

A multifunctional quasi-solid-state polymer electrolyte with highly selective ion highways for practical zinc ion batteries

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The uncontrolled dendrite growth and detrimental parasitic reactions of Zn anodes currently impede the large-scale implementation of aqueous zinc ion batteries. Here, we design a versatile quasi-solid-state polymer electrolyte with highly selective ion transport channels via molecular crosslinking of sodium polyacrylate, lithium magnesium silicate and cellulose nanofiber. The abundant negatively charged ionic channels modulate Zn²⁺ desolvation process and facilitate ion transport. Moreover, an in-situ formed Zn-Mg-Si medium-entropy alloy on Zn anode allows for an improved Zn nucleation kinetics and homogeneous Zn deposition. These combined advantages of the polymer electrolyte enable Zn anodes to achieve an average Coulombic efficiency of 99.7 % over 2400 cycles and highly reversible cycling up to 600 h with large depth of discharge of 85.6%. The resultant Zn || V₂O₅ offers a stable long-term cycling performance and its pouch cell achieves a cycling capacity of 1.13 Ah at industrial-level loading mass of 31.3 mg.

Aqueous zinc ion batteries (AZIBs) have emerged as a prospective alternative for energy storage systems in the “post-lithium” era, due to their advantageous characteristics of high safety, cost-effectiveness and environmentally benignity^{1,2}. However, AZIBs still face the significant challenges, such as the accretion of inactive by-product on the surface of Zn anodes because of excessive free water and subsequent side reactions. This dramatically deteriorate the issues related to local chemical corrosion, passivation, and hydrogen evolution, resulting in low Coulombic efficiency (CE) and irreversible Zn loss. More pressingly, the boom of intractable Zn dendrites initiated by the limited nucleation sites and heterogeneous Zn plating are prone to puncture

the separator during repeated electrochemical testing and cause permanent device failure, posing a critical obstacle to the practical application of highly stable AZIBs^{3,4}. Thereout, it is imperative to open up efficient pathways to fundamentally conquer the challenges of dendrite growth and internal short circuits.

Quasi-solid-state polymer electrolytes (QSPEs) as a promising kind of “beyond aqueous” electrolytes that reconcile mechanical properties of solid electrolytes and ionic diffusion behaviors of liquid electrolytes are triggered to break through the aforesaid obstacles in AZIBs. Since QSPEs can avoid liquid leakage with high flexible and elasticity of polymer matrices, they are helpful to stabilize solid-

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electrolyte interface (SEI) and prevent electrode corrosion and Zn protuberances formation^{5,6}. Various polymer matrices, such as polyvinyl alcohol⁷, polyacrylamide⁸, and polysaccharide⁹, have been employed for the preparation of QSPEs. However, they often encounter the cruxes of low ionic conductivity and high interfacial impedance due to less water content. To address these problems, the incorporation of molecular-level designed microchannels within QSPEs, which could regulate solvation structure of Zn^{2+} ions and promote ion transport behavior to enhance Zn^{2+} deposition kinetics, has been identified as an efficient approach¹⁰. In response, researches have reported that the polymer networks with charged anionic or cationic groups possess a unique zincophilic ability, allowing for homogenized ion distributions and three-dimensional (3D) diffusion mechanism on Zn anode^{11,12}. In addition, the charged groups (e.g., carboxyl, sulfonate, phosphate and hydroxyl groups) inherently contribute to a firm adherence between substrate and polymer electrolyte, which in turn restrains interfacial dislocation and maintains stable electrode reactions. Unfortunately, establishing Zn^{2+} ion migration channels in the polymer networks comes with a downside - it reduces the selectivity of ions, resulting in high voltage hysteresis and the formation of by-product³. The challenge lies in reconciling the conflicting requirements of ion sieving and migration in QSPEs. When Zn ions infiltrate the polymer electrolytes, they can interact with the charged groups, altering the original hydrogen-bond networks. This leads to an increase in free water content and water activity, weakening water retention and even compromising electrode stabilities. Additionally, achieving a balance between mechanical properties and ionic conductivity of QSPEs is difficult. Because strong mechanical properties rely on high polymer crystallinity, whereas high ionic migration and conductivity necessitate amorphous and loosely-structured microenvironments within the polymer networks¹³. Thus, there is an urgent need to enhance both ionic conductivity and selectivity, while maintaining mechanical strength, to enable high-performance AZIBs.

Here, to cope with these above-mentioned challenges, we designed a versatile QSPE with rapid Zn-ion diffusion, high selectivity and strong mechanical properties through the cross-linking of sodium polyacrylate (PAAS), lithium magnesium silicate (LMS) and cellulose nanofiber (CNF). PAAS and LMS were first dissolved in CNF solution to establish physical entanglement and after dried, followed by complete Zn^{2+} ion exchange in ZnSO_4 solution. The prepared polymer electrolyte is designated as PLCZ. For comparative purposes, we also prepared a polymer electrolyte without the LMS additive (PCZ) and an aqueous ZnSO_4 electrolyte equipped with a CNF separator (CZ). The LMS platelets, consisting of silicate tetrahedrons and intermediate octahedrons of Li and Mg ions coordinated with oxygen atoms and hydroxyl groups, create an anisotropic charge distribution where the silicate tetrahedron layers induce a negative charge and Mg-O octahedrons in the platelet edge have positive charge (Supplementary Fig. S1)^{14,15}. Therefore, the Mg-O octahedrons allow for easy bonding with the carboxylate ($-\text{COO}^-$) groups in polymer chain via electrostatic interaction, orchestrating the assembly of microchannels constituted by $-\text{COO}^-$ groups and silicate tetrahedrons (Fig. 1a). Then, by selectively gathering Zn^{2+} ions in the created microchannels through LMS and PAAS, ion migration in and out of the PLCZ electrolyte can be rapidly forced by concentration gradients and electric fields. The constructed ion migration channels effectively modulate Zn^{2+} solvation structure and repel SO_4^{2-} anions, thus relieving by-product generation. Excitingly, a compact and firm SEI protection of Zn-Mg-Si medium-entropy alloy (MEA) is in-situ made through the co-reduction of LMS and Zn^{2+} ions. The resultant MEA SEI owns ultrahigh Young's modulus (11.07 GPa) and brilliant zincophilic affinity, bringing uniform Zn deposition of (002) planes and effective dendrite suppression. The superb features of the PLCZ enable Zn||Zn and Zn|| V_2O_5 batteries to exhibit highly stable cycling performances.

Results

Electrolyte structures and properties

The abundant presence of $-\text{COO}^-$ favors PAAS polymer chains to readily form hydrogen bonding bridges or electrostatic interactions with diverse molecules (such as H_2O , cellulose, polyvinyl alcohol, metal cations, etc.). Building upon this understanding, this work employs a rational design based on molecular engineering utilizing various constituents for the creation of a versatile QSPE with ion-sieving capabilities. As depicted in Supplementary Fig. S2a, the synthesis of the PLCZ polymer electrolytes involved the blending of PAAS and LMS in a cellulose dispersion solution, followed by Zn^{2+} ion exchange procedure, facilitating the formation of a well-connected cross-linked molecular network. The $-\text{COO}^-$ groups in PAAS can establish physical connection with cellulose nanofiber matrix (Supplementary Fig. S2b). Furthermore, owing to the positive charge induced by Mg-O octahedron in the edge of LMS, the larger number of $-\text{COO}^-$ negative charges in PAAS chain also provide opportunity to cohere with LMS sheets via electrostatic interactions (Supplementary Fig. S2c)^{15,16}. Afterwards, the resulting PAAS-LMS-CNF membrane (Supplementary Fig. S3) was immersed in ZnSO_4 solution to ensure sufficient ion exchange. The negative charge of $-\text{COO}^-$ can facilitate the permeation of Zn^{2+} ion by metal coordination bonds and concentration gradients, which thus speeds up Zn^{2+} diffusion in the PLCZ electrolyte and more importantly, restructure the solvation structure of hydrated Zn^{2+} by substituting partial water molecules (Fig. 1a and Supplementary Fig. S2d)¹⁷. On the other hand, the outer negative charges on the LMS platelet surface result in the selective adsorption of Zn^{2+} ion into the interparticle nanogaps of LMS platelets^{18,19}. Such unique selective aggregation of Zn^{2+} ion confers upon LMS platelets and PAAS chains the ability to work as "ion transfer pumps", which in turn renders a fast ion transportation, even ion nucleation and homogeneous Zn deposition during Zn plating/stripping process^{20,21}. Molecular dynamics (MD) simulations were conducted to validate the above inferences (Fig. 1b and Supplementary Fig. S4). The radial distribution function (RDF) of the CZ liquid electrolyte reveals a prominent peak of $\text{Zn}^{2+}\cdots\text{O}$ (H_2O) at 2.75 Å, with the coordination number (CN) of 6.06, indicative of the typical Zn^{2+} solvation sheath structure ($[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$) in the liquid solution²². However, the PCZ and PLCZ electrolytes exhibit reduced CN values of 4.30 and 3.75, respectively. This decrease is attributed to the electrostatic interactions of $-\text{COO}^-$ group and LMS with Zn^{2+} ions, which efficiently displace the coordinated water molecules around Zn^{2+} ions and alter the solvation structures to $[\text{Zn}(\text{H}_2\text{O})_4(\text{COO})]^{+}$ in PCZ and $[\text{Zn}(\text{H}_2\text{O})_3(\text{COO})\text{LMS}]^{+}$ in PLCZ. Additionally, the PLCZ polymer electrolyte realizes rapid Zn^{2+} ion diffusion and intercalation with high self-diffusion coefficient (Ds) of $7.55 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ (Fig. 1c and Supplementary Fig. S5), due to the formed highly selective transportation microchannels by $-\text{COO}^-$ within PAAS chain and LMS platelets. Figure 1d shows the digital photographs of the PLCZ electrolyte, which exhibits a complete structure and no visible damages even after kneading, highlighting its good flexibility and restorability. The strain-stress tests of the PLCZ with and without ZnSO_4 immersion validate that the Hofmeister effect of Zn^{2+} ion greatly improves the mechanical properties of the PLCZ (Supplementary Figs. S6 and S7). The optimum ratio of the components for the fabrication of the PLCZ electrolytes was determined through galvanostatic cycling tests conducted on Zn||Zn symmetric cells. The $\text{P}_{0.1}\text{L}_{0.1}\text{CZ}$ achieves a lower and flatter voltage polarization throughout charge-discharge cycling at the current densities spanning from 0.5 to 10 mA cm^{-2} and returning to 0.5 mA cm^{-2} when in comparison to CZ, PCZ and another PLCZ electrolytes (Supplementary Fig. S8), meaning a reduced Zn deposition barriers and high reversibility of Zn deposition/dissolution, which is also proved by the Zn nucleation overpotential in Supplementary Fig. S9. Scanning electron microscope (SEM) was employed to observe the surface and internal structure of the PLCZ electrolyte. The PLCZ electrolyte features a sleek and consistent surface (Fig. 1e) and a dense

texture in its cross-section (Fig. 1f and Supplementary Fig. S10), contributing to reinforce interfacial stability between the electrolyte and Zn anode and to set up an effective bridge for fast Zn ion transportation. In comparison, the CZ shows a loose and porous structure (Supplementary Fig. S11) and the PCZ also displays a rugged texture (Supplementary Fig. S12). This non-uniform morphologies of both the CZ and PCZ are postulated to disrupt the concentration distribution of Zn^{2+} flux on Zn anode, thereby resulting in the dendrite formation²³.

The intermolecular interactions in the CZ, PCZ and PLCZ were investigated by Fourier transform infrared (FTIR) spectra. The FTIR peaks centered at 1403 and 1540 cm^{-1} are originated from the characteristic symmetric and asymmetric $-\text{COO}^-$ stretching vibrations (Fig. 2a), respectively²⁴. Compared with the pristine PAAS aqueous gel, symmetric and asymmetric $-\text{COO}^-$ stretching vibrations after ion exchange of the PCZ experience a notable blue shift, due to the metal coordination with Zn^{2+} ions with electrostatic forces, highly advantageous for the confinement and control of Zn^{2+} ion migration along the polymer chain. Moreover, the coordination between $-\text{COO}^-$ and Zn^{2+} ion also promotes the reconstruction of the solvation structure of hydrated Zn^{2+} ions. In a similar manner, a further blue shift in

asymmetric and symmetric $-\text{COO}^-$ stretching of the PLCZ towards higher wavenumbers is also observed and stemmed from the electrostatic interactions between $-\text{COO}^-$ and LMS (Supplementary Fig. S13). The existence of internal molecular interactions in electrolyte supports the high stability of the PLCZ and enhances its mechanical property. Besides, FTIR spectra of the CZ show the stretching vibration of the O-H bonds at 3245 cm^{-1} (Fig. 2b). The utilization of PAAS polymer and LMS causes the stretching vibration blue shifting to 3272 cm^{-1} of the PCZ and 3281 cm^{-1} of the PLCZ, suggesting an improved immobilization of water molecules through hydrogen bonding. This immobilization serves to block free water and alleviate the effects of HER, as well as anode corrosion²⁵. Raman spectra also evidence this tendency. The Raman signal at 449 cm^{-1} derived from the $\text{Zn}-\text{OH}_2$ vibration²⁰ exhibits a decrease in peak intensity and an obvious blue shift from the CZ to PLCZ (Fig. 2c and Supplementary Fig. S14), indicating a weakening of the initial hydrogen bonds stemming from free water molecules. Likewise, the Raman vibration of $\nu(\text{SO}_4^{2-})$ generates similar variations amongst the electrolytes (Fig. 2d), implying an impaired electrostatic coupling between Zn^{2+} and SO_4^{2-} ions in the PLCZ electrolytes and consequently, a low possibility of Zn^{2+} -

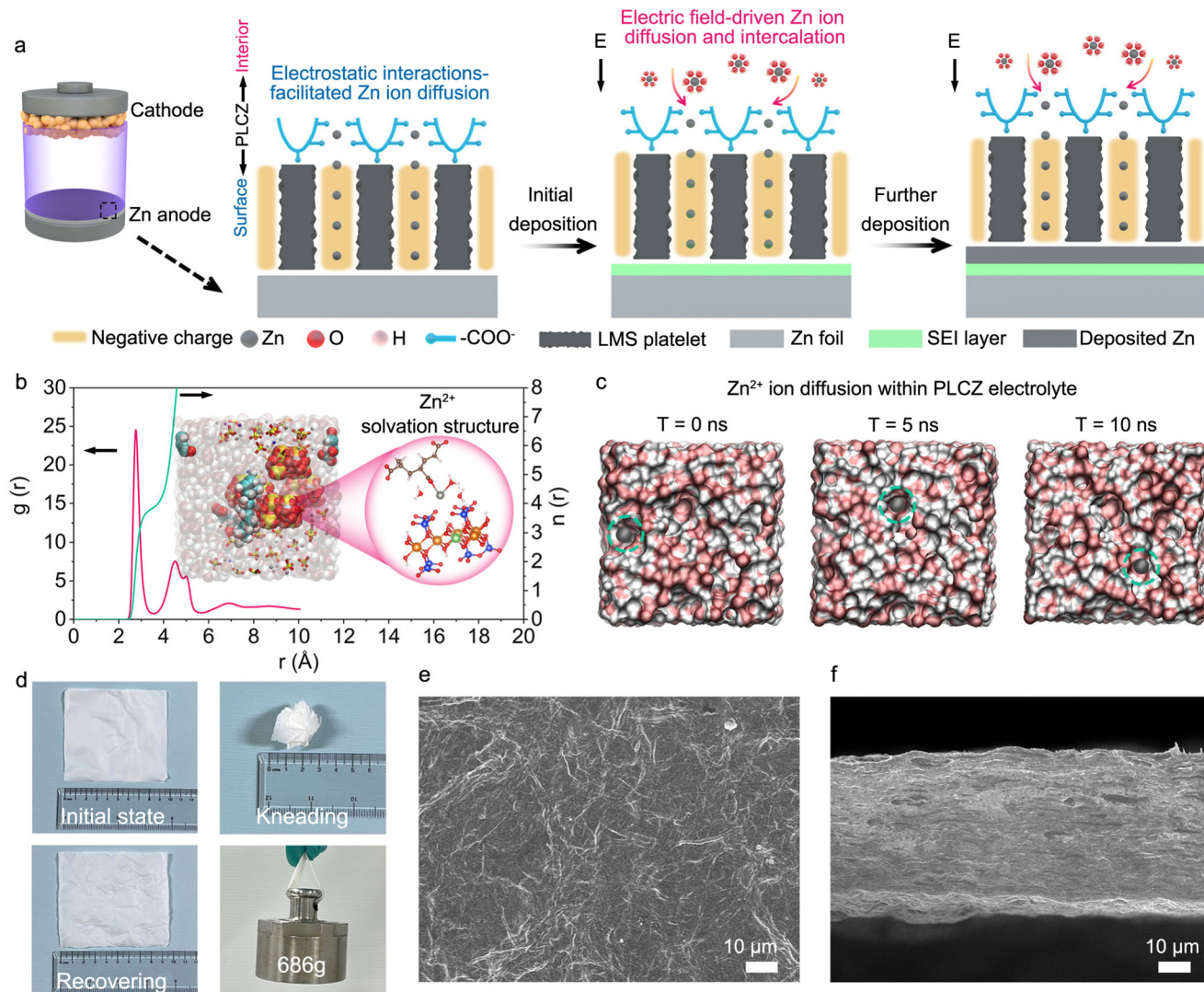


Fig. 1 | The solvation structure of Zn^{2+} ions and morphology characterization of electrolyte. a Schematically illustrating the Zn^{2+} ion diffusion and transport cross the PLCZ polymer electrolyte. **b** The simulated RDF of Zn^{2+} -O (H_2O) and the coordination numbers of Zn^{2+} with water molecules with the corresponding Zn^{2+} solvation structure in the PLCZ electrolytes. **c** The Zn^{2+} diffusion within the PLCZ

electrolyte from the 3D snapshots of $T = 0$ ns to 10 ns. **d** The digital photographs of the designed PLCZ electrolyte under initial state, kneading and recovering and the corresponding strain-stress test. SEM images of the PLCZ electrolyte on **(e)** the top view and **(f)** cross-sectional view.

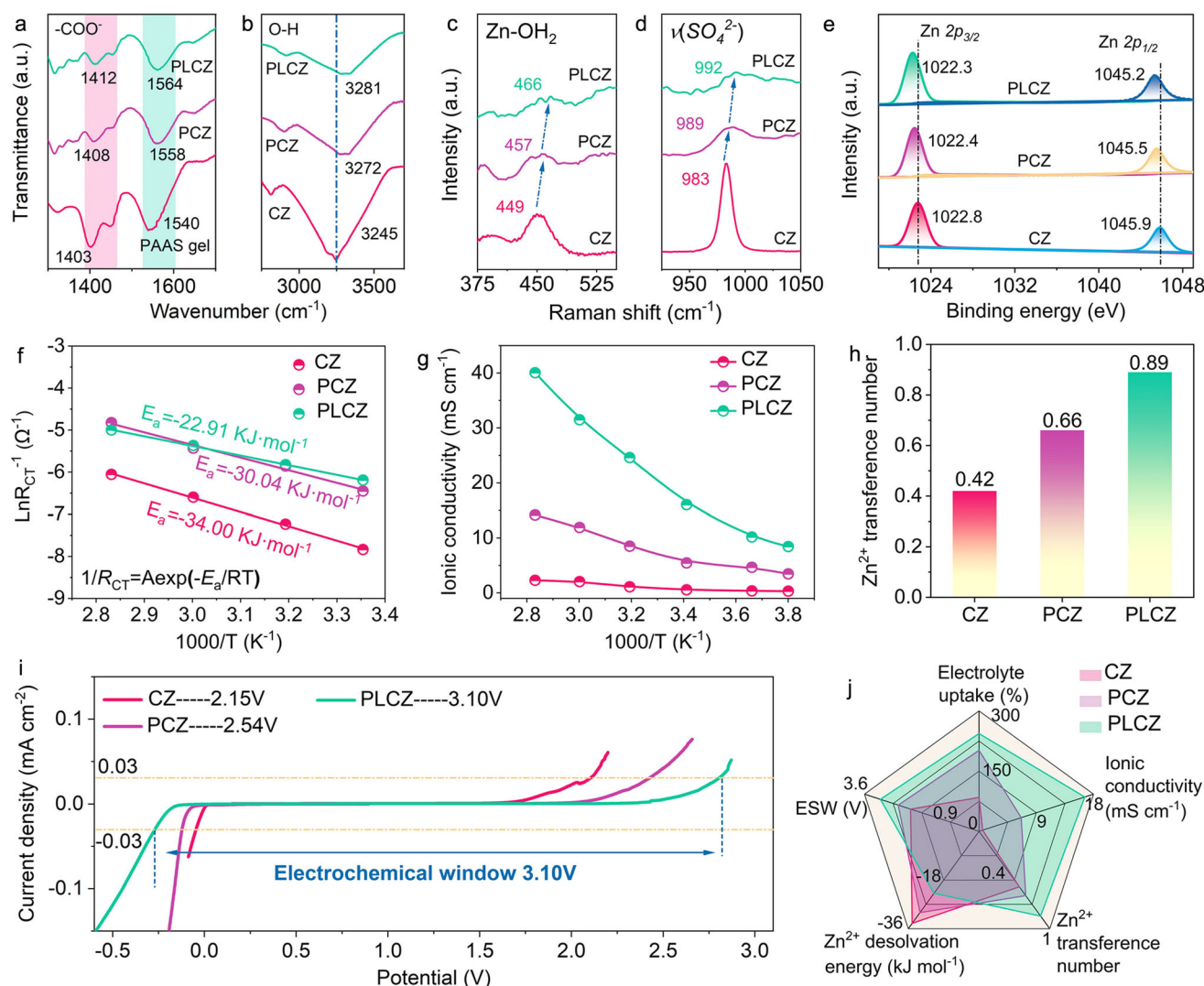


Fig. 2 | The spectra analyses and electrochemical properties of electrolytes.

FTIR spectra focused on (a) the asymmetric and symmetric -COO⁻ stretching and (b) the stretching vibration of the O-H bonds. In the low wavenumber region, pure PAAS gel serves as the reference to assess the impact of Zn²⁺ and LMS on the -COO⁻ groups within the PAAS chain. In the high wavenumber region, CZ electrolyte is used as a benchmark for examining the influence of PAAS and LMS on water

molecules. c Raman spectra of (c) Zn-OH and (d) ν(SO₄²⁻) vibrations and (e) Zn 2p XPS spectra of CZ, PCZ and PLCZ electrolytes. The electrochemical characterizations of CZ, PCZ and PLCZ electrolytes. f The calculated activation energy (Eₐ), (g) ionic conductivity at different temperatures, (h) Zn²⁺ transference number and (i) ESW. j Radar diagram comparing the electrochemical performances of CZ, PCZ and PLCZ electrolytes.

(H₂O)₆ · SO₄²⁻ solvation structure formation (Supplementary Fig. S15)²⁶. The high-resolution XPS spectra of Zn 2p in electrolytes are shown in Fig. 2e. Leveraging the intense electrostatic interactions between Zn²⁺ ions and -COO⁻ groups as well as LMS platelets, the binding energy of Zn 2p in the PLCZ is significantly lower than that in CZ. This observation further substantiates the synergistic effect of -COO⁻ groups and LMS platelets in controlling the coordination environment of Zn²⁺ ions and preventing the formation of undesirable [Zn(H₂O)₆]²⁺ solvation structure.

The desolvation energy barrier of Zn at the interface between electrolyte and Zn anode was evaluated by calculating the Zn²⁺ activation energy (Eₐ)^{27,28}. Figure 2f and Supplementary Fig. S16 show that the Eₐ of Zn²⁺ in the PLCZ is -22.91 kJ mol⁻¹, which is more positive than the CZ (-34.00 kJ mol⁻¹) and PCZ (-30.04 kJ mol⁻¹). This manifests a low desolvation barrier of Zn²⁺ and improved Zn²⁺ transport kinetics achieved by the PLCZ²⁹. Accordingly, by virtue of the enhanced dissociation capability of Zn²⁺, the PLCZ demonstrates a larger ionic conductivity across a temperature range from 263.15 to 353.15 K (Fig. 2g and Supplementary Fig. S17). In comparison, the CZ and PCZ

show lower ionic conductivity. Moreover, as presented in Fig. 2h and Supplementary Fig. S18, the PLCZ also achieves a significantly higher Zn²⁺ transference number of 0.89, outperforming CZ (0.42) and PCZ (0.66), as well as recently reported liquid and solid-state electrolytes^{4,12,24,30–34} (Supplementary Fig. S19). Furthermore, the designed PLCZ shows a better electrolyte uptake property, with a high value of 243.6% (Supplementary Fig. S20), indicating a high hydrophilicity and electrolyte reservoir enabled by intermolecular cross-linked polymer networks and LMS platelets. The electrochemical stable window (ESW) of electrolytes as a vital criterion of electrolyte stability was examined in Zn||stainless steel (SS) asymmetric cells using linear sweep voltammetry (LSV). The Zn||SS cell with the CZ expresses a narrow ESW of 2.15 V (Fig. 2i), which aligns with the value of ZnSO₄ aqueous electrolyte³⁵. After binding PAAS and LMS, the ESWs gain extension and the PLCZ exhibits the widest ESW of 3.10 V. Such broad ESW results from the exhaustion of free water molecules in the polymer networks. As contrastively depicted in the radar diagram (Fig. 2j), the all-around merits of the PLCZ electrolyte, including high ionic conductivity, large Zn²⁺ transference number, low Zn²⁺

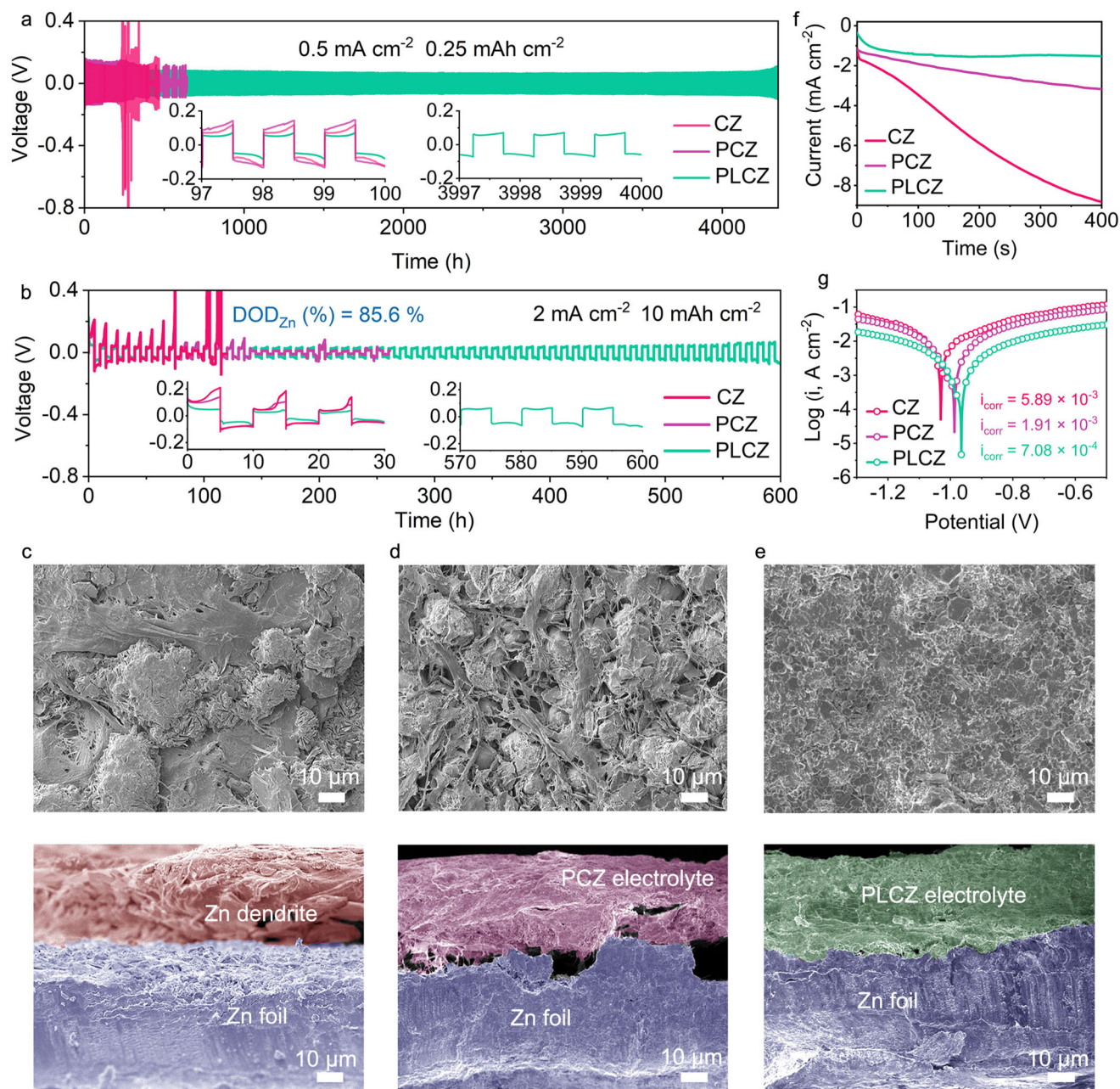


Fig. 3 | Electrochemical performance of Zn||Zn symmetric cells. Cycling performances of Zn||Zn symmetric cells with the CZ, PCZ and PLCZ at (a) 0.5 mA cm⁻², 0.25 mAh cm⁻² and (b) 2 mA cm⁻², 10 mAh cm⁻². The electrolyte thickness of PLCZ here is 128 μm. SEM images of the Zn anodes on the top view and side view of (c) CZ,

(d) PCZ and (e) PLCZ after 200 cycles. For easy of result comparison and analysis, the Zn dendrite, Zn foil, PCZ electrolyte and PLCZ electrolyte are colored with red, blue, pink and green, respectively. f FCA tests and (g) Tafel plots of the CZ, PCZ and PLCZ.

desolvation energy, wide ESW and high electrolyte uptake, clearly surpass those of the CZ and PCZ.

Electrochemical performance of symmetric cells

The cycling stability of Zn||Zn cells was systematically scrutinized to validate the efficacy of the polymer electrolyte in augmenting the electrochemical reversibility of the Zn anode. The PLCZ symmetric cell with the electrolyte thickness of 128 μm demonstrates an exceptionally prolonged lifespan exceeding 4400 h at 0.5 mA cm⁻² and 0.25 mAh cm⁻², nearly 22 and 10 times greater than those of CZ (203 h) and PCZ (443 h) respectively, as illustrated in Fig. 3a and Supplementary Fig. S21a. The amplified voltage profiles provide the further affirmation of the consistent and minimal voltage hysteresis throughout the entire cycling process. The PLCZ symmetric cell also exhibits a

duration of 1200 h at 5 mA cm⁻² and 2.5 mAh cm⁻² (Supplementary Figs. S21b and S22). When under the current density of 10 mA cm⁻² and 1 mAh cm⁻², it sustains an impressive cycle lifespan of 1400 h (7000 cycles) without discernible voltage fluctuation (Supplementary Fig. S23). Even under higher current densities (20 mA cm⁻², 5 mAh cm⁻² and 40 mA cm⁻², 1 mAh cm⁻²), the PLCZ symmetric cells still maintain better cycling lifespans and stabilities than that of the CZ and PCZ electrolytes (Supplementary Figs. S24 and S25). More importantly, the performance of the PLCZ cell remains better even when subjected to a large depth of discharge (DOD) of Zn anode (85.6 %), by a sustained lifespan of 600 h, whereas cells utilizing CZ and PCZ cease operation after just a few cycles (Fig. 3b). This underscores the commendable Zn utilization rate and energy density facilitated by the PLCZ. These outcomes prove the efficacy of the PLCZ electrolyte, with its rapid ionic

transport pathways and effective ion separation, on lowering the energy barrier for Zn deposition/dissolution and bolstering the cycling reversibility of the Zn anode.

SEM was carried out to compare the morphology of Zn electrodes after different cycles (50, 100 and 200). As shown in Supplementary Fig. S26 and Fig. 3c, d, distinct Zn protrusions with interposed cellulose nanofibers are observed on the surfaces of Zn electrodes when using the CZ and PCZ. In stark contrast, the PLCZ electrolyte yields a uniform and flat surface morphology (Fig. 3e). Notably, the cross-sectional view reveals intimate adhesion between the PLCZ polymer electrolyte and Zn electrode, while significant cavity and ravine are clear between the PCZ and electrode due to pronounced Zn dendrite growth. This observation indicates that the PLCZ is capable of establishing a robust solid-electrolyte interface and facilitating limited volume expansion toward Zn electrode³⁶. These different Zn deposition/dissolution behaviors of the electrolytes are further disclosed by confocal laser scanning microscopy (CLSM), in which the PLCZ causes a more compact surface with the reduced surface roughness of 1.6 (Supplementary Fig. S27). The surface morphology of the CZ, PCZ and PLCZ after different cycles was also investigated (Supplementary Fig. S28). Unwanted dendrite agglutination and penetration are generated on the surface of the CZ and PCZ at the 100th and 200th cycles, which would pierce them and eventually lead to the failure of batteries. Surprisingly, the PLCZ electrolyte maintains a clean and undamaged structure even after 200 cycles.

Chronoamperometry (CA) was utilized to obtain a comprehensive understanding of Zn^{2+} deposition behavior (Fig. 3f). Both CZ and PCZ electrolytes undergo a continuous increase in current density within 400 s, indicative of a persistent 2D diffusion and vertical Zn deposition behavior. However, owing to the favorable migration paths created by PAAS chains and LMS platelets, Zn^{2+} ions initially follows a 2D diffusion process for the first 100 s before transitioning to stable 3D spatial accumulation, causing homogeneous Zn deposition. Tafel curves were conducted to monitor the surface corrosion of Zn electrodes in the electrolytes. Figure 3g demonstrates that the PLCZ polymer electrolyte achieves a smaller corrosion current density (i_{corr}) of $7.08 \times 10^{-4} \text{ A cm}^{-2}$ than the CZ ($5.89 \times 10^{-3} \text{ A cm}^{-2}$) and PCZ ($1.91 \times 10^{-3} \text{ A cm}^{-2}$). This implies that the PLCZ effectively mitigates the intractable corrosion issue of Zn electrode. On account of the improved anti-corrosion and less free water in the electrolyte, the PLCZ significantly elevates the onset potential of OER and HER at various temperatures, compared with the CZ and PCZ (Supplementary Fig. S29). Consequently, symmetric cells with the PLCZ electrolyte all deliver superior cycling stability over 4200 h at 273.15 K, 1600 h at 313.15 K and 400 h at 333.15 K (Supplementary Fig. S30). These PLCZ-enabled symmetric cells exhibit exceptionally long cycling lifespans at high current densities and areal capacities across wide temperature range, surpassing previously reported state-of-the-art (quasi)-solid-state electrolytes (Supplementary Fig. S31)^{7,11,36–52}.

Formation and properties of medium-entropy alloy layer

The CE of Zn deposition/dissolution, a pivotal parameter evaluating reversibility, was examined in Zn||Cu asymmetric cells¹². The high stability and reversibility of Zn deposition/dissolution by the PLCZ are evident through a steady CE of 99.7% over 2400 cycles (Fig. 4a and Supplementary Fig. S32). In contrast, the CZ and PCZ systems experience rapid cycling deterioration after only 110 and 580 cycles, respectively. The stability of the PLCZ cell is also demonstrated at harsher cycling condition (Supplementary Fig. S33). The PLCZ polymer electrolyte enhances key aspects of the electrochemical performance of Zn anode by facilitating rapid Zn^{2+} transport, promoting uniform Zn nucleation and delaying surface corrosion and side reactions. These improvements contribute to the stable cycling performance in Zn||Cu cells. Cyclic voltammetry (CV) analyses of the asymmetric cells reveal

that the PLCZ reduces the nucleation overpotential to a mere 23 mV while maintaining strong current density (Supplementary Fig. S34), indicating its ability to optimize reaction kinetics for fast and uniform Zn deposition and dissolution³⁸. SEM images of Cu electrodes alongside their digital photographs provide further evidences that after cycling, the PLCZ results in a smooth and dendrite-free Zn deposition/dissolution behavior, contrasting with the messy feature of the CZ and PCZ electrolytes (Fig. 4b). To deepen understanding of the superior stability of Zn||Cu cells with the PLCZ, the surface chemical information of Zn anodes after 10 cycles were probed by X-ray photoelectron spectroscopy (XPS) spectra. Figure 4c illustrates the recorded Si 2p and Mg 1s XPS peaks detected on the Zn surface, with peaks at 100.5 and 1301.6 eV corresponding to Zn_xSi_y ^{53,54} and Zn_xMg_y ^{55,56}, respectively. As Ar^+ etching time increases gradually, the XPS peaks of alloy components of Zn_xSi_y and Zn_xMg_y are preserved, while the emergence of new peaks at 102.4 and 1303.8 eV, attributed to Si-O⁵⁷ and Mg-O⁵⁸ bonds in the LMS material, indicates an interfacial reduction reaction between Zn anode and the PLCZ electrolyte, leading to the formation of a Zn-Mg-Si MEA SEI during cycling. Energy-dispersive X-ray spectroscopy (EDS) mapping depict the uniform distribution of Zn, Mg and Si elements, proving the existence of the Zn-Mg-Si SEI on the Zn surface (Supplementary Fig. S35). X-ray absorption spectra (XAS) of Zn anode after depositing different Zn capacities (1, 3 and 5 mAh cm^{-2}) were used to investigate the local structure and chemical environment of Si and Mg atoms. The Si and Mg atoms in the Zn anodes show a much higher oxidation state than their metallic foils due to the existence of Si-O and Mg-O bonds (Fig. 4d, e). With increasing deposited Zn, their oxidation states gradually decrease compared with the case of 1 mAh cm^{-2} . This arises from the electron transfer from Zn to Si and Mg atoms for the formation of metallic Si and Mg in the Zn-containing alloy components. Distinct changes in the *r*-space curves of the Si K-edge and Mg K-edge are observed as increasing deposited Zn, signifying the coordination variation of Si and Mg, which corroborates the increased formation of Zn_xSi_y and Zn_xMg_y components (Fig. 4f, g). Figure 4h schematically represents the formation of the MEA layer from the PLCZ electrolyte. Additionally, density functional theory (DFT) calculations were conducted to assess the binding energy of each component with Zn^{2+} ion as a reflection of their zincophilic capacity. The calculated binding energies for H_2O , Si, Mg, Zn_3Si , MgZn and SiZn_3 are -0.5, -0.59, -0.66, -1.04, -1.77 and -2.65 eV (Fig. 4i), respectively. These results indicate that the Zn-containing MEA layer has higher chemical affinity towards Zn^{2+} ions, conducive to the homogeneous nucleation and Zn^{2+} deposition with a lower Zn nucleation barrier.

It is widely recognized that inadequate SEI robustness fails to accommodate the volume fluctuations in repeated Zn deposition/dissolution processes, resulting in the accumulation of Zn dendrite and dead Zn in mechanically weak areas⁴⁹. The local mechanical strength of the SEIs was assessed using atomic force microscopy (AFM). The force-displacement curves from nanoindentation experiments on Zn electrodes after cycling are plotted in Supplementary Fig. S36. The force-displacement curves of Zn electrodes with the PLCZ during loading and unloading process are more reversible than those with the CZ and PCZ, indicating that the formed MEA SEI layer by the PLCZ exhibits greater reversibility and elastic deformation, while the $\text{Zn}(\text{OH})_2$ -based SEIs of the CZ and PCZ demonstrate more elastic-plastic deformation characteristics. Furthermore, the MEA SEI displays a notably higher and uniform Young's modulus of 11.07 GPa (Supplementary Figs. S37 and S38), in contrast to the SEIs of the CZ (2.05 GPa) and PCZ (3.03 GPa). AFM images further illustrate the better uniformity and smoothness of the MEA SEI layer surface than $\text{Zn}(\text{OH})_2$ -based SEIs (Supplementary Fig. S39), emphasizing the significance of a robust MEA SEI in alleviating Zn dendrite growth and preserving SEI integrity during cycling.

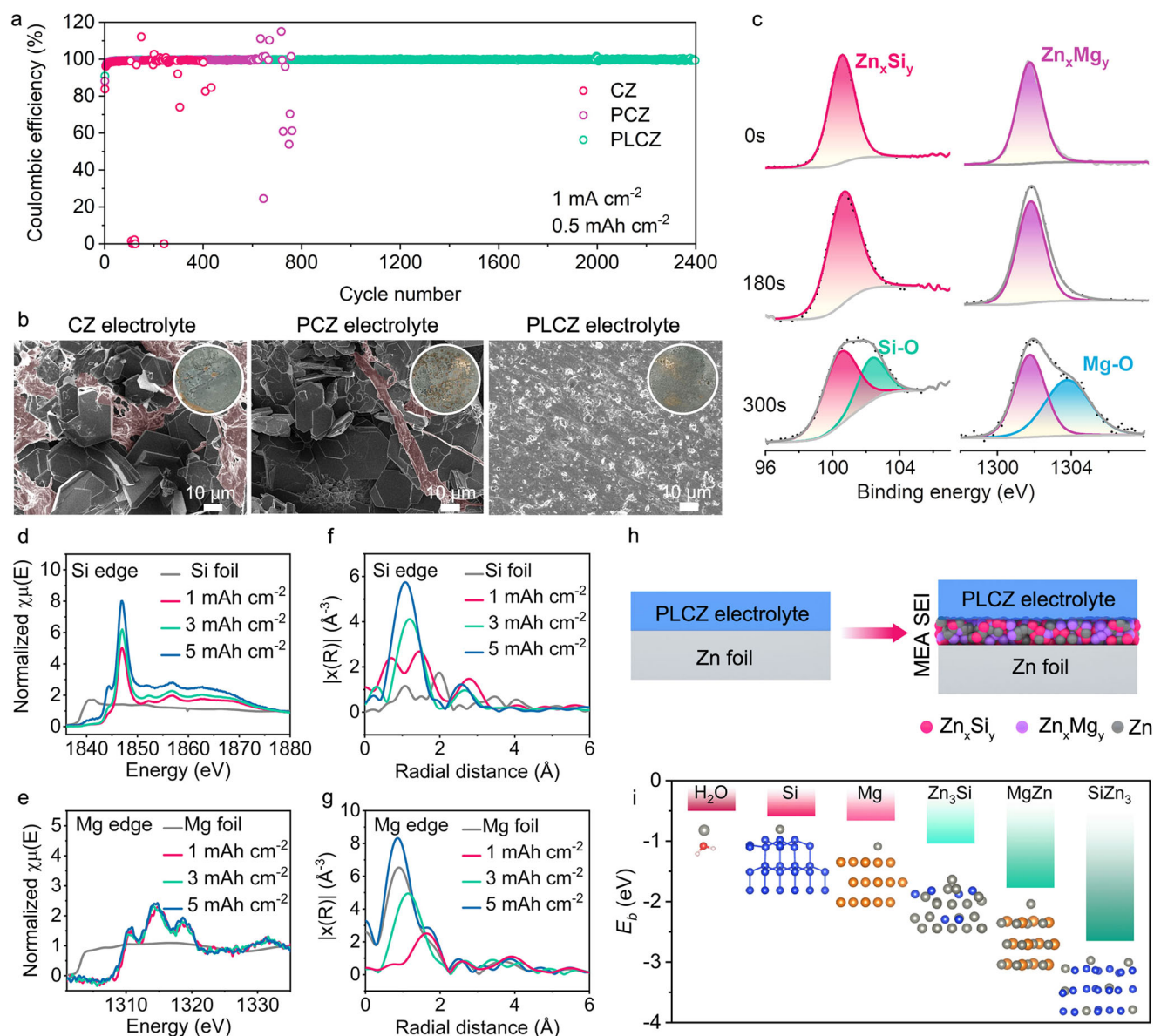


Fig. 4 | The formation and characterization of alloy protection layer. **a** Cycling performance of Zn||Cu asymmetric cells as well as the corresponding **(b)** SEM images of Cu cathode of the CZ, PCZ and PLCZ (insets: digital photographs of Cu electrodes). The red color in the SEM images represent the CNF fiber. **c** Si 2p and Mg 1s XPS spectra of the cycled Zn anodes of PLCZ electrolyte. XANES spectra and the

corresponding r-space data of **(d, f)** Si K-edge and **(e, g)** Mg K-edge of Zn anodes after deposited different Zn capacities with PLCZ electrolyte. **h** Schematically illustrating the formation of MEA SEI layer on Zn anode. **i** The calculated E_b of Zn on the alloy ingredients.

Zn deposition mechanism of electrolytes

In-situ Raman spectroscopy was performed to investigate the coordination changes of Zn²⁺ ion at the electrolyte-electrode interface. The experimental configuration, as drawn in Supplementary Fig. S40, encompassed a photoelectrochemical cell with a micron-sized Ag layer on the electrolyte as the working electrode and Zn foil as the counter/reference electrode. The Raman signal peaks located at 1418, 1661, and 1748 cm⁻¹, corresponding to symmetric and asymmetric -COO⁻ vibrations and C=O structure, respectively³⁹, exhibit a red shift to lower Raman shifts during electroplating process (Fig. 5a). This phenomenon can be ascribed to the weakening of coordination between Zn²⁺ ions and the -COO⁻ groups due to the reduction of Zn²⁺ to Zn⁰. To track the evolution of Zn morphology over multiple cycles, in-situ micro-computed tomography (micro-CT) measurements were conducted on symmetric cells (Supplementary Fig. S41). Visualization of different substances with varying densities was achieved through color

differentiation in the micro-CT images. As illustrated in Fig. 5b and Supplementary Fig. S42, the CZ liquid electrolyte evidences dispersive dendrites and surface corruptions on the Zn surface at the 30th cycle, which progressively worsened in subsequent cycles. Similarly, the PCZ electrolyte exhibits a comparable phenomenon that Zn electrode displays a rough surface at 50th cycles and then deteriorates. In contrast, the Zn electrode with the PLCZ maintains a consistently smooth surface throughout the cycling process, illustrating a uniform and stable Zn²⁺ ion flux within the electrolyte. Micro-CT measurements of Zn electrodes disassembled from the cells were conducted. Conspicuously, the Zn electrodes with the CZ and PCZ electrolytes exhibit a coarse morphology characterized by numerous humps and corrosion pits, whereas the PLCZ electrolyte facilitates the attainment of a glossy and unblemished Zn surface (Supplementary Fig. S43). X-ray diffraction (XRD) patterns of Zn electrodes reveal the deep reasons into the variations in morphology and are shown in Supplementary

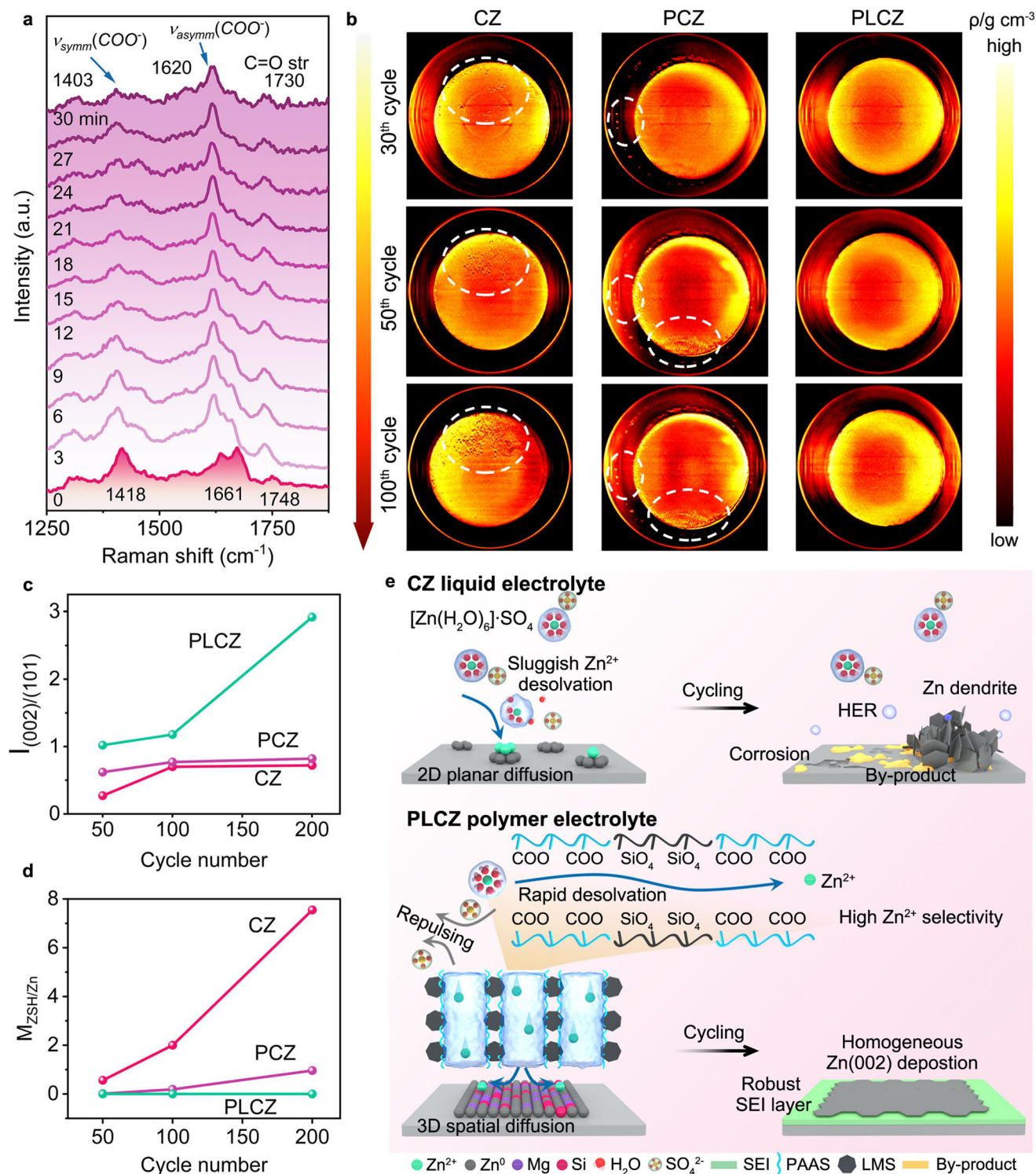


Fig. 5 | The deposition behavior and mechanism of Zn²⁺ ions. a The in-situ Raman spectra of Zn||Ag cell during deposition. **b** The micro-CT images of Zn||Zn cells at different cycles CZ, PCZ and PLCZ electrolytes. Color representation: orange/yellow circle for cathode case, orange/yellow circle wafer for Zn electrode, orange/

yellow dot for Zn dendrite, black/wine red dot for corrosion pit. The calculated (c) $I_{(002)/(101)}$ and (d) $M_{\text{ZSH/Zn}}$ on Zn anodes based on XRD patterns. **e** Schematically illustrating the Zn deposition in CZ liquid and PLCZ electrolytes.

Fig. S44. In the CZ and PCZ, although the Zn(002) peak intensity gradually improves from 50th to 200th cycles, the intensity ratios ($I_{(002)/(101)}$) of Zn(002) to Zn(101) remain below 1.0 (Fig. 5c). This suggests that the deposited Zn predominantly grows along the Zn(101) plane with unordered growth of Zn dendrites. Conversely, the $I_{(002)/(101)}$ of the PLCZ is 1.02 at the 50th cycle and then greatly improves to 2.92

after 200 cycles. This confirms that the PLCZ effectively controls the desired orientation of Zn deposition for a dendrite-free Zn topography. Besides, the cycled Zn electrodes in the CZ and PCZ electrolytes exhibit strong XRD peaks at 8.11, 16.2 and 24.8°, reflecting the formation of $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot 5\text{H}_2\text{O}$ (ZSH) by-product. As a comparison, no distinct by-product peaks are detected in the PLCZ. To provide a

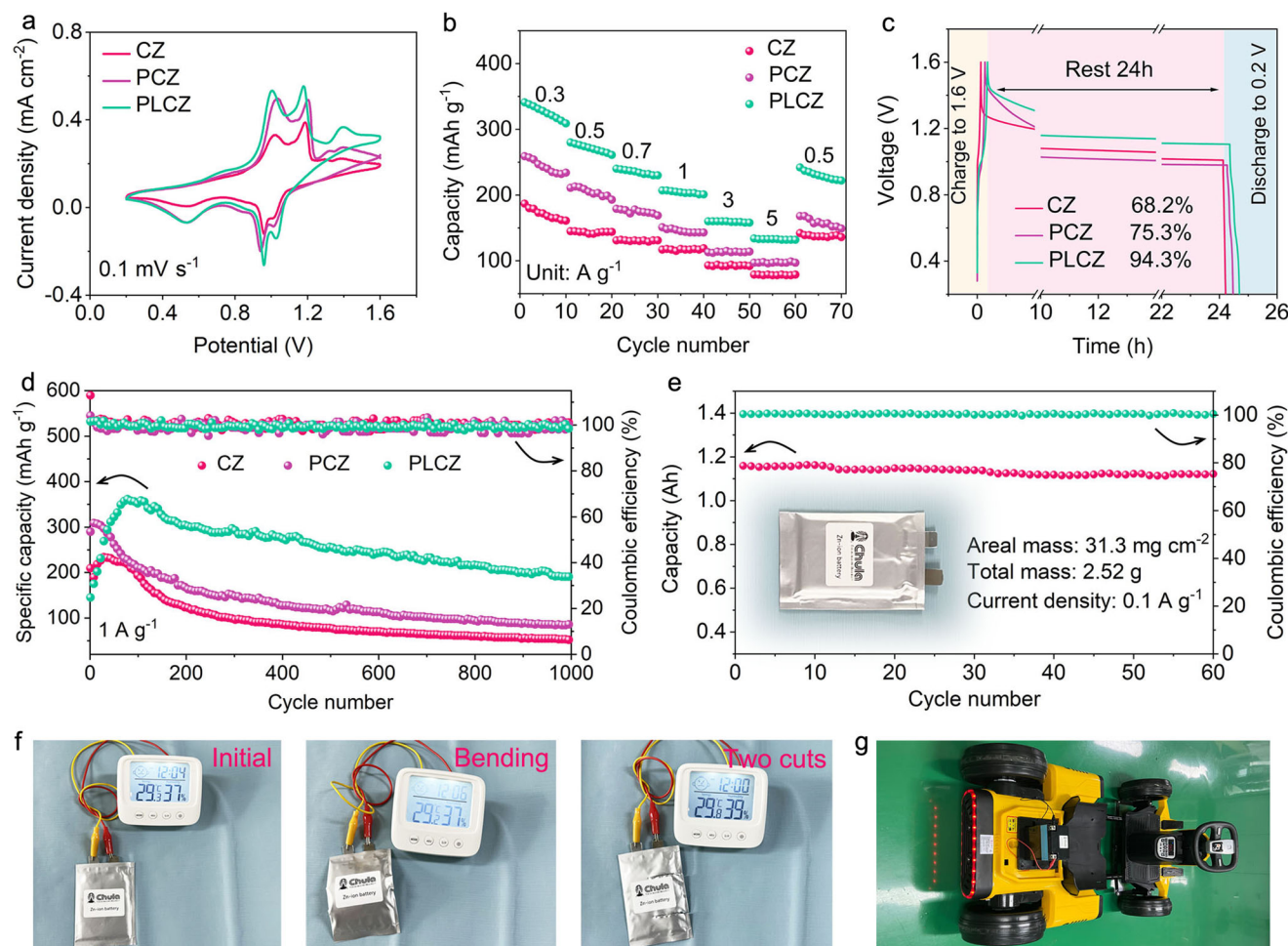


Fig. 6 | Electrochemical performance and application of Zn || V₂O₅ full cells. a CV curves Zn || V₂O₅ cells with CZ, PCZ and PLCZ. The electrode area is 1.54 cm². **b** rate performances of Zn || V₂O₅ cells with CZ, PCZ and PLCZ. **c** Capacity retention test after charging to 1.6 V, resting 24 h and discharging to 0.2 V. **d** Long-term cycling

performances of full cells. **e** Cycling performance of pouch cell with PLCZ. The digital photographs of pouch cell **f** supporting electronic device under initial state, bending and cutting and **(g)** running a toy car.

visual comparison of ZSH accumulation in these electrolytes at each cycle, the mass ratios ($M_{\text{ZSH/Zn}}$) of ZSH to Zn phases on the Zn surface were determined based on the XRD patterns (Fig. 5d). XPS spectra of S 2p further evidence that the PLCZ electrolyte successfully inhibits the formation and accumulation of ZSH during cycling (Supplementary Fig. S45), thus favoring the improved CE and durability of Zn electrode. Electrochemical impedance spectra (EIS) of symmetric cells at various cycles were measured to evaluate electrolyte resistance (R_s), SEI resistance (R_{SEI}) and charge-transfer resistance (R_{CT}). In Supplementary Fig. S46, compared to the CZ and PCZ, the PLCZ obtains smaller and more stable R_{SEI} and R_{CT} values, resulting from the highly conductive MEA SEI and the suppressive by-product. The Zn deposition mechanisms in the CZ liquid and PLCZ electrolytes were schematically illustrated in Fig. 5e. Zn²⁺ ions in CZ aqueous electrolyte tend to laterally diffuse along the rough surface and deposit at energetically favorable sites, finally generating the fatal dendrites. Meanwhile, water-induced side reactions aggravate H₂O decomposition and increase local pH value near the Zn electrode. This unfavorable environment promotes the precipitation of [Zn(H₂O)₆]SO₄ complex and the generation of ZSH by-product. On the contrary, the PLCZ electrolyte leverages the charged -COO⁻ groups of polymer chains and LMS platelets to establish high-speed pathways for Zn²⁺ ion transportation through electrostatic interactions. This interaction spontaneously influences solvation structure and expedites desolvation behavior. During subsequent deposition, Si and Mg atoms

concurrently deposit with Zn ion to form a robust MEA SEI with a strong affinity for Zn. Such unique SEI extends spatial movement of Zn and guides the favorable deposition of Zn(002) planes, ultimately yielding an ultra-stable Zn electrode.

Practical application of such polymer electrolyte

To assess the practical viability and reliability of the polymer electrolyte, Zn || V₂O₅ cells were assembled. The V₂O₅ cathode material exhibits a strong resemblance to the characteristic XRD peaks of orthorhombic V₂O₅ (PDF # 85-0601, Supplementary Fig. S47) and showcases an irregular rod-like morphology (Supplementary Fig. S48). The CV curve with the PLCZ shows a higher current density in comparison to that of the CZ and PCZ electrolytes, confirming the enhancement in charge/ion transport dynamics and redox activity of the PLCZ (Fig. 6a). With the abundance of charged groups and species, robust SEI formation and high ionic conductivity of the PLCZ, the full cell outputs a higher discharge capacity of 327.5, 272.9, 238.6, 203.7, 164.9 and 134.6 mAh g⁻¹ at 0.3, 0.5, 0.7, 1, 3 and 5 A g⁻¹ (Fig. 6b), outperforming those of the CZ and PCZ electrolytes. Such superior rate performance of the PLCZ cell is also supported by the lower internal electronic resistance before and after cycling (Supplementary Fig. S49). Resting experiments were conducted to examine electrochemical stability of cells using different electrolytes (Fig. 6c). After 24 h of rest, the PLCZ cell maintains a higher open-circuit voltage of 1.1 V with a satisfactory self-discharge capacity retention of 94.3 %,

ascertaining the suppressed side reactions and surface corrosion by the PLCZ³². In the long-term cycling measurement (Fig. 6d), the PLCZ cell exhibits a delightful specific capacity of 192.9 mAh g⁻¹ after 1000 cycles, whereas the CZ liquid electrolyte and PCZ cells start to degrade after several dozen cycles. This striking disparity in cycling performance can be primarily attributed to the distinctive properties of the PLCZ electrolyte, which effectively creates a swift ionic transportation path and eliminates the adverse effects caused by Zn dendrite and by-product. This can be supported by the XRD patterns (Supplementary Fig. S50) and SEM images (Supplementary Fig. S51). Moreover, Zn||V₂O₅ cells with the PLCZ were exposed to more challenging temperatures of 273.15, 313.15 and 333.15 K (Supplementary Fig. S52), which shows a more stable and reversible cycling capacity. The practicability and compatibility of the PLCZ design can be also observed when coupled with other cathode materials, including MnO₂, LiFePO₄ and (NH₄)₂V₁₀O₂₅·8H₂O (Supplementary Fig. S53).

To further notarize the efficacy of the PLCZ electrolyte in large-scale practical operation, a pouch cell with ultrahigh loading mass of V₂O₅ (31.3 mg cm⁻², total 2.52 g) was assembled. The pouch cell with the PLCZ delivers a discharge capacity of 1.13 Ah with energy density of 358.7 Wh Kg⁻¹ at 0.1 A g⁻¹ (Fig. 6e). And the pouch cell shows similar capacity-voltage curves at different cycles (Supplementary Fig. S54). Impressively, it can power up digital thermometer under varying conditions and survive being cut twice without short circuits, indicating the high steadiness and safety (Fig. 6f). More importantly, twelve pouch cells in series smoothly run a high-voltage toy car (12 V), as present in Fig. 6g and Supplementary Movie 1. These pouch cells verify the potential of the as-designed PLCZ electrolyte for the commercialization of AZIBs.

Discussion

We present a multifunctional PLCZ polymer electrolyte with tailored ion channels, effectively suppressing dendrite growth, electrode corrosion and by-product generation. Owing to the constructed ionic channels, the designed PLCZ electrolyte can motivate fast and uniform Zn²⁺ ion transport, regulate ionic solvation structure and reduce free water content. The experimental results and theoretical calculations demonstrate that the in-situ formed robust MEA SEI with abundant zincophilic alloy ingredients enables a 3D spatial ion diffusion and ensures a homogeneous Zn(002) deposition. Consequently, Zn||Zn cells of the PLCZ electrolyte can stably operate at various temperatures, even at a deeper DOD of 85.6% with current density of 2 mA cm⁻² and areal capacity of 10 mAh cm⁻². Furthermore, Zn||Cu asymmetric cells of the PLCZ electrolyte achieve an ultralong cycling over 2400 cycles with a high and stable average CE of 99.7%. The PLCZ electrolyte causes an improved Zn²⁺ reaction kinetics and discharge capacity to Zn||V₂O₅ full cells. Their assembled pouch cells with the industry-level mass loading of 31.3 mg cm⁻² obtains high discharge capacity of 1.13 Ah and also show the potential for severe operating conditions such as bending, shear damage and high temperatures. Overall, our electrolyte design represents an innovative approach to high-performance and stable Zn ion batteries.

Methods

Preparation of electrolytes

The PLCZ quasi-solid-state electrolyte was prepared by a sample ion-exchange method. 30 g polymethyl cellulose nanofiber dispersion (CNF, solid content ~2%) was added into 50 ml DI water. A certain amount of PAAS (0.05 g, 0.1 g, 0.25 g and 0.5 g) was added into the above solution and intensely stirred for 30 min, formed solution A. A certain amount of LMS (0.05 g, 0.1 g, 0.25 g and 0.5 g) was dispersed in 50 ml DI water with stirring for 30 min, formed solution B. Then, solution A and solution B were mixed together and stirred for 5 h. After that, the resultant PAAS-LMS-CNf solution was poured into Teflon petri dish and then dried at 348.15 K for 12 h. The formed polymer film

is shown in Supplementary Fig. S3. Subsequently, the polymer film was first soaked in DI water for 10 min and then immersed in 2 M ZnSO₄ solution for 24 h. According to the used amount of PAAS and LMS, the prepared quasi-solid-state electrolyte was marked as P_{0.05}L_{0.05}CZ, P_{0.1}L_{0.05}CZ, P_{0.1}L_{0.1}CZ, P_{0.1}L_{0.25}CZ, P_{0.25}L_{0.25}CZ and P_{0.5}L_{0.5}CZ. The optimal amounts of PAAS and LMS in solid-state solution were investigated through the galvanostatic charge-discharge (GCD) test of symmetric cells at various current densities from 0.5 to 10 mA cm⁻². The CNF separator was prepared without any PAAS and LMS additives. The batteries using CNF separator and 2 M ZnSO₄ (120 μL) aqueous solution was labelled as CZ. The PCZ quasi-solid-state electrolyte containing 0.1 g of PAAS was also prepared.

Synthesis of V₂O₅ cathode material

10 g NH₄VO₃ was put into a crucible and heated at 673.15 K for 2 h with ramping rate of 10 K min⁻¹. After cooling down, the synthetic V₂O₅ powder was fully ground.

Characterization

X-ray diffraction (XRD) patterns were acquired using Rigaku D X-ray diffractometer. Surface composition and elemental information were obtained through X-ray photoelectron spectroscopy (Thermo ESCA-LAB 250XI, XPS) and X-ray absorption spectroscopy (XAS). The morphology was observed via scanning electron microscopy (SEM) and 3D laser microscope (Olympus LEXT OLS5000). Raman spectroscopy was tested by a Thermo Fisher DXR. Fourier Transform infrared spectroscopy (FTIR) analysis was performed with Perkin Elmer, spectrum One Bruker, covering a wavenumber range of 400–4000 cm⁻¹. All AFM measurements and Nanoindentation measurements were conducted using a Hysitron TI 950 TriboIndenter with a diamond indenter tip (radius of 50 nm). Zn foils with the diameter of 1.4 cm were cleaned by ethanol and deionized water, respectively, and dried by nitrogen gas before test. Indentation depths were controlled within 30 nm and the loading/unloading rates were set as 0.2 mN s⁻¹ with a holding time of 5 s for each segment. In-situ micro-CT (Bruker skyscan 1173) was employed to observe Zn dendrite growth and by-product distribution on the surface of Zn anode, when Zn||Zn symmetric cell was cycled at current density of 5 mA cm⁻²/2.5 mAh cm⁻².

Theoretical calculations

The calculation in this study were performed on the Vienna ab-initio simulation package (VASP)⁶⁰ with density functional theory (DFT) as the basis. The projector augmented wave (PAW)⁶¹ method together with the Perdew-Burke-Ernzerhof (PBE)⁶² exchange-correlation functional were utilized to calculate self-consistency and total energy. The plane-wave basis cutoff was set at 500 eV for all calculations. To achieve convergence, the energy and stress accuracies were set at 1 × 10⁻⁵ eV/atom and 0.02 eV/Å, respectively. The K-point meshes employed were 5 × 4 × 1 for H₂O, 4 × 6 × 1 for Mg, 5 × 5 × 1 for Si, 5 × 5 × 1 for MgZn, 4 × 4 × 1 for Zn₃Si, and 3 × 7 × 1 for ZnSi₃ substrates. The binding energy (*E_b*) of Zn²⁺ ion on the substrate was calculated by the Eq. (1):

$$E_b = E_{\text{total}} - E_{\text{sub}} - E_{\text{Zn}} \quad (1)$$

Where *E_{total}*, *E_{sub}*, *E_{Zn}* refer to the energies of Zn²⁺ ion adsorbed on substrate, the substrate and Zn²⁺ ion.

Zn ion desolvation and transport within the polymer electrolyte were investigated by using the classical MD simulations for three systems i.e. (1) The 36 ZnSO₄ and 1000 water molecules; (2) The 2 PAAS, 1 cellulose, 36 ZnSO₄ and 1000 water molecules were randomly added into simulation system; (3) The 5 LMS, 2 PAAS, 1 cellulose, 36 ZnSO₄ and 1000 water molecules were randomly added into simulation system. The all molecules were randomly added into each simulation system. This study used DLPOLY 4.10 package⁶³. MD simulations were initiated with a box size of 40 × 40 × 40 Å³ and conducted under the

Nose-Hoover ensemble⁶⁴ at 298 K. Short-range interactions were truncated at a cutoff radius of 12 Å. Long-range interactions were addressed using the Ewald summation method⁶⁵. To achieve equilibration of system, the simulations were commenced by using the NPT ensemble for 2 ns and a stepping time of 1 fs. Production runs were executed under the NVT ensemble for a duration of 20 ns. Trajectories from the last 10 ns of the simulation were analyzed to compute RDFs.

The interaction of water molecules was described using the SPC/E model⁶⁶, where the bond distances and angles were kept constant. The interactions for other atom types were modeled using the DREIDING force field⁶⁷. Lennard-Jones (LJ) parameters for different atom pairs (σ_{ij} , ϵ_{ij}) were derived from the parameters of pure atom types (σ_{ii} , ϵ_{jj}) according to the Lorentz-Berthelot mixing rules⁶⁸:

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2}; \epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}} \quad (2)$$

Partial atomic charges, excluding those of water molecules, were obtained by the ORCA program. The charges were determined based on the HF/6-31 G(d) level of theory and electrostatic potential (ESP) fitting using the CHELPG method⁶⁹.

Battery assembly

Symmetric cells (Zn||Zn), asymmetric cells (Zn||Cu) and full cells (Zn||V₂O₅) were assembled at room temperature and tested in CR2032-type coin cells. The diameter of anode and cathode electrodes was 14 mm and the corresponding electrode area was 1.54 cm². The diameter of CNF separator and polymer electrolyte was 19 mm. The thickness of Zn anode was 50 µm. For V₂O₅ cathode electrode, V₂O₅, conductive carbon and PVDF in a mass ratio of 7:2:1 were stirring for 2 h after adding NMP. The resultant slurry was then coated on carbon paper and dried at 343.15 K in oven overnight. The average loading mass of V₂O₅ on carbon paper was 1.4 mg cm⁻².

Electrochemical performance

The charge-discharge cycling performance of the batteries was conducted on NEWARE battery testing system. The EIS, CA and CV measurements were performed using CHI660E workstation. The electrochemical stable window of solid-state electrolyte was evaluated in Zn||stainless steel (SS) asymmetric cell by linear scan voltammetry (LSV) at 5 mV s⁻¹ under various temperatures. The ionic conductivity (σ) was obtained via testing the resistance of Zn||Zn symmetric cells ranging from 0.05 Hz to 100 KHz, and calculated via the following Eq. (3)⁷⁰:

$$\sigma = LR \times A \quad (3)$$

where A , R and L are the resistance, surface area and thickness of the CNF separator and solid-state electrolytes, respectively.

The Zn²⁺ transference number was determined by the resistance of Zn||Zn before and after CA, and calculated via the following Eq. (4)⁷¹:

$$t_{\text{Zn}^{2+}} = \frac{I_s(\Delta V - I_0 R_0)}{I_0(\Delta V - I_s R_s)} \quad (4)$$

Where I_0 and R_0 represent the current and resistance before CA, respectively. I_s and R_s are the current and resistance when the current keeps steady at CA plot, respectively. ΔV is the applied voltage polarization (5 mV).

The Zn²⁺ desolvation energy was tested the resistance of Zn||Zn at various temperature and calculated via the Arrhenius Eq. (5)⁶:

$$\frac{1}{R_{\text{ct}}} = A \exp\left(-\frac{E_a}{RT}\right) \quad (5)$$

Where E_a , R_{ct} , R , T and A represent the activation energy, charge transfer resistance, molar gas constant, absolute temperature and Arrhenius constant, respectively.

Data availability

All data that support the findings of this study are deposited in the Figshare database (<https://doi.org/10.6084/m9.figshare.25569885>). The other data are available from the corresponding author on request.

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- S.G. and R.C. carried out the theoretical calculations. K.L. and W.L. conducted the XAS tests. T.P. and T.B. provided the Raman characterization. X.Z., J.Q. and Y.H. directed the project and afforded experimental guidance. C.Y. wrote the manuscript. Y.S. and Y.H. commented and revised the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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Author contributions

All the authors contributed to this work. C.Y. and P.W. fabricated the materials and performed experimental characterizations and analyses.