonate salts, calcium lignosulfonate (CaSL) is an attractive precursor for designing interfacial electrolyte additives due to its abundant biomass-

derived availability and its unique Ca^{2+} -bridged polyanionic structure. Compared with lignosulfonate salts containing monovalent counterions, the divalent Ca^{2+} in calcium lignosulfonate can coordinate with sulfonate and oxygen-containing groups on neighboring lignosulfonate chains, forming a more compact ionically cross-linked macromolecular framework. Such a structure suggests that calcium lignosulfonate possesses a high density of potentially active functional groups and multiple coordination sites, which could be beneficial for Zn^{2+} regulation and interfacial adsorption once these sites are fully released [28]. However, in the original calcium lignosulfonate salt, Ca^{2+} counterions interact with sulfonate and other oxygen-containing groups, thereby weakening their accessibility and interaction capability toward Zn^{2+} and the Zn surface [29]. Therefore, removing Ca^{2+} from calcium lignosulfonate is expected to release active functional groups and eliminate counterion-induced interference.

To address this issue, calcium lignosulfonate was directionally converted into lignosulfonic acid using an H-type cation-exchange resin, removing Ca^{2+} and activating the interfacially active functional groups. The obtained lignosulfonic acid was subsequently employed as a functional electrolyte additive, and its concentration was systematically optimized to regulate the Zn/electrolyte interface. For comparison, lignosulfonic acid derived from the more commonly used sodium lignosulfonate was also investigated. The results demonstrate that, after Ca^{2+} removal, the lignosulfonic acid molecules enriched with polar functional groups ($-\text{SO}_3\text{H}$, $-\text{OH}$, and $-\text{COOH}$) exhibit strong affinity toward the Zn surface and preferentially adsorb at the Zn/electrolyte interface. Such preferential adsorption reconstructs the original water-rich electric double layer into a water-deficient inner Helmholtz layer dominated by organic molecular adsorption. Consequently, the lignosulfonate additive enables the assembled Zn||Zn symmetric cell to operate stably for 1600 h at 1 mA cm^{-2} and 1 mAh cm^{-2} , and allows the Zn||Cu cell to sustain 1500 plating/stripping cycles at 2 mA cm^{-2} with an average Coulombic efficiency of 99.59%. Moreover, the Zn|| MnO_2 full cell delivers stable cycling performance over 2000 cycles at 0.5 A g^{-1} with an average Coulombic efficiency of 99.63%. This work provides new insight into the rational

design of sustainable biomass-derived electrolyte additives for high-performance AZIBs.

2 Experimental Section

2.1 Preparation of the Electrolyte

Calcium lignosulfonate (CaSL) was converted into lignosulfonic acid through an H-type cation-exchange process. A 732 strongly acidic cation-exchange resin in the H^+ form was used for the ion-exchange treatment. Before use, the resin was immersed in $1\text{ mol}\cdot\text{L}^{-1}$ HCl for 12 h to ensure conversion to the H^+ form and was subsequently rinsed repeatedly with deionized water until the effluent reached a neutral pH. A total of 10 g of CaSL was dissolved in 60 mL of deionized water to prepare a CaSL solution. The prepared CaSL solution was then poured into the pretreated H-type resin and allowed to undergo ion exchange at $25\text{ }^{\circ}\text{C}$ for 5 h. After ion exchange, the liquid extract was collected in a beaker, and the resin was further rinsed with deionized water until the eluate became colorless. The collected fractions were combined and centrifuged. The obtained solid fraction was collected, frozen overnight, and subsequently freeze-dried for three days to obtain the lignosulfonic acid (CL), which was used as the electrolyte additive.

A 2M aqueous ZnSO_4 solution was prepared as the baseline electrolyte and denoted as ZSO. Subsequently, CL was introduced into the baseline electrolyte at volume fractions of 0.1%, 0.2%, 0.3%, 0.4%, and 0.5%, and the resulting electrolytes were denoted as ZSO/CL-0.1, ZSO/CL-0.2, ZSO/CL-0.3, ZSO/CL-0.4, and ZSO/CL-0.5, respectively.

2.2 Electrochemical measurement

All electrochemical tests were conducted using CR2032 coin cells. $\text{Zn}||\text{Zn}$ symmetric cells were assembled with zinc foil serving as both the working and counter electrodes. For the $\text{Zn}||\text{Cu}$ asymmetric configuration, zinc foil and copper foil were employed as the working and counter electrodes, respectively. $\text{Zn}||\text{MnO}_2$ full cells were fabricated using MnO_2/CNT as the working electrode and zinc foil as the counter electrode. A 2M aqueous ZnSO_4 solution was used as the baseline electrolyte, with CL

introduced as the functional additive. Glass fiber (GF/D) was selected as the separator in all cell assemblies.

Galvanostatic charge-discharge (GCD) measurements were carried out using a CT3001K battery testing system. Electrochemical measurements, including cyclic voltammetry (CV), linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS), chronoamperometry (CA) and Tafel tests, were performed on a Modulab XM electrochemical workstation. EIS and CA measurements were conducted under a constant polarization voltage of 20 mV. The Zn^{2+} transference number ($t_{\text{Zn}^{2+}}$) was calculated according to the Bruce-Vincent method using the impedance and polarization results based on Equation (1):

$$t_{\text{Zn}^{2+}} = \frac{I_s(\Delta V - I_0 R_0)}{I_0(\Delta V - I_s R_s)} \quad (1)$$

where ΔV represents the applied polarization voltage (20 mV). I_0 and R_0 denote the current and resistance in the initial state, while I_s and R_s correspond to the steady-state current and resistance.

The activation energy (E_a) for ion desolvation was evaluated using the Arrhenius equation based on the interfacial charge-transfer resistance (R_{ct}) obtained from EIS measurements:

$$1/R_{ct} = A \exp\left(-\frac{E_a}{RT}\right) \quad (2)$$

where A is the frequency factor, R is the molar gas constant, and T is the absolute temperature.

The electrical double-layer capacitance (EDLC) of Zn symmetric cells with different electrolytes was further determined from CV curves collected within the non-faradaic potential region according to Equation (3):

$$C = i_c / \nu \quad (3)$$

where i_c represents the capacitance current and ν represents the scan rate.

2.3 Materials characterization

Surface morphology and elemental composition were characterized using scanning electron microscopy (SEM, JEOL JSM-7200F) equipped with an energy-dispersive X-ray spectrometer (EDS, Oxford X-Max50X). Fourier transform infrared (FTIR) spectra

were recorded within the wavenumber range of 400-4000 cm^{-1} using KBr pellets (Thermo Scientific iN10). Elemental distribution on the sample surface was characterized by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha). The crystal structure of the materials was determined by X-ray diffraction (XRD, Shimadzu XRD-7000) with Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The wettability of the electrolyte on the electrode surface was evaluated using a contact angle measuring instrument (OCA100). Nuclear magnetic resonance (NMR) spectrum was recorded with a JEOL-ECZR 600 MHz instrument. Zeta potential and particle size were characterized by dynamic light scattering (DLS) using a Zetasizer Pro instrument (Malvern Panalytical, UK). Molecular weight analysis was performed via gel permeation chromatography (GPC) on an Agilent 1260 Infinity system (Agilent Technologies, USA).

2.4 Theoretical calculation

Density functional theory (DFT) calculations were carried out using the Materials Studio package. The electrostatic potential distribution and adsorption energies of various adsorbates were evaluated using the DMol3 and Forcite modules, respectively. The exchange-correlation interactions were described within the generalized gradient approximation (GGA) framework employing the Perdew-Burke-Ernzerhof (PBE) functional. A double numerical plus polarization (DNP) basis set was adopted to represent the electron-nucleus interactions, and a smearing value of 0.001 Ha (1 Ha = 27.21 eV) was applied to improve convergence. Structural optimizations were performed with convergence thresholds of 1.0×10^{-5} Ha for energy, 0.002 Ha $\text{\AA}^{-1}$ for maximum force, and 0.005 $\text{\AA}$ for maximum displacement. To avoid spurious interactions between periodic images, a vacuum layer of 30 $\text{\AA}$ was introduced along the Z-direction in the surface slab model.

The corresponding adsorption energy was determined from equation (4):

$$E_{ads} = E_{total} - E_{slab} - E_a \quad (4)$$

where E_{ads} , E_{total} , E_{slab} , and E_a are the adsorption energy, the total energy of the adsorption systems, the energy of the pristine slab, and the energy of the isolated adsorbate, respectively.

Given the relatively large molecular size and complex atomic composition of lignosulfonate in the adsorption model, the Forcite module was further employed to evaluate adsorption energies using a classical force-field approach. The Zn metal surfaces of (002), (101) and (100) facets were constructed with four atomic layers and expanded into a $4 \times 5 \times 1$ supercell. The COMPASS III force field was used throughout the simulations, and atomic charges were assigned consistently within the same framework. Both electrostatic and van der Waals interactions were calculated using the Ewald summation method. The convergence tolerance for energy was set to 2×10^{-5} kcal mol⁻¹, and the force tolerance was 0.001 kcal mol⁻¹.

3 Results and discussion

As shown in Fig. 1a, the electrostatic potential (ESP) distributions of H₂O, SO₄²⁻, and the lignosulfonate model molecule were analyzed to evaluate their charge characteristics. The lignosulfonate molecule displays a highly heterogeneous charge distribution, with electron density localized on the oxygen atoms of sulfonate (-SO₃⁻) groups. These electron-rich regions act as nucleophilic sites for Zn²⁺ coordination, indicating strong interfacial affinity toward Zn species. To further elucidate the electronic interaction with the Zn surface, frontier molecular orbital analysis was performed (Fig. 1b). Compared with H₂O and SO₄²⁻, lignosulfonate possesses a higher HOMO energy level, a relatively lower LUMO energy level, and a narrower HOMO-LUMO energy gap. These electronic features suggest that lignosulfonate can more readily participate in interfacial electron transfer and spontaneously adsorb onto the Zn surface. To quantitatively evaluate the interfacial adsorption behavior, DFT calculations were further performed on different Zn crystal planes, and the corresponding adsorption energies were calculated according to Equation (4) (Fig. 1c). The adsorption energies of lignosulfonate on Zn(100), Zn(101), and Zn(002) surfaces were calculated to be -3.854, -3.650, and -4.286 eV, respectively, all significantly stronger than those of H₂O and SO₄²⁻. These results demonstrate the strong adsorption affinity of lignosulfonate toward Zn surfaces, enabling it to outcompete water molecules and sulfate anions during interfacial adsorption.

Based on these theoretical insights, liginosulfonate salts were initially introduced as electrolyte additives. However, the performance of CaSL was unsatisfactory (Fig. S1, 2). A 30-day immersion test of Zn foil (Fig. S3) reveals severe surface corrosion after soaking, with pronounced Ca enrichment detected in the corrosion products. To address this issue, a cation-exchange strategy was designed to remove Ca^{2+} from calcium liginosulfonate, yielding CL, as illustrated in Fig. 1d. This process effectively eliminates the influence of hetero cations and fully exposes the active functional groups ($-\text{SO}_3\text{H}$, $-\text{OH}$, $-\text{COOH}$).

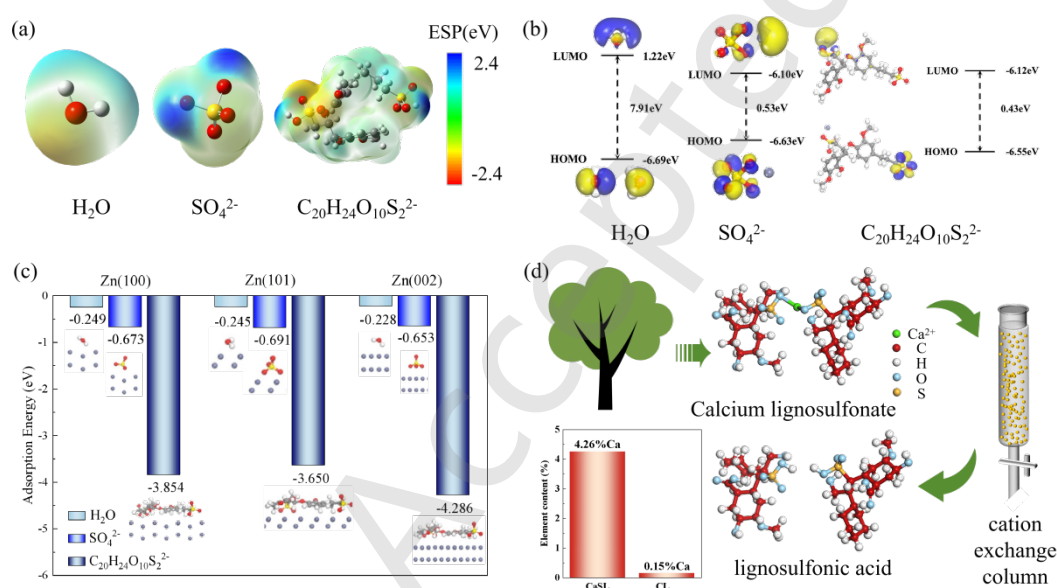


Fig. 1 (a) The electrostatic potential mapping results of H_2O , SO_4^{2-} and $\text{C}_{20}\text{H}_{24}\text{O}_{10}\text{S}_2^{2-}$. (b) LUMO and HOMO iso-surfaces of H_2O , SO_4^{2-} and $\text{C}_{20}\text{H}_{24}\text{O}_{10}\text{S}_2^{2-}$. (c) Adsorption energy of H_2O , SO_4^{2-} and $\text{C}_{20}\text{H}_{24}\text{O}_{10}\text{S}_2^{2-}$ with different crystal face. (d) The preparation process of CL.

The obtained CL shows a dried particulate morphology after ion-exchange treatment (Fig. 2a). Corresponding EDS elemental mapping (Fig. S4) further confirms the uniform distribution of C, O and S elements throughout the sample, while no obvious Ca signal is detected, demonstrating the effective removal of Ca^{2+} . The particle size distribution in Fig. 2b shows a relatively narrow distribution with an average size of 85.95 nm, suggesting nanoscale uniformity. GPC results (Fig. 2c) show a broad molecular weight distribution with a number-average molecular weight (M_n) of 559, reflecting the intrinsic polydispersity of lignin-derived materials.

To confirm the effectiveness of the cation-exchange process, XPS was conducted.

As shown in Fig. 2d, compared with CaSL, the survey spectrum of CL shows the complete disappearance of the Ca 2p signal, evidencing the effective removal of Ca^{2+} [30]. Meanwhile, the relative intensities of O 1s, C 1s, and S 2p signals remain prominent, indicating that the main lignosulfonate framework is preserved after treatment. This result validates the design strategy proposed in Fig. 1f, which eliminates inactive metal cations to release functional groups. Notably, the high-resolution S 2p spectra (Fig. 2e, f) exhibit a clear positive shift from 167.7 eV in CaSL to 168.4 eV in CL. This shift is attributed to the disruption of Ca^{2+} -sulfonate coordination, which reduces electron shielding around sulfur atoms and leads to decreased electron density. As a result, the binding energy increases, indicating the transformation from metal-coordinated sulfonate ($\text{Ca}^{2+}\text{-SO}_3^-$) to more free sulfonate groups. The O 1s spectra further support this interpretation (Fig. S5, 6). A slight shift toward higher binding energy (from 532.4 to 532.7 eV) is observed after Ca^{2+} removal, indicating a similar decrease in electron density around oxygen atoms. This suggests that the oxygen atoms in the sulfonate groups become more electron-deficient after dissociation of $\text{Ca}^{2+}\text{-SO}_3^-$ interactions, consistent with the S 2p results [31]. In addition, the C 1s spectra show subtle changes in the relative intensities of C-O and O-C=O components, implying a modification in the local chemical environment of oxygen-containing functional groups [32]. Although the carbon backbone remains intact, the redistribution of electron density induced by Ca^{2+} removal slightly alters the electronic structure of adjacent carbon atoms.

The FTIR spectra (Fig. 2g) provide complementary evidence for this structural evolution. Both CL and CaSL exhibit similar characteristic bands of lignin, including aromatic skeletal vibrations at 1598, 1509 and 1423 cm^{-1} , as well as C-O and C-H vibrations associated with guaiacyl units at 1262 and 1026 cm^{-1} , confirming that the primary lignin backbone is preserved after treatment [33, 34]. However, distinct differences are observed in functional group regions. A new peak at 1706 cm^{-1} in CL corresponds to the C=O stretching of -COOH, whereas CaSL predominantly contains -COO⁻ groups [35]. More importantly, the characteristic O=S=O vibration shifts to 1208 cm^{-1} in CL, which is assigned to protonated sulfonic acid groups (-SO₃H), while in CaSL the sulfonate groups (-SO₃⁻) exhibit lower wavenumbers due to resonance

stabilization and coordination with Ca^{2+} [36, 37]. The removal of Ca^{2+} weakens this resonance effect, strengthens the $\text{S}=\text{O}$ bonds, and shifts the vibration to higher wavenumber [38]. These FTIR results are in excellent agreement with the XPS analysis, both indicating decreased electron density and the formation of more chemically active sulfonic groups after ion exchange.

After confirming the structural and chemical activation of CL, its influence on the electrolyte environment was investigated. The ^1H NMR spectra (Fig. 2h) show that the water proton signal in the baseline ZSO electrolyte, located at 4.665 ppm, shifts to 4.658 ppm upon the addition of CL. This chemical shift reflects a change in the hydrogen-bond network of the aqueous electrolyte [39]. Specifically, the interaction between CL functional groups and water molecules alters proton environment, suggesting reduced activity of free water and strengthened intermolecular interactions, which suppress water-induced side reactions. Finally, ionic conductivity and pH measurements (Fig. 2i) show that the ionic conductivity first increases and then decreases with increasing CL concentration. At low concentrations, the partial dissociation of acidic groups may increase the number of mobile ions, whereas at higher concentrations, CL- Zn^{2+} interactions and macromolecular crowding restrict ion migration. Meanwhile, the continuously decreasing pH is consistent with the presence of acidic functional groups, such as $-\text{SO}_3\text{H}$ and $-\text{COOH}$. The FTIR spectra (Fig. S7) remain largely unchanged, indicating that CL does not substantially alter the bulk solvation structure but mainly regulates the local interfacial environment near the Zn surface.

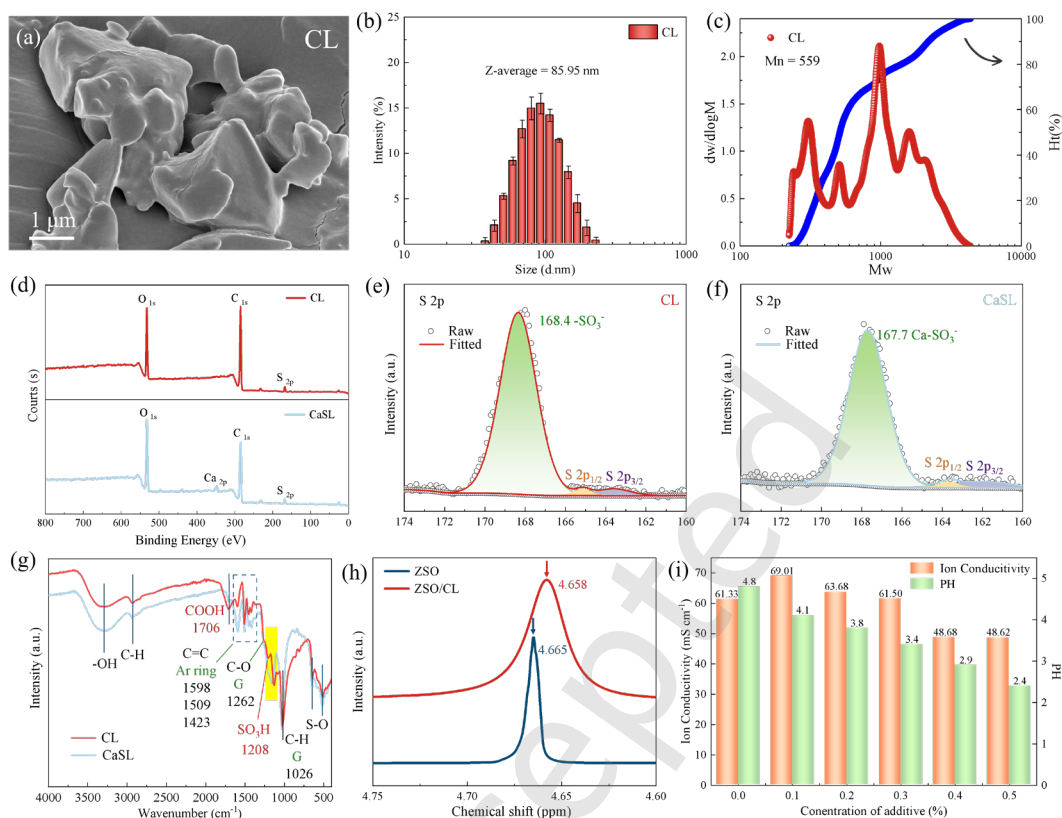


Fig. 2 (a) SEM images of CL. (b) Particle size distribution of CL. (c) Molecular weight distribution of CL. (d) XPS survey spectra of CL and CaSL. (e) high-resolution S 2p spectra of CL. (f) high-resolution S 2p spectra of CaSL. (g) FTIR spectra of CL and CaSL. (h) ^1H NMR spectra of ZSO and ZSO/CL electrolytes. (i) The pH value and Ion conductivity of different electrolytes.

To evaluate the effect of CL on the electrochemical performance of the Zn anode, Zn||Zn symmetric cells were first assembled using different electrolytes to investigate their long-term cycling stability. As shown in Fig. 3a, at a current density of 1 mA cm^{-2} with a plating/stripping capacity of 1 mAh cm^{-2} , all CL-containing electrolytes exhibit longer cycling lifespans than the pristine ZSO electrolyte, indicating that the additive effectively improves the stability of Zn plating/stripping. Among them, the ZSO/CL-0.2 electrolyte delivers the best performance, maintaining stable cycling for over 1600 h with a low voltage hysteresis of 40 mV. In contrast, the cell using pristine ZSO electrolyte fails within 200 h and shows severe voltage fluctuations. Notably, comparison with previously reported Zn-based electrolyte systems (Fig. 3b and Table S1) demonstrates that the ZSO/CL-0.2 electrolyte delivers markedly enhanced cycling durability and interfacial stability.

To further probe the reversibility of Zn plating/stripping, Zn||Cu asymmetric cells were tested at 1 mA cm^{-2} with a deposition capacity of 0.5 mAh cm^{-2} . As illustrated in Fig. 3c, all CL-containing electrolytes exhibit improved cycling stability and Coulombic efficiency (CE) compared with the pristine ZSO electrolyte, indicating that the introduction of lignosulfonic acid enhances the reversibility of Zn plating/stripping. Among these electrolytes, ZSO/CL-0.2 delivers the best performance, maintaining stable cycling over 1500 cycles with an average CE of 99.03 %. In contrast, the cell using ZSO electrolyte shows initial activation behavior followed by pronounced CE fluctuation and rapid decay, indicating poor reversibility and eventual short-circuit failure. When the testing conditions are increased to 2 mA cm^{-2} and 1 mAh cm^{-2} (Fig. 3d), the ZSO/CL-0.2 electrolyte still maintains excellent stability with an average CE as high as 99.59 % over more than 1500 cycles, whereas the ZSO-based cell exhibits drastic voltage instability after only 398 cycles. The voltage-capacity profiles further reveal the differences induced by the additive (Fig. 3e, f). The Zn||Cu cell with ZSO/CL-0.2 electrolyte shows highly overlapping curves during cycling, indicating excellent reversibility and stable interfacial kinetics, with a voltage hysteresis of only 115.64 mV even after 1500 cycles. By contrast, the ZSO electrolyte displays obvious voltage fluctuations as early as the 406th cycle, along with a much larger voltage hysteresis of 185.39 mV, reflecting severe polarization and unstable Zn deposition behavior.

Based on these results, ZSO/CL-0.2 is identified as the optimal electrolyte and further evaluated for rate performance. As shown in Fig. 3g, ZSO/CL-0.2 delivers a highly stable voltage response over a wide current range from 0.5 to 8 mA cm^{-2} and fully recovers when the current density returns to 0.5 mA cm^{-2} . In contrast, the ZSO-based cell suffers from irreversible performance degradation after cycling at high current densities. Overall, these results demonstrate that the introduction of CL significantly improves the reversibility of Zn plating/stripping.

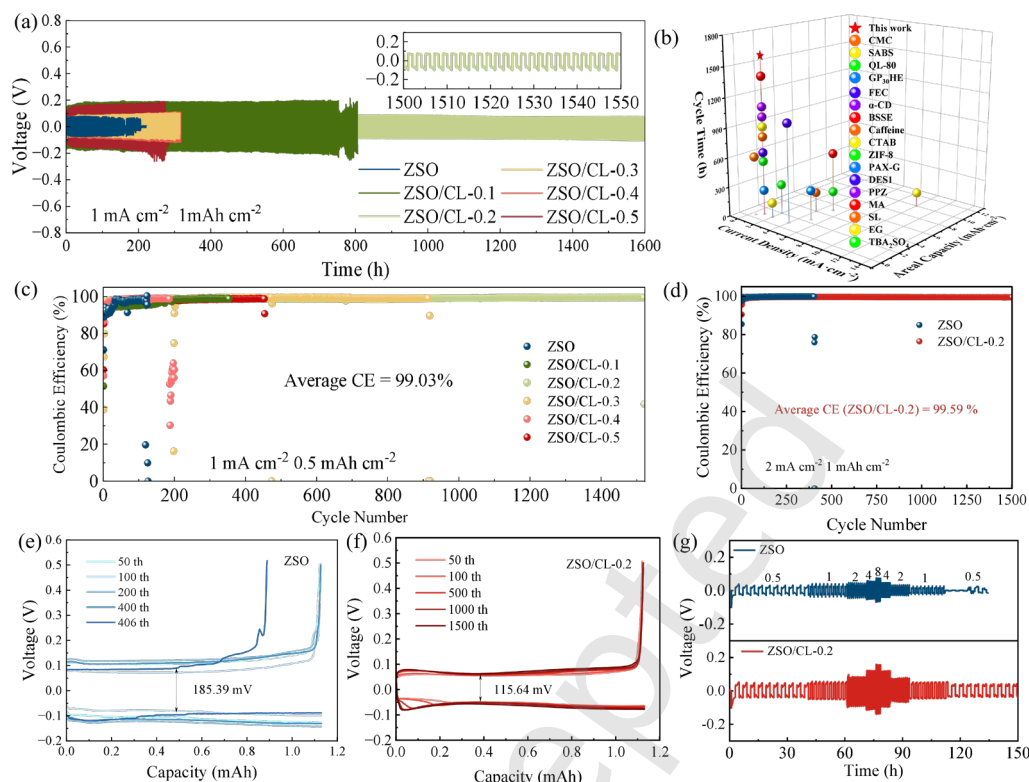


Fig. 3 (a) Cycling performance of symmetric batteries assembled by ZSO/CL-x electrolytes. (b) Comparison of the cycling performance with recent works, with detailed information provided in Table S1. (c) Electroplating/stripping curves of Zn||Cu asymmetric batteries assembled with ZSO/CL-x electrolytes at 1 mA cm⁻² and 0.5 mAh cm⁻². (d) Electroplating/stripping curves of Zn||Cu asymmetric batteries assembled with ZSO and ZSO/CL-0.2 electrolytes at 2 mA cm⁻² and 1 mAh cm⁻². (e) Capacity-voltage curves of ZSO electrolyte during Zn⁰ plating/stripping. (f) Capacity-voltage curves of ZSO/CL-0.2 electrolyte during Zn⁰ plating/stripping. (g) Rate performance of symmetric batteries assembled by ZSO and ZSO/CL-0.2.

To elucidate the mechanism by which CL stabilizes the Zn anode, systematic characterizations were carried out from three aspects: suppression of water-induced side reactions, regulation of Zn²⁺ deposition behavior, and the unique functional-anion effect of CL compared with sodium lignosulfonate derived lignosulfonate. First, the ability of CL to suppress interfacial side reactions was evaluated by long-term Zn foil immersion, corrosion, and hydrogen evolution tests. As shown in Fig. 4a, the Zn foil immersed in pristine ZSO electrolyte for 30 days exhibits a rough and uneven surface covered with abundant irregular corrosion products. Consistently, the XRD pattern (Fig.

4b) displays characteristic diffraction peaks assigned to zinc hydroxide sulfate hydrate (PDF#39-0688, $\text{Zn}_4\text{SO}_4(\text{OH})_6(\text{H}_2\text{O})_5$)^[40]. In contrast, although slight surface roughness remains on the Zn foil immersed in ZSO/CL-0.2, no detectable crystalline byproduct peaks are observed by XRD, indicating that the formation of crystalline byproducts is substantially suppressed. Furthermore, the markedly reduced ZHS-related S 2p signals in the XPS spectrum (Fig. S8) confirm that CL effectively inhibits the formation and accumulation of ZHS on the Zn surface^[41]. Meanwhile, Tafel analysis using a pH-matched ZSO electrolyte (pH 3.8) as the control shows that the corrosion current density decreases from $5.751 \times 10^{-3} \text{ mA cm}^{-2}$ in ZSO to $0.776 \times 10^{-3} \text{ mA cm}^{-2}$ in ZSO/CL-0.2 (Fig. 4c). The corresponding corrosion potential shifts positively from -0.968 to -0.934 V. As the two electrolytes have the same pH, the markedly lower corrosion current density indicates that CL suppresses Zn corrosion beyond the effect of bulk electrolyte acidity. The suppression of corrosion side reactions was further verified by in situ hydrogen evolution observations and hydrogen evolution potential measurements. As shown in Fig. 4d, hydrogen bubbles appear much later and in significantly smaller quantities in the ZSO/CL-0.2 electrolyte compared with pristine ZSO. In addition, the ZSO/CL-0.2 electrolyte exhibits a higher hydrogen evolution overpotential (Fig. S9). At a current of 5 mA, the potential of the ZSO electrolyte is -0.122 V, whereas that of the ZSO/CL-0.2 electrolyte shifts to -0.182 V, indicating that hydrogen evolution becomes thermodynamically less favorable after the introduction of CL. These results confirm that CL effectively suppresses hydrogen evolution and corrosion reactions at the Zn/electrolyte interface, thereby improving interfacial thermodynamic stability.

Second, the influence of CL on Zn^{2+} deposition kinetics and interfacial ion transport was investigated. The voltage-capacity profiles of Zn||Cu asymmetric cells at 2 mA cm^{-2} (Fig. 4e) show that the Zn deposition overpotential decreases from 55.8 mV in the pristine ZSO electrolyte to 44.95 mV after introducing CL into the electrolyte. Accordingly, the CV curves (Fig. S10) exhibit a significantly reduced nucleation overpotential in the ZSO/CL-0.2 electrolyte. To further elucidate the regulatory effect

of CL on interfacial Zn deposition, EIS and CA measurements were conducted under a constant polarization voltage of 20 mV. According to the Bruce-Vincent method (Equation (1)), the Zn^{2+} transference number was calculated from the impedance and polarization results (Fig. 4f, Fig. S11 and Table S2) [42]. After the addition of CL, the Zn^{2+} transference number increases from 0.50 to 0.62, indicating enhanced Zn^{2+} transport capability within the electrolyte. The increased Zn^{2+} transference number alleviates ion depletion and concentration gradients at the Zn/electrolyte interface [43]. In addition, dynamic contact angle measurements show that the contact angle of the pristine ZSO electrolyte decreases by only 20.64% within 10 min, whereas the ZSO/CL-0.2 electrolyte exhibits a larger reduction of 24.77% (Fig. 4g and Fig. S12), indicating improved interfacial wettability. The enhanced wettability can be attributed to the abundant polar functional groups of CL, which improve electrolyte spreading on the Zn surface and promote more uniform Zn^{2+} flux. Therefore, CL not only suppresses side reactions but also regulates interfacial Zn^{2+} transport and deposition, contributing to uniform and reversible Zn plating/stripping.

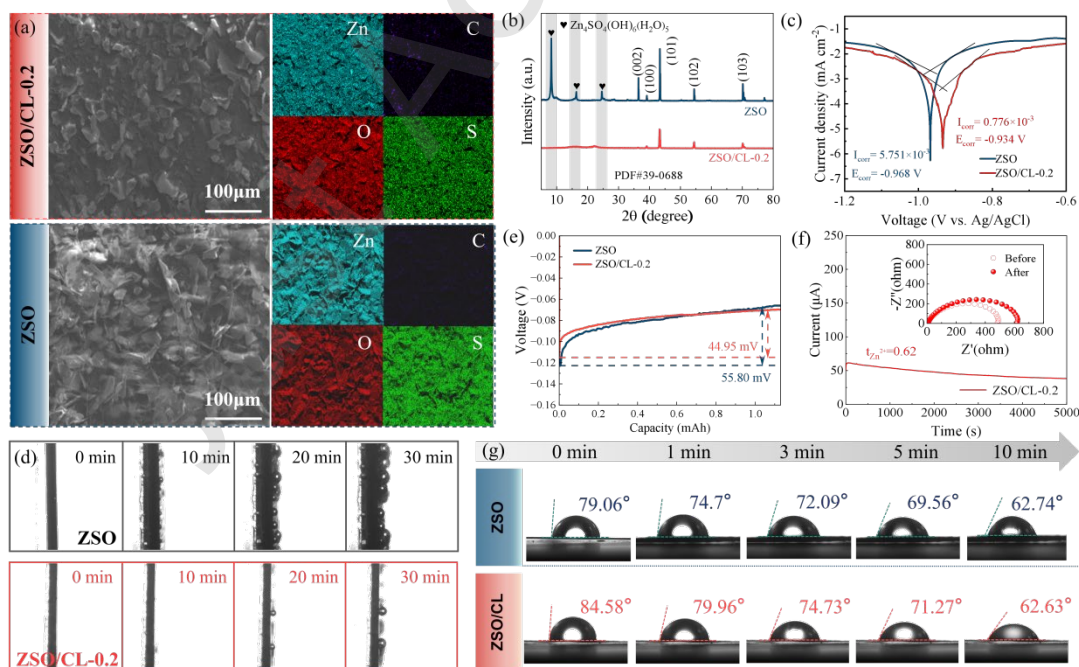


Fig. 4 (a) SEM and EDS images of Zn foils soaked in ZSO and ZSO/CL-0.2 electrolytes for 30 days. (b) XRD patterns of Zn foils soaked in ZSO and ZSO/CL-0.2 electrolytes for 30 days. (c) Tafel curves of ZSO and ZSO/CL-0.2 electrolytes. (d) In-situ hydrogen evolution image of Zn foils

soaked in ZSO and ZSO/CL-0.2 electrolytes. (e) Nucleation overpotential of Zn||Cu batteries assembled with ZSO and ZSO/CL-0.2 electrolytes. (f) EIS tests and i-t curves of ZSO/CL-0.2 electrolyte. (g) Change of contact angle of ZSO and ZSO/CL-0.2 electrolytes on zinc foil surface with time.

Finally, to demonstrate that the superior regulation effect originates from the unique structure of CL rather than merely from the presence of lignosulfonate species, sodium lignosulfonate (NaSL) was subjected to the same ion-exchange treatment to obtain protonated lignosulfonate (NL), and its physicochemical properties were systematically investigated. Although NL exhibits a morphology similar to that of CL (Fig. S13), EDS and ICP results reveal that residual Na^+ remains in NL after ion exchange, with a Na content of 0.79 %, which is significantly higher than the residual Ca content in CL (0.15 %). This suggests that ion exchange with the H-type resin effectively displaces Ca^{2+} from its interactions with the sulfonate groups under the present treatment conditions. Moreover, NL shows a larger average particle size of 116.63 nm and a higher number-average molecular weight of 986 (Fig. S14, 15, 16), whereas CL possesses a smaller particle size (85.95 nm) and a lower molecular weight (559). As NL and CL originate from different lignosulfonate precursors, these differences do not indicate their relative degrees of depolymerization during ion exchange, but may contribute to their different dispersion behaviors in the electrolyte. The smaller molecular size and lower molecular weight of CL are beneficial for molecular dispersion, interfacial adsorption, and ion transport in the electrolyte.

The FTIR spectra of NL and NaSL are shown in Fig. S17. Similar to the CL system, the ion-exchange treatment preserves the primary lignin framework while altering the local chemical environment of sulfonic functional groups. However, distinct differences are observed between CL and NL. In the enlarged FTIR spectra (Fig. 5a), the band associated with sulfonic groups appears at 1153.92 cm^{-1} for CL, at a higher wavenumber than the corresponding band of NL at 1133.38 cm^{-1} . Repeated measurements show the same relative peak-position trend (Fig. S18), confirming that this spectral difference is reproducible. The two samples also exhibit different features in the $580\text{--}620\text{ cm}^{-1}$ region, where vibrations associated with metal-oxygen (M-O)

interactions may contribute. The more pronounced feature in NL is consistent with its higher residual Na^+ content and the persistence of counterion-oxygen interactions, whereas the altered feature in CL is consistent with its lower residual metal-ion content. These observations suggest that CL contains more effectively activated sulfonic acid groups with enhanced polarity and interfacial interaction capability, whereas residual Na^+ in NL partially preserves ionic shielding and weakens the activation effect of the sulfonic groups. The differences in molecular structure further influence the physicochemical properties of the corresponding electrolytes. The ZSO/NL electrolyte exhibits noticeably poorer solubility and transparency than ZSO/CL in Fig. S19, indicating inferior dispersion behavior of NL in aqueous electrolyte. Viscosity and zeta potential results (Fig. 5b) further support this conclusion. The viscosity of ZSO/CL is $2.71 \text{ mPa}\cdot\text{s}$, lower than that of ZSO/NL ($2.88 \text{ mPa}\cdot\text{s}$), suggesting that the smaller CL molecules induce less resistance to ion migration and maintain better electrolyte fluidity. Meanwhile, the absolute zeta potential value of CL (13.29 mV) is higher than that of NL (11.47 mV), indicating weaker intermolecular aggregation tendency and improved colloidal stability in the electrolyte. These characteristics favor more uniform molecular dispersion and interfacial adsorption of CL on the Zn surface.

Temperature-dependent EIS measurements were performed to further clarify the influence of CL on interfacial ion-transfer behavior. As shown in Fig. 5c and Fig. S20, the charge-transfer resistance (R_{ct}) of the cells containing ZSO/NL (313Ω) and ZSO/CL (702Ω) at 20°C is higher than that of pristine ZSO electrolyte (249Ω). This increase in R_{ct} can be attributed to the strong coordination interaction between sulfonic groups and Zn^{2+} ions, together with the steric hindrance effect introduced by lignosulfonate molecules. However, as the temperature increases, the R_{ct} values of all electrolytes gradually converge to approximately 100Ω at 60°C . According to the Arrhenius relationship (Equation (2)), the apparent activation energy for interfacial charge transfer (E_{a}) was calculated from the temperature-dependent impedance results (Fig. 5d). The ZSO/CL electrolyte exhibits the highest E_{a} value ($31.88 \text{ kJ mol}^{-1}$), significantly larger than those of pristine ZSO ($15.21 \text{ kJ mol}^{-1}$) and ZSO/NL ($21.99 \text{ kJ mol}^{-1}$). These results indicate that the strongly adsorbed CL layer moderately restricts interfacial charge

transfer, thereby suppressing excessive local charge transfer and uncontrolled Zn growth.

The EDLC of Zn symmetric cells assembled with different electrolytes was further analyzed based on CV curves collected in the non-faradaic region (Fig. 5e and Fig. S21). According to Equation (3), the calculated EDLC values are summarized in Fig. 5f. The electrolyte containing CL exhibits a significantly lower EDLC ($65.43 \mu\text{F cm}^{-2}$) than pristine ZSO electrolyte ($253.35 \mu\text{F cm}^{-2}$) and ZSO/NL electrolyte ($75.46 \mu\text{F cm}^{-2}$). The reduced EDLC indicates that lignosulfonate molecules preferentially adsorb onto the Zn surface to form a new dipole layer rather than allowing water molecules to dominate the original interfacial structure [44]. Consistent with the temperature-dependent EIS results, lignosulfonate exhibits strong interfacial affinity and forms an adsorbed layer on the Zn surface. This layer alleviates local concentration polarization and homogenizes the interfacial Zn^{2+} flux, thereby promoting controlled and uniform Zn deposition.

Fig. 5g schematically illustrates the interfacial regulation mechanism of CL at the Zn anode/electrolyte interface. In conventional ZSO aqueous electrolytes, the negatively charged Zn surface rearranges interfacial ions and orients water dipoles, forming a water-rich electrical double layer (EDL) [45-47]. In such an interfacial environment, abundant active water molecules directly contact the Zn surface, accelerating parasitic reactions such as hydrogen evolution, Zn corrosion, and byproduct formation. Consequently, the interface becomes highly unstable, leading to dendrite growth, and rapid cell failure. Upon introducing CL into the electrolyte, CL molecules preferentially adsorb onto the Zn surface under the external electric field, spontaneously forming a self-assembled interfacial layer. Owing to the abundant polar functional groups and strong interfacial affinity of CL, this organic layer effectively blocks the direct water-Zn contact, suppressing water-induced side reactions and corrosion. Moreover, the preferential adsorption of CL reconstructs the interfacial EDL structure and forms a water-deficient inner Helmholtz layer, reducing the proportion of active interfacial water molecules near the Zn surface. The corresponding decrease in electrical double-layer capacitance (EDLC) confirms the formation of a dipole layer

dominated by adsorbed CL molecules instead of water. Furthermore, the adsorbed CL layer homogenizes the interfacial electric field and Zn^{2+} flux, alleviating localized concentration polarization and promoting uniform Zn deposition. The steric hindrance effect of the CL layer further suppresses uncontrolled lateral Zn growth and dendrite formation, yielding a dense and dendrite-free Zn deposition morphology. Benefiting from the synergistic effects of interfacial adsorption, EDL reconstruction, and interfacial Zn^{2+} regulation, the Zn anode exhibits reduced polarization, enhanced reversibility, improved corrosion resistance, and significantly prolonged cycling stability.

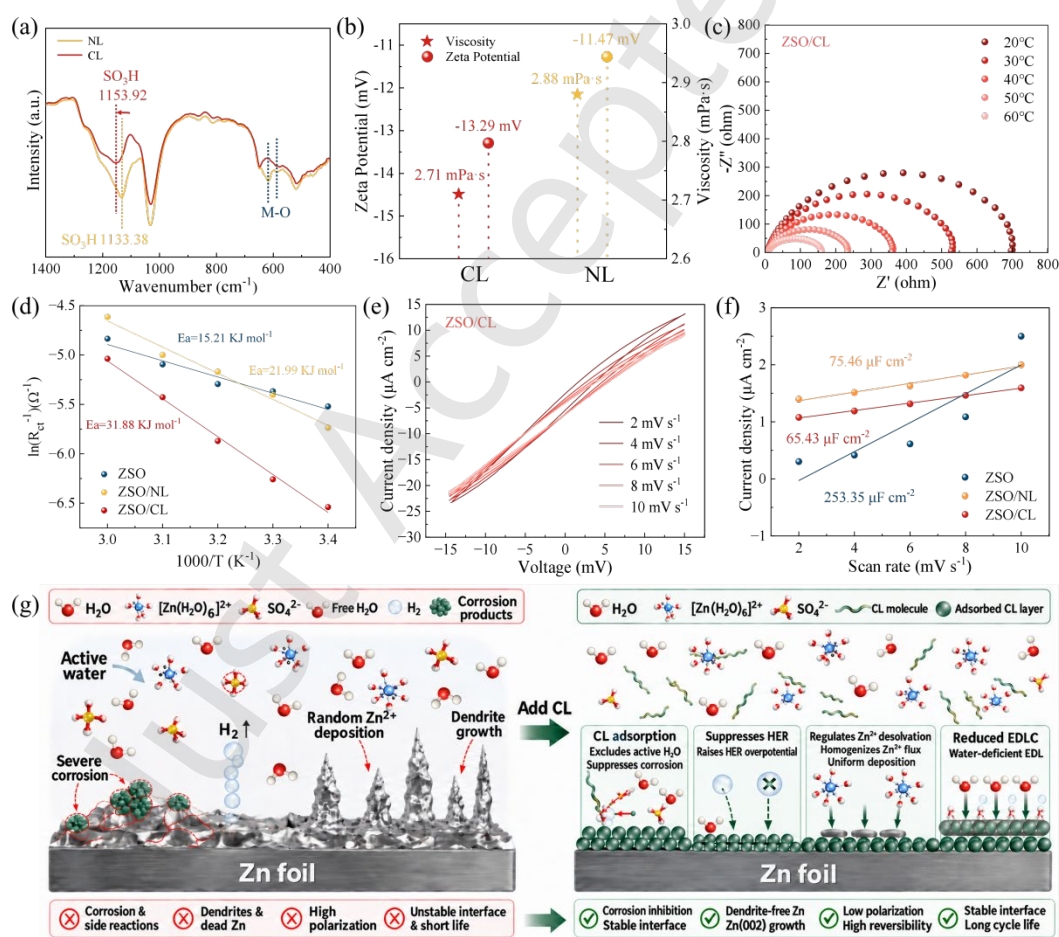


Fig. 5 (a) Local magnified FTIR images of CL and NL. (b) The viscosity and zeta potential of CL and NL. (c) EIS test of ZSO/CL-0.2 electrolytes at different temperature. (d) Apparent activation energy for interfacial charge transfer of ZSO, ZSO/NL-0.2 and ZSO/CL-0.2 electrolytes. (e) CV curves at different scan rate of ZSO/CL-0.2 electrolytes. (f) The relationship curve between current density and scanning rate. (g) Mechanism of lignosulfonic acid regulating zinc anode/electrolyte

interface.

To evaluate the practical applicability of the electrolyte, Zn||MnO₂ full cells were assembled using the pristine ZSO electrolyte and the modified ZSO/CL-0.2 electrolyte. As shown in Fig. 6a, at 0.5 A g⁻¹, the Zn||MnO₂ cell with the CL additive maintains a capacity of 102.43 mAh g⁻¹ after the initial decay within the first 100 cycles and delivers a prolonged cycling stability over 2000 cycles with a capacity retention of 85.82%. In contrast, the cell with the ZSO electrolyte suffers rapid capacity fading, retaining only 63.5 mAh g⁻¹ after the initial decay and failing after 656 cycles. Furthermore, the introduction of CL significantly improves the CE of the full cell, achieving an average CE of 99.63% over 2000 cycles, which indicates that CL effectively enables long-term cycling stability. The charge-discharge profiles in Fig. 6b reveal that, upon adding CL, the inflection point of the discharge curve shifts to higher capacity, indicating a prolonged proton-dominated interfacial reaction stage [48], which creates a more favorable environment for subsequent Zn²⁺ intercalation. Collectively, these results demonstrate that CL can effectively regulate the electrode/electrolyte interface, as evidenced by enhanced capacity retention and high CE over 2000 cycles.

Fig. 6c compares the rate performance of Zn||MnO₂ full cells with different electrolytes. The cell with CL delivers high specific capacities of 205.9, 199.8, 173.4, 122.5, and 65.7 mAh g⁻¹ at current densities of 0.3, 0.5, 1, 3, and 5 A g⁻¹, respectively. When the current density returns to 0.3 A g⁻¹, the capacity recovers to 186.5 mAh g⁻¹, demonstrating excellent reversibility. In contrast, the ZSO-based cell shows much lower capacities under identical conditions, confirming that CL significantly enhances both reversibility and rate performance. The corresponding GCD curves in Fig. 6d further support this conclusion. The CV curves of the full cells are presented in Fig. 6e. Both electrolytes exhibit two pairs of redox peaks with similar shapes, corresponding to the two voltage plateaus observed in Fig. 6b, indicating that the CL does not alter the intrinsic energy storage mechanism of MnO₂ [49]. Notably, the cell with CL shows significantly enhanced redox peak currents, suggesting improved electrochemical activity. Meanwhile, the oxidation peaks shift positively and the reduction peaks shift negatively, leading to increased voltage polarization. This behavior is closely related to

the preferential adsorption of lignosulfonate molecules on the Zn surface. The adsorption layer blocks active H₂O sites within the EDL, suppressing the hydrogen evolution reaction and thereby increasing the contribution of the main redox reactions. The peak shifts are consistent with the EIS results, as shown in Fig. S22. The charge transfer resistance of the ZSO/CL-0.2 electrolyte is 336.10 Ω , which is higher than that of the ZSO electrolyte (106.51 Ω). The increase is attributed to the formation of a dynamically adsorbed interfacial layer by lignosulfonate molecules, which slightly retards interfacial ion transport but effectively stabilizes the interface.

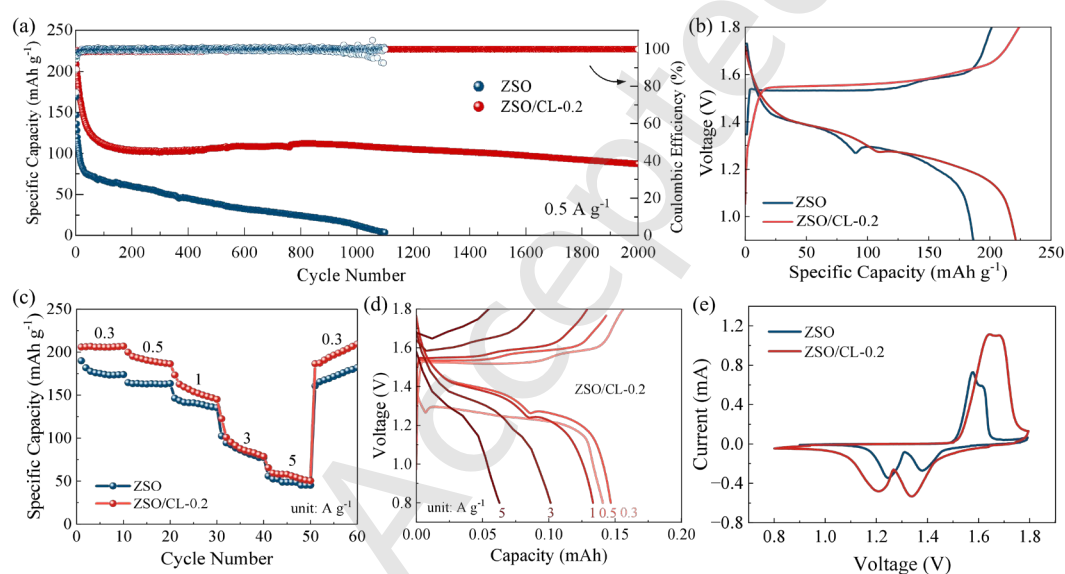


Fig. 6 (a) Long cycle performance of Zn||MnO₂ battery with ZSO and ZSO/CL-0.2 electrolytes. (b) GCD curve of Zn||MnO₂ batteries using ZSO and ZSO/CL-0.2 electrolytes. (c) Rate performance of the Zn||MnO₂ batteries assembled with ZSO and ZSO/CL-0.2 electrolytes. (d) GCD curves of the Zn||MnO₂ batteries assembled with ZSO/CL-0.2 electrolytes at different current density. (e) CV curve of the Zn||MnO₂ batteries assembled with ZSO and ZSO/CL-0.2 electrolytes.

4 Conclusion

In summary, a biomass-derived CL additive was successfully introduced into ZnSO₄ electrolyte to stabilize the Zn anode/electrolyte interface for AZIBs. The removal of inactive Ca²⁺ from the biomass effectively activates the abundant polar functional groups (-SO₃H, -OH, and -COOH), thereby enhancing its interfacial adsorption capability toward the Zn surface. The preferential adsorption of CL

reconstructs the original water-rich electric double layer into a water-deficient interfacial layer, which effectively blocks direct contact between active water molecules and Zn metal, suppresses hydrogen evolution and corrosion, and mitigates the formation of harmful byproducts. Meanwhile, the multifunctional groups and steric hindrance of CL homogenize the interfacial electric field and Zn^{2+} flux, alleviating concentration polarization. Benefiting from these synergistic effects, the optimized ZSO/CL-0.2 electrolyte enables the assembled Zn||Zn symmetric cell to operate stably for 1600 h at 1 mA cm^{-2} and 1 mAh cm^{-2} , while allowing the Zn||Cu cell to sustain 1500 plating/stripping cycles at 2 mA cm^{-2} with an average CE of 99.59%. The Zn|| MnO_2 full cell delivers stable cycling performance over 2000 cycles at 0.5 A g^{-1} with an average CE of 99.63%. This work highlights the great potential of sustainable biomass-derived additives for electrolyte engineering and provides a promising strategy for the development of highly stable and durable AZIBs.

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None.

Author contribution statement

Chenlu Wang: Writing-original draft, Investigation, Funding acquisition. YiQiu Gao: Data curation. Hanyi Liu: Data curation. Ning Cao: Supervision, Funding acquisition. Jingyi Guan: Methodology, Funding acquisition. Shiyu Du: Resources. Lixia Zhou: Investigation. Xiaobei Zang: Writing-review & editing, Project administration, Funding acquisition. All authors have approved the final manuscript.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Use of AI statement

During the preparation of this work, the authors used Doubao in order to draw the background image of the Graphical Abstract. After using this tool, the authors reviewed and edited the content as needed and take full responsibility for the content of the publication.

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