

Zn-ion ultrafluidity by coupling ion-sieving and Zn ion replenishment for highly reversible Zn-metal anode chemistry

Taesoon Hwang^{2,§}, Hongwei Tao^{3,§}, Yuxuan Yang¹, Qianzheng Jin¹(✉)

¹ Zhengzhou University, Zhengzhou 450001, China

² Department of Materials Science and Engineering, University of Texas at Dallas, Richardson 75080, Texas, USA

³ Institute of Smart City and Intelligent Transportation, Southwest Jiaotong University, Chengdu 611756, China

§ Taesoon Hwang and Hongwei Tao contributed equally to this work.

Nano Res., **Just Accepted Manuscript** • <https://doi.org/10.26599/NR.2026.94909106>

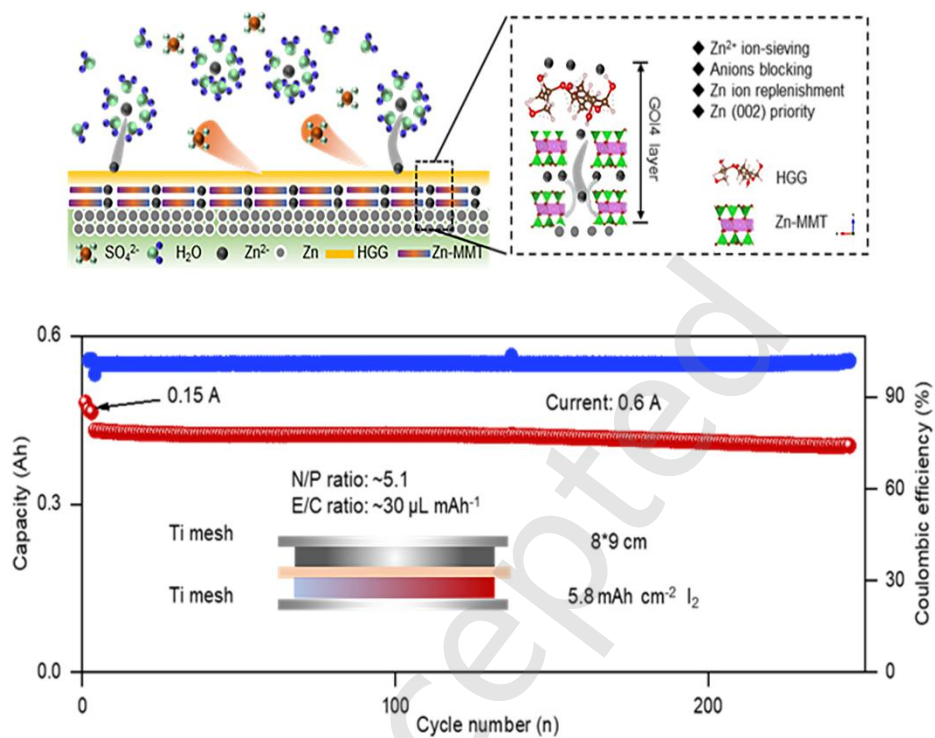
<https://www.sciopen.com/journal/1998-0124> on Aug. 10, 2026

© The Authors(s)

Just Accepted

This is a “Just Accepted” manuscript, which has been examined by the peer-review process and has been accepted for publication. A “Just Accepted” manuscript is published online shortly after its acceptance, which is prior to technical editing and formatting and author proofing. Tsinghua University Press (TUP) provides “Just Accepted” as an optional and free service which allows authors to make their results available to the research community as soon as possible after acceptance. After a manuscript has been technically edited and formatted, and the page proofs have been corrected, it will be removed from the “Just Accepted” web site and published officially with volume and article number (e.g., *Nano Research*, **2025**, *18*, 94906990). Please note that technical editing may introduce minor changes to the manuscript text and/or graphics which may affect the content, and all legal disclaimers that apply to the journal pertain. In no event shall TUP be held responsible for errors or consequences arising from the use of any information contained in these “Just Accepted” manuscripts. To cite this manuscript please use its Digital Object Identifier (DOI®), which is identical for all formats of publication.

TABLE OF CONTENTS (TOC)



Zn-ion ultrafluidity is constructed by designing a gradient organic-inorganic layer at interface to achieve highly reversible Zn-metal anode chemistry.

Zn-ion ultrafluidity by coupling ion-sieving and Zn ion replenishment for highly reversible Zn-metal anode chemistry

Taesoon Hwang^{2,§}, Hongwei Tao^{3,§}, Yuxuan Yang¹, and Qianzheng Jin¹  

¹ Zhengzhou University, Zhengzhou 450001, China

² Department of Materials Science and Engineering, University of Texas at Dallas, Richardson 75080, Texas, USA

³ Institute of Smart City and Intelligent Transportation, Southwest Jiaotong University, Chengdu 611756, China

[§] Taesoon Hwang and Hongwei Tao contributed equally to this work.

Received: 25 June 2026; Revised: 10 August 2026; Accepted: 10 August 2026

 Address correspondence to qzjin@zzu.edu.cn

 Cite this article: Nano Research, 2026, 19, 94909106 <https://doi.org/10.26599/NR.2026.94909106>

ABSTRACT: The commercialization of aqueous zinc-ion batteries (AZIBs) is hindered by the poor reversibility of Zn-metal anodes, which suffer from dendrite growth, hydrogen evolution reaction (HER), and corrosion. This work designs a gradient organic-inorganic (GOI4) protective layer on the Zn anode, which is composed of a Zn-rich inorganic montmorillonite (Zn-MMT) sub-layer and an organic hydroxypropyl guar gum (HGG) top-layer. The -OH of HGG acts as valve for gating Zn^{2+} 'on' and anions 'off' states to block water and SO_4^{2-} , while close-fitting Zn-rich MMT at interface can provide rapid interfacial Zn^{2+} replenishment to homogenize ion flux and its feasible mechanical strength promises suppression of dendrites formation. Through theoretical calculation, the lower transfer energy barrier of Zn^{2+} in GOI4 layer provides unique benefits to accelerating fast Zn migration, decreasing the concentration polarization. Consequently, the GOI4@Zn symmetric cell achieves exceptional cycling stability over 2700 hours at $0.25 \text{ mA cm}^{-2}/0.25 \text{ mA cm}^{-2}$ and operates reliably even at ultrahigh current density (5 mA cm^{-2} , 1 mAh cm^{-2} for 4000 h). When paired with I_2 @PAC cathode, the full cell also demonstrates long-term cycling (e.g., 20,000 cycles with 87.5% capacity retention). This work provides a feasible strategy for developing highly reversible Zn anodes for practical AZIBs.

KEYWORDS: Zn-metal battery, anion blocking, ion sieve, Zn replenishment, organic-inorganic layer

1 Instruction

Rechargeable batteries coupling with aqueous based electrolyte has motivated intensive researches since the plentiful electric vehicle and energy storage power station powered by non-aqueous Li-ion batteries suffer from the unexpected combustion and explosion [1-4]. Aqueous zinc-ion batteries (AZIBs) offer the most promising alternative for large-scale energy storage systems with the advantages of low cost, volumetric energy density and environmental friendliness [5]. However, the commercialization of AZIBs faces challenges in achieving highly stable and reversible zinc (Zn) anode, particularly at high depths of discharge (DOD) and high current condition, which is attributed to the side reactions of hydrogen evolution reaction (HER), metal corrosion, and irregular dendrite growth [6]. Inhomogeneous Zn electrodeposition presents more reactive sites in the aqueous electrolytes, exacerbating these adverse side reactions, and finally leading to the failure of AZIBs.

Realizing a reversible, well-oriented and dense zinc electrodeposition during the repeated plating/stripping process needs to minimize the active surface exposed to electrolyte and suppress the dendrite growth [7]. Highly concentrated electrolytes can achieve high reversibility but the low-cost and high ionic conductivity merits of aqueous

electrolyte are significantly compromised [8]. Engineering solid electrolyte interface (SEI) at anode surface provides promising advantages to solve these problems through separating H_2O from the anode and allowing for ion transfer. For example, Lu constructed an organic/inorganic dual-phase SEI through electrolytes design, and realized ordered zinc electrodeposition process under SEI [9]. However, less of these works achieve long-cycling life over 2000 h at an ultrahigh capacity ($>20 \text{ mAh cm}^{-2}$) [10]. The unsatisfactory performances can be attributed to ignored facts: 1) inadequate replenishment of Zn^{2+} due to their inability to balance lower charge transfer resistance at fast Zn^{2+} diffusion rate [11]; 2) visible dissolution of ZnF_2 -riched composite in aqueous electrolyte [12]; 3) weak stress tolerance under nano-meter level thickness of SEI [13]. Therefore, feasible strategies that can improve anode stability while maintaining the high safety merits are urgently needed.

Due to the versatility of different components in the composite artificial interface layer (AIL), great efforts on multifunctional AILs have recently been devoted to Zn anode protection for designing durable and stable AZIBs. For example, Sun [14] reported a unique multi-filtration-concentration gradient interlayer integrating a three-dimensional (3D) structure to suppress Zn dendrite growth

and parasitic reactions. But the top layer of gradient structure with hydrophobic property may lead to larger deposition potential. Deng [15] synthesized a double-layer gradient coating consisting of zincophilic organic outlayer (OSA/PAM) and inside metal Sn, which can facilitate the desolvation process of $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ and decrease the deposition barrier. However, there exists some question associated with metal layer. The Zn^{2+} is deposited on the surface of metal layer, which will lead to the separation between metal and organic layer during the repeated plating/stripping process. The substitution of metal layer using ion-conductivity ZnO accompanying external PVA is alternative solution [16]. But, to the requirement of high current densities, it is insufficient since it can't supply sufficient Zn^{2+} during plating process. Therefore, these structures present challenges for stable cycling of Zn anode, especially at high capacities.

Herein, we construct a gradient layer (GOI4@Zn) with Zn^{2+} -rich replenishment through a spin coating method, where Zn-based montmorillonite (Zn-MMT) inorganic is below the organic hydroxypropyl guar gum (HGG) layer. Unlike the conventional artificial SEI layer, the abundant Zn^{2+} in the inorganic layer provides rapid interfacial ion replenishment, eliminating the concentration gradient and reducing the nucleation barrier. The strong negative surface of outside organic as ion-sieving captures more Zn^{2+} to facilitate the uniform zinc ions flow and exclude formation of basic zinc sulfate (ZHS) at electrolyte-anode interface. The lower desolvation energy during Zn penetrating to the layer significantly enhances the Zn^{2+} transport kinetics. In addition, the organic/inorganic composite provides strong mechanical strength to accommodate the volumetric changes during the depositing/stripping process. As a result, the assembled GOI4@Zn cell delivers an excellent cycling performance and a high average CE of 99.8%. Even at a current density of $50 \text{ mA cm}^{-2}/50 \text{ mAh cm}^{-2}$, GOI4@Zn symmetrical battery operates for 3000 h. Additionally, the GOI4@Zn|| I_2 @PAC cell demonstrates stable cycling performance with a capacity retention rate of 87.5% after 20000 cycles at 2 A g^{-1} . This work offers an economical and user-friendly approach to designing GOI4@Zn anode, enhancing the feasibility of widespread practical applications for AZIBs.

2 Results and discussion

2.1 Design of the organic-inorganic layer GOI4.

The GOI4@Zn electrode was synthesized by spinning the solution containing Zn-based MMT and hydroxypropyl guar gum (HGG) on the surface of Zn foil. The thin gradient GOI4 layer is composed of inorganic interlayer and organic outlayer, where MMT is mainly located below the HGG layer. The HGG with strong negative charge acts as filter to realize the Zn^{2+} sieving and anions blocking, and meanwhile prevents reactive H_2O to reach the zinc electrode surface to suppress the hydrogen evolution reaction (HER). The Zn-based MMT at interface is Zn container to avoid the formation of charge space especially at high current density (Fig. 1(a)). The Fig. 1(b) reveals that surface of GOI4@Zn is uniform and smooth, and a thickness of $\sim 10 \text{ }\mu\text{m}$ is observed from the cross-sectional SEM image. The EDS mapping

images (Fig. 1(c)) display the distribution of elements Zn, C, O, Si, Mg, further confirming the specific configuration. The Zn content of Zn-based MMT is about 5% (Fig. S1 and Table S1). Based on electron localized function (ELF), there are four sites for Zn existence with similar value of -10.7 eV/f.u (Fig. 1(d) and S2), which provides possible actives for potential fast Zn supplement. Fig. 1(e) shows that Al_{2p} spectrum of GOI4 shifts to lower binding position, indicative of Al-O-C formation responsible for the mechanical integrity during the volumetric change. Infrared (IR) spectroscopy results (Fig. 1(f)) manifest absorption peaks at 848 cm^{-1} corresponding to Al-O stretching vibrations from the MMT [17]. The peak intensity becomes weaker can be attributed to the Al-O-C between MMT and HGG. These oxygen-containing structures in Zn-MMT and HGG exhibit strengthened surface negative charge density enabling priority of the interfacial Zn ion distribution (Fig. 1(g) and 1(h)) and act as nanofluidic concentrators for the efficient trapping and release of collected ions [18], which promotes homogeneous deposition. This can be further demonstrated by lower contact angle (Fig. S3). The GOI4 presents strong mechanical strength to accommodate volumetric change for prohibiting short circuit since it has sufficient young's modulus (Fig. 1(i) and 1(j)) [19]. The optimized GOI layer is chose to be GOI4 since its excellent electrochemical stability (Fig. S4).

2.2 The Regulation of stability of Zn plating/stripping process.

The morphologies and structures are investigated since the deposition behaviors of Zn^{2+} give an important influence on the cycling reliability of Zn batteries. We analyzed the Zn anode surface morphology evolution under the artificial SEI layer using ex-situ scanning electron microscopy (SEM). At the depositing capacity of 1 mAh cm^{-2} , irregular and smaller Zn particles are observed on the surface of pure Zn anode, which is expected to pierce the glass fibers because of its large "hill" shape after the capacity is increased to 3 mAh cm^{-2} (Fig. 2(a)). This inhomogeneous growth of Zn dendrites poses serious risks of short circuiting and potential safety concerns during battery operation. In contrast, for GOI4@Zn (Fig. 2(b)), planar and large stacks with obvious grain boundary are observed on the surface at 1 mAh cm^{-2} , which gradually covered whole surface through connecting with stacks at 3 mAh cm^{-2} , indicating that GOI4 layer with rich Zn supplement can arrange the Zn^{2+} to deposit uniformly with oriented morphologies. The deposition process from particles to oriented stacks benefits to achieve uniform deposition enabling long life span. After cycling 400 h, the pure Zn delivers abundant stacks appearing inside the glass fibers (Fig. S5). Through 3D confocal laser scanning microscope measurements (3D CLSM), it further shows that bare Zn anode is more irregular compared to deposited Zn under GOI4 (Fig. 2(c)). This structure sparks numerous parasitic reaction sites and defects, which promotes nucleation and growth of more Zn grains as well [20]. For GOI4@Zn, it is still maintained by uniform surface with compact polycrystalline, indicating that the interface layer produces favorable advantages rendering Zn anode with the uniform plating behaviors (Fig. 2(d)). The section-cross SEM

image of Zn anode shows that the surface of pure Zn anode is consisted by separated and porous Zn islands clamping massive glass fibers, while GOI4@Zn presents textured oriented stacks (Fig. S6).

optical microscopy was carried out to visually survey the growing morphologies at a current density of 5 mA cm^{-2} . At initial 10 min in Fig. S7, the surface of GOI4@Zn is obviously covered by a planar Zn layer, and as an increase of time, the

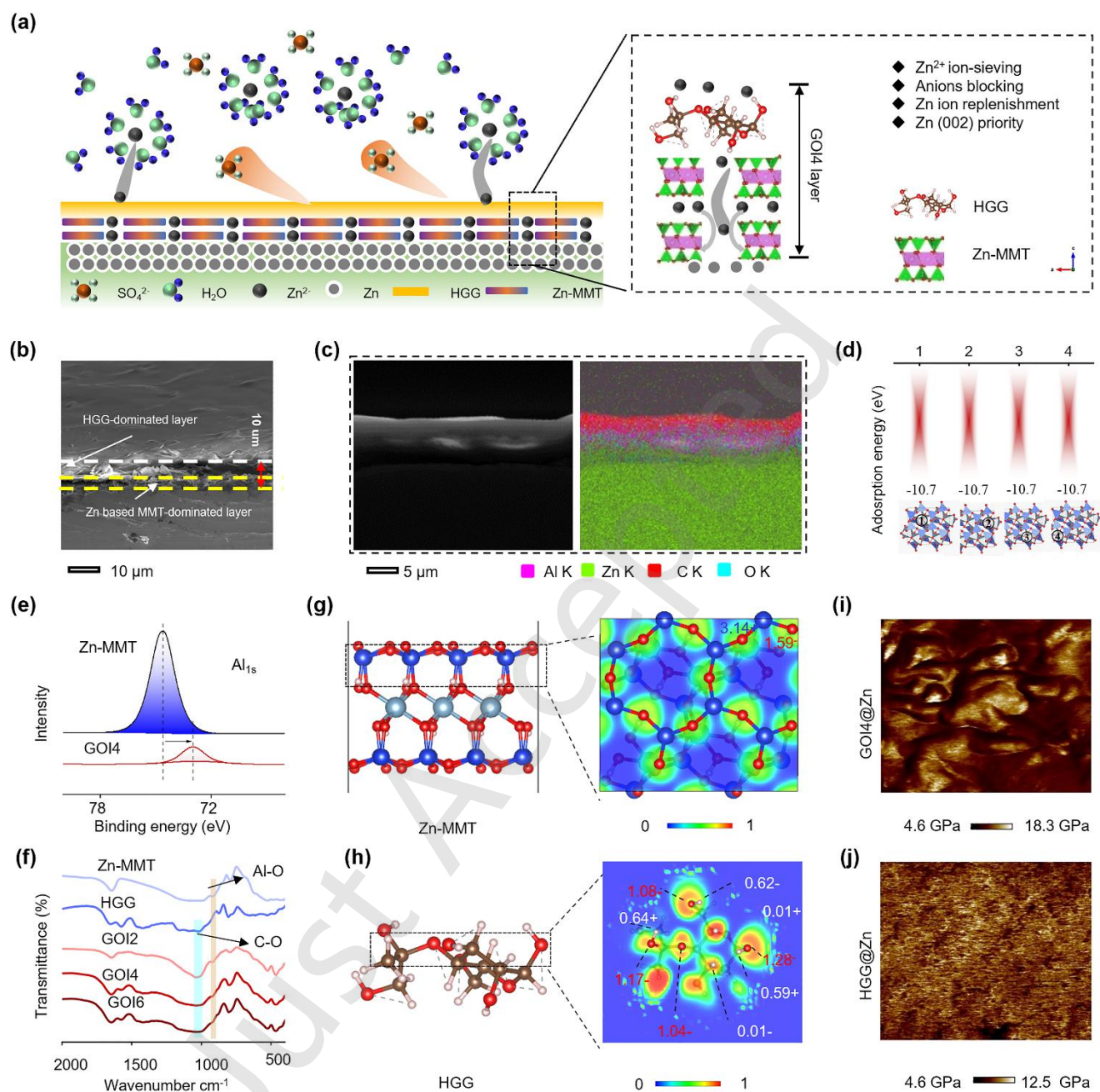


Figure 1 Design of the organic-inorganic layer GOI4. a) Schematic process of Zn^{2+} ion-sieving and transport through GOI4 layer. b) The SEM image of GOI4@Zn and corresponding EDS (c). d) The stable existing sites of Zn^{2+} in Zn-MMT. e) Fitted XPS spectrum of Al_{1s} and FTIR (f) of Zn-MMT, HGG and GOIs layers. g, h) The electron localized function of Zn-MMT and HGG, respectively. i, j) Young's modulus of GOI4@Zn and HGG@Zn,

The nucleation, growth and development of Zn anode during the plating process were further understood by chronoamperometry (CA) measurements at potential of 0.15 V. In Fig. 2(e), the current of pure Zn anode continuously increases even at 200 s, suggestive of 2D growth to form irregular dendrites responsible for enlarged surface. On the contrary, the current-time curve reveals that GOI4@Zn electrode shows the immediate current rise, indicative of fast nucleation after Zn^{2+} contact electron at the interface. The current then maintains constant value implying 3D growth model where abundant nucleation sites connect to construct density morphologies along the surface [21, 22]. The in-situ

deposited Zn grows along the surface without significant dendritic protrusions. As a comparison, the surface of pure Zn is rapidly occupied by isolated protrusions, which gradually develops into large zinc dendrites over time. The uncontrollable growth, especially at high capacities, poses a risk of short circuiting. The ratio of Zn_{002} to Zn_{100} is an important index reflecting the texture properties of deposited Zn, which indirectly illustrates the reversibility of electrochemical behaviors. In Fig. S8, the XRD shows that an enormous rise of the ratio is observed for GOI4@Zn at different operational capacities, while it is decreased for pure Zn (Table S2), implying the controllable and

homogeneous plating process enabled by Zn-rich GO14 layer.

(Fig. S9) show an obvious side product for pure Zn after 7

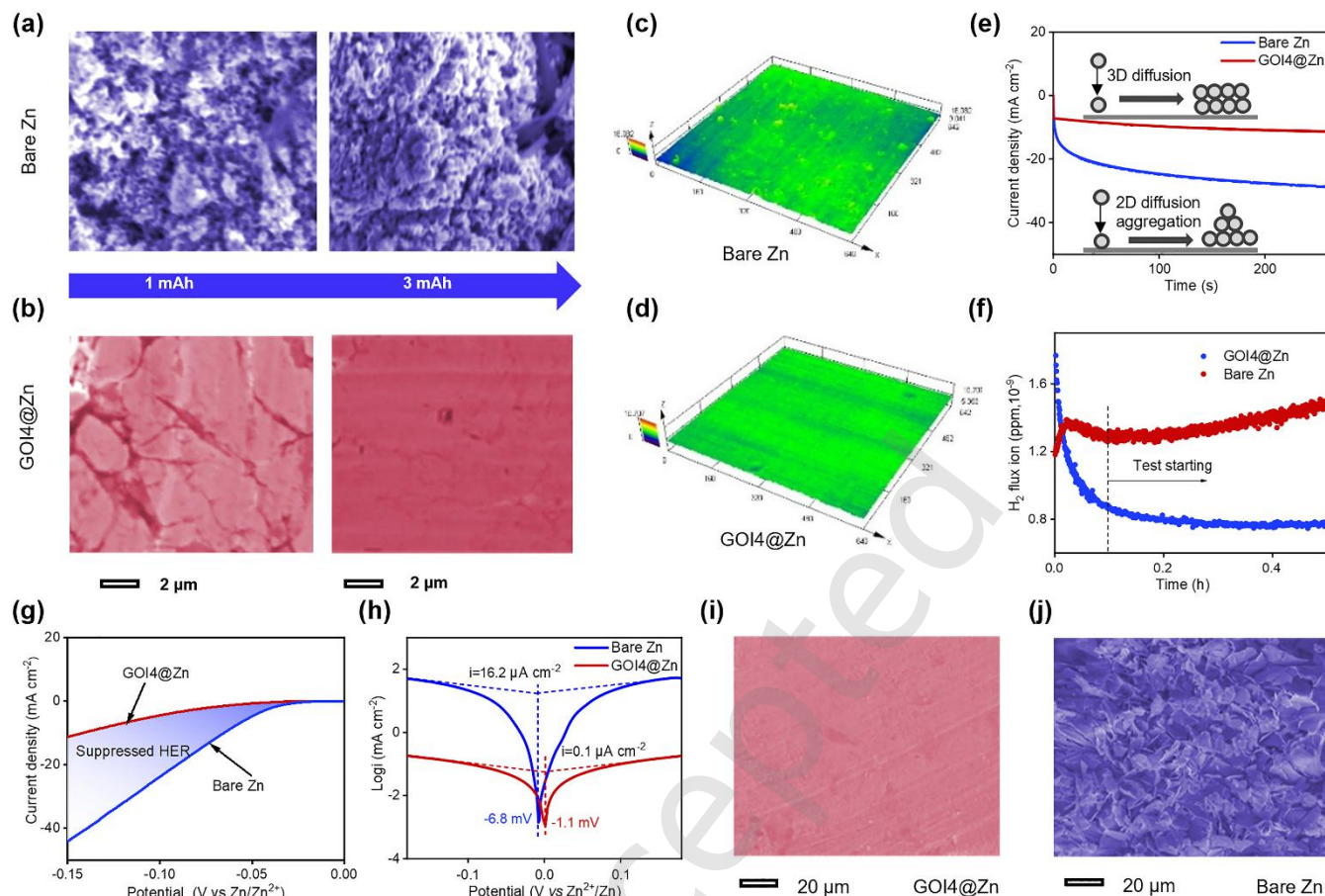


Figure 2 The effect of GO14 on the reversibility of deposition behaviors. a) The deposition morphologies of bare Zn and (b) Zn anode after peeling off the GO14 layer. c) The 3D CLSM images of bare Zn and (d) Zn under GO14 layer. e) The CA curves of bare Zn and GO14@Zn. f) In-situ DEMS of GO14@Zn and bare Zn symmetrical cells. g, h) The HER measurement and LSV test for bare Zn and GO14@Zn, respectively. i, j) The corrosion morphologies of Zn anode under GO14 layer and bare Zn anode after soaking in electrolyte for 7 days, respectively.

The suppression of hydrogen evolution reaction (HER) is crucial since metal corrosion at interface will affect transfer process of Zn²⁺ and final morphologies as well as reversibility of plating/stripping process [23, 24]. Differential electrochemical mass spectrometry (DEMS) was explored to determine HER of Zn symmetrical cells during the Zn stripping/plating at a current density/capacity of 2 mA cm⁻² for 0.5 h. As shown in Fig. 2(f), compared to the pure Zn cell, GO14@Zn symmetrical cell generates little H₂ peak, while an improved H₂ evolution flux is captured for pure Zn symmetrical cell as an increase of cycling time. The HER potential is tested in Na₂SO₄ electrolyte (Fig. 2(g)). Notably, the onset potential of HER of GO14@Ti shows a significant shift to -0.15 V from -0.1 V, which confirms the ability of GO14 layer to suppress the decomposition of H₂O. The linear scanning voltammetry (LSV) tests were performed to evaluate the inhibition property of metal corrosion (Fig. 2(h)). Compared to high corrosion current (16.2 μA cm⁻²) of pure Zn, the GO14@Zn is 0.1 μA cm⁻², meaning that the protective layer successfully inhibits occurrence of HER. In addition, the corrosion potential of bare Zn is measured to be -6.8 mV and then shifts to -1.1 mV after coating GO14, further implying the organic-inorganic SEI is able to strip solvation H₂O and preclude penetration of free H₂O. The self-stability during rest time is of significance for long lifespan, which can be reflected by corrosion of metal anode. The XRD patterns

days soaking in electrolyte, while there is no appearance of additional peak features for GO14@Zn, indicating the chemical stability at interface [25]. From SEM image of soaked anode, the surface of Zn anode under GO14 layer preserves its initial smooth morphologies (Fig. 2(i)), while abundant micro sheets are observed for Zn anode without protective layer (Fig. 2(j)). These results again confirm the effective restriction of by-products generation through GO14 protective layer, contributing to less propensity of uncontrollable growth, demonstrate by higher the coulombic efficiency based on the Aurbach CE value (Fig. S10).

2.3 Fast Zn²⁺ migration mechanism

The deposition process of Zn²⁺ is involved with the desolvation behaviors, penetration from SEI and electrochemical reduction, which are intimately related to the interfacial properties. The desolvation process is characterized by desolvation energy calculated by Arrhenius equation based on the temperature-dependent EIS measurements (Fig. S11). The values of GO14@Zn and pure Zn are 20.4 and 30.3 KJ mol⁻¹, respectively, demonstrating that GO14 layer promotes fast detaching of solvated water, leading to quick ion transfer (Fig. 3(a)) [26, 27]. Based on the ion transfer number measurement (Fig. S12 and S13), the GO14@Zn and pure Zn electrode exhibit 0.36 and 0.09, respectively, further confirming that the organic-inorganic

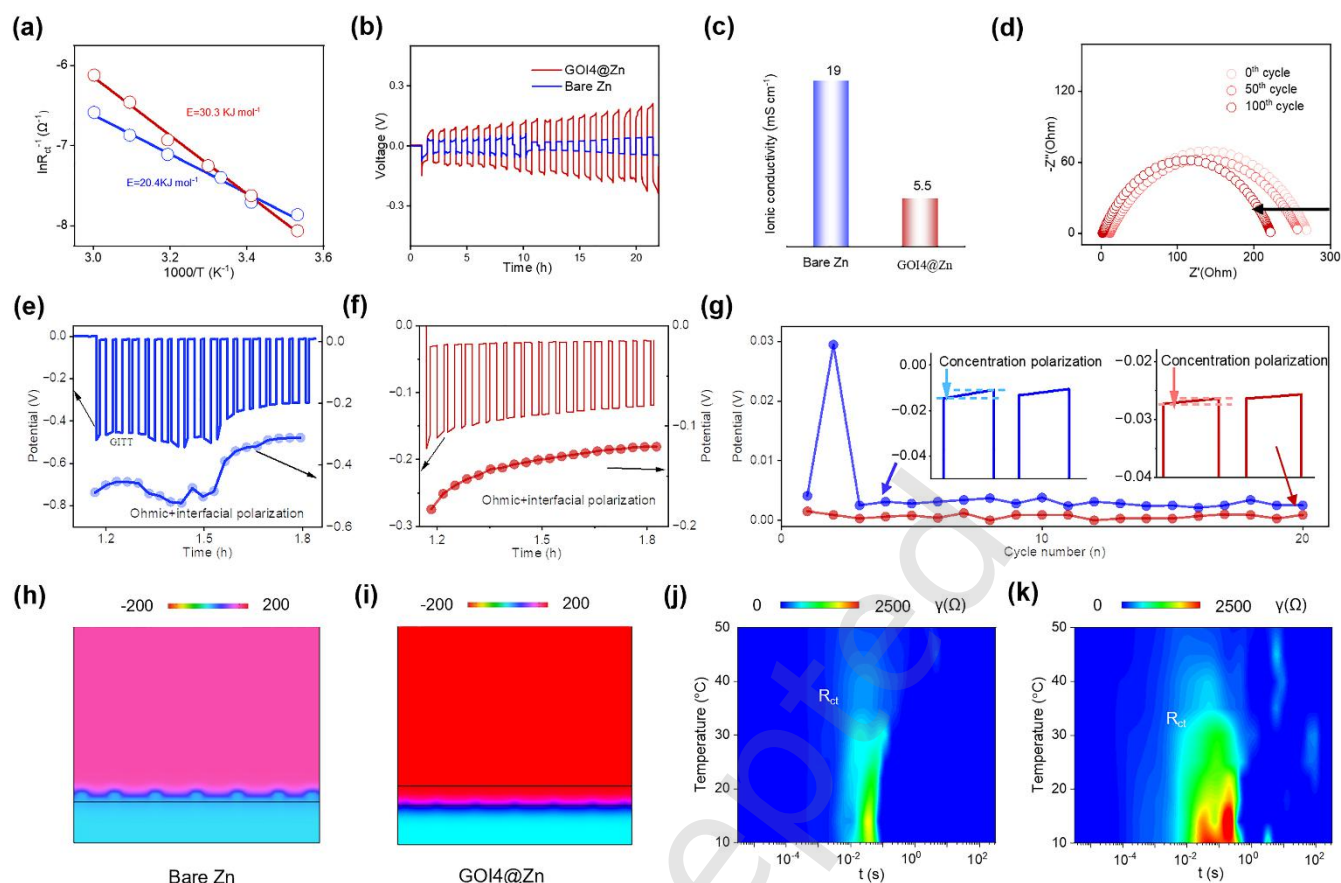


Figure 3 The Zn^{2+} migration mechanism of GOI4@Zn and bare Zn. a) The desolvation energy. b) The critical current density. c) The ion conductivity. d) EIS curves of GOI4@Zn|| GOI4@Zn at different cycles. e, f) The GITT curves and ohmic+interfacial polarization potential. g) The concentration polarization potential. h, i) The concentration gradient at anode interface. j) The distribution of relaxation times (DRT) measurements of GOI4@Zn and Zn symmetrical cells (k) at different temperatures.

layer can improve ion transfer performance. The acceleration effect enables the anode with favorable merit for high current tolerance. The critical current/capacity test shows critical current density of GOI4@Zn is higher than that of pure Zn anode (Fig. 3(b)), which is related to the higher ion conductivity (Fig. 3(c) and Fig. S14). The excellent transport performance can be demonstrated by impedance spectrum characterization at different cycles (Fig. 3(d)), where GOI4@Zn has lower resistances than those of pure Zn (Fig. S15), suggesting that GOI4 can enable fast ion transfer owing to the supplement of Zn^{2+} at interface and intrinsic electron-rich structure. Galvanostatic intermittent titration technique (GITT) was used to titrate an uncycled battery. Compared to bare Zn, GOI4@Zn displays lower potential caused by ohmic and electrochemical polarization (Fig. 3(e) and 3f). In addition, its lower concentration polarization also contributes to lower potential response (Fig. 3(g)), demonstrating that GOI4@Zn effectively captures Zn^{2+} and accelerates their transport.

To understand the nucleation and growing mechanism of density Zn, simulation was adapted using COMSOL Multiphysics based on an established electrodeposition model. In Fig. 3(h), significant concentration gradient is observed over the whole surface of bare Zn, granting inclination to produce the disordered dendrites, especially under high current density. In contrast, the thin GOI4 layer exhibits uniform ion flux with higher values owing to its

electronegative properties and rich adsorption sites (Fig. 3(i)). This intrinsic electric drive force can accelerate the Zn transfer and homogenize Zn^{2+} distribution avoiding the charge space. As deposition time increases to 50 s, there is no significant dendrite morphologies on the GOI4@Zn anode, ensuring Zn homogenous deposition throughout the electrode compared to the pure Zn (Fig. S16). To avoid the erroneous pre-modeling of the equivalent circuit model method that leads to possible misunderstandings, the distribution of relaxation time (DRT) analysis that directly distinguishes the relaxation time (τ) constants of the principal electrochemical processes was used [28]. The deconvoluted charge transfer resistance (R_{ct}) of the GOI4@Zn symmetrical cell is far lower than those of Zn symmetrical cell at all temperatures (Fig. 3(j) and 3k), denoting much faster interfacial kinetics enabled by GOI4 layer.

2.4 The work mechanism of Zn-ion ultrafluidity

In-situ FTIR spectra (Fig. 4(a)) were recorded in one cycle to investigate the mechanism of Zn^{2+} plating/stripping behaviors on GOI4@Zn. During the discharge process, the relative band intensity of -OH vibration of HGG at $\sim 3400 \text{ cm}^{-1}$ is gradually weakened [29, 30], indicating that Zn^{2+} is adsorbed on the sites of HGG side chain. Then, the -OH peak intensity recovers its pristine state during the charge process, suggesting that Zn^{2+} is quickly detached from these sites. The density function theory (DFT) was carried out to

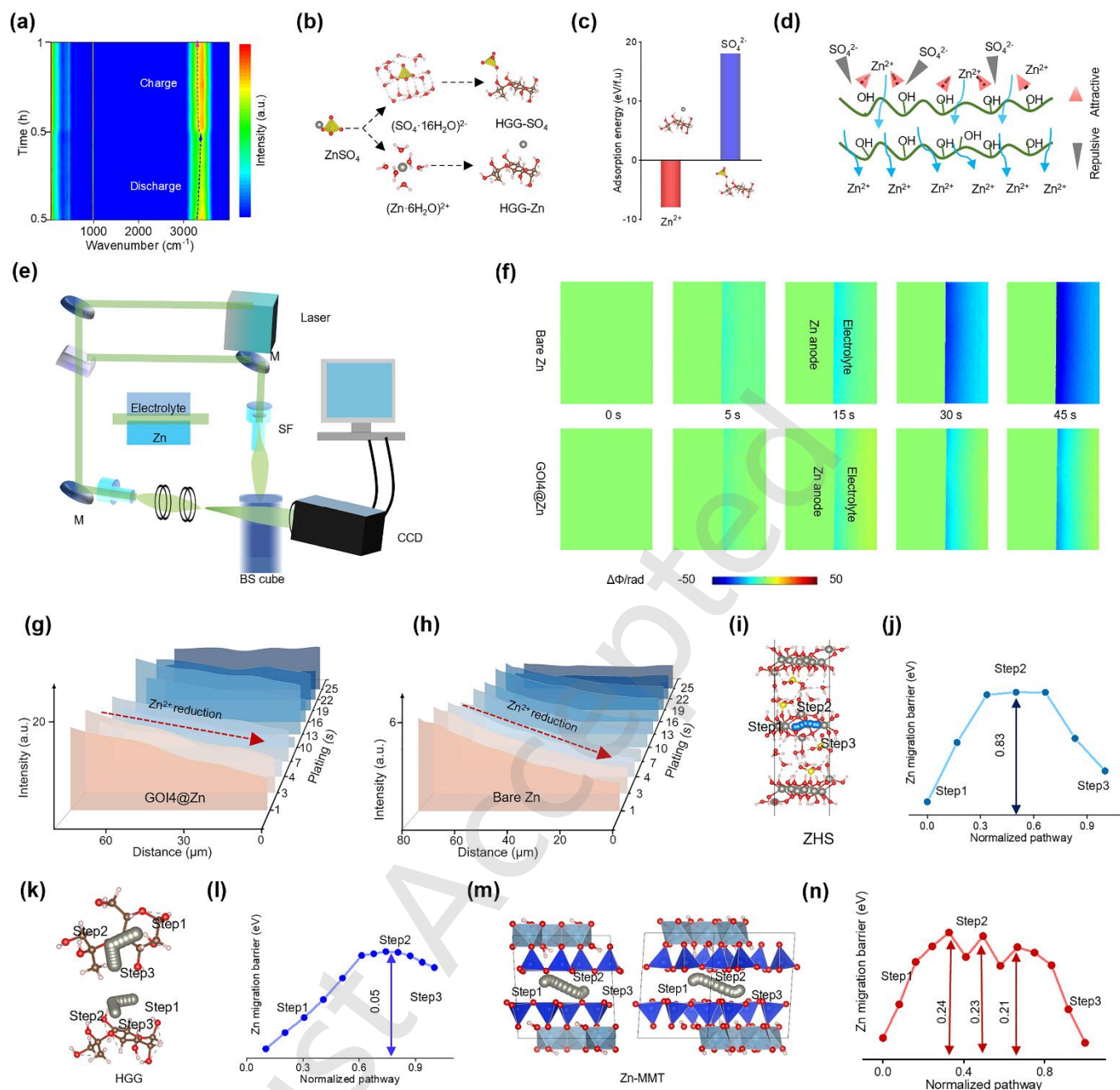


Figure 4 The work mechanism of Zn-ion ultrafluidity. a) The in-situ FTIR of GOI4@Zn for one cycle. b) The possible binding models of HGG with Zn²⁺/SO₄²⁻. c) The adsorption energy of HGG with Zn²⁺/SO₄²⁻. d) The Zn²⁺/SO₄²⁻ ion-sieving accelerating channel model generated by the top HGG layer. e) The Diagram of the EDH. f) In-situ EDH projection of bare Zn and GOI4@Zn electrodes at different deposition times and g, h) corresponding 3D area charts of concentration in normal direction of anode (10 mA cm⁻²). The transport pathway of ZHS (i), HGG (k) and Zn-MMT (m). The corresponding transfer energy barriers: ZHS (j), HGG (l), Zn-MMT (n).

analyze the adsorption and deposition behaviors. The binding models of HGG with Zn²⁺ and SO₄²⁻ is shown in Fig. 4(b). The calculated adsorption energy of HGG on Zn²⁺ and SO₄²⁻ are -6 eV and 17.5 eV (Fig. 4(c)), respectively, implying the HGG selectively adsorbs Zn²⁺ and enforces SO₄²⁻ blocking [31]. Therefore, ZHS formation can be suppressed. The ion transfer path can be illustrated in Fig. 4(d), where Zn²⁺ initially uniformly adsorbs near -OH sites of HGG accompanying the repulsion of SO₄²⁻, and then fast transfers between chains of HGG.

The Zn²⁺ transport is tested using in-situ electrochemical digital holography (EDH) in Fig. 4(e) during plating for 45s. The evolution process of Zn²⁺ concentration during plating at

interface (Fig. 4(f)) is tracked by measuring optical path length distribution [32]. Compared to the bare Zn, the interfacial color near GOI4@Zn is less changed at initial time (0-5s), indicating that GOI4 effectively absorbs Zn ions. In the subsequent deposition process (15-45s), the interfaces of bare Zn and GOI4@Zn become blue, indicating that Zn²⁺ is constantly consumed. However, the blue color of GOI4@Zn is lower and more uniform, indicating that the nanofluid layer keeps the high concentration state and homogenizes the ion flux on the interface. The 3D area charts derived from EDH show the intensity corresponding to concentrations at different times. During the whole migration, the concentration of GOI4@Zn is 4 times higher than that of bare

Zn. At time range of 1-10 s, GOI4@Zn presents slower concentration fading, and then maintains a high concentration nearly a constant during 15-25 s (Fig. 4(g)), whereas bare Zn exhibits a noticeable decrease during continuous electroreduction (Fig. 4(h)). The high concentration distribution further demonstrates that GOI4 layer can create nanofluid to regulating Zn^{2+} flux.

Therefore, the work mechanism of GOI4 for long reversible cycles can be attributed to three aspects. Firstly, the outlayer organic removes the solvated H_2O preventing accumulation of corrosion products and rearranges the ion distribution at the interface. Secondly, the inside inorganic with rich Zn can replenish Zn^{2+} to avoid the formation space charge responsible for uncontrollable deposition. Thirdly,

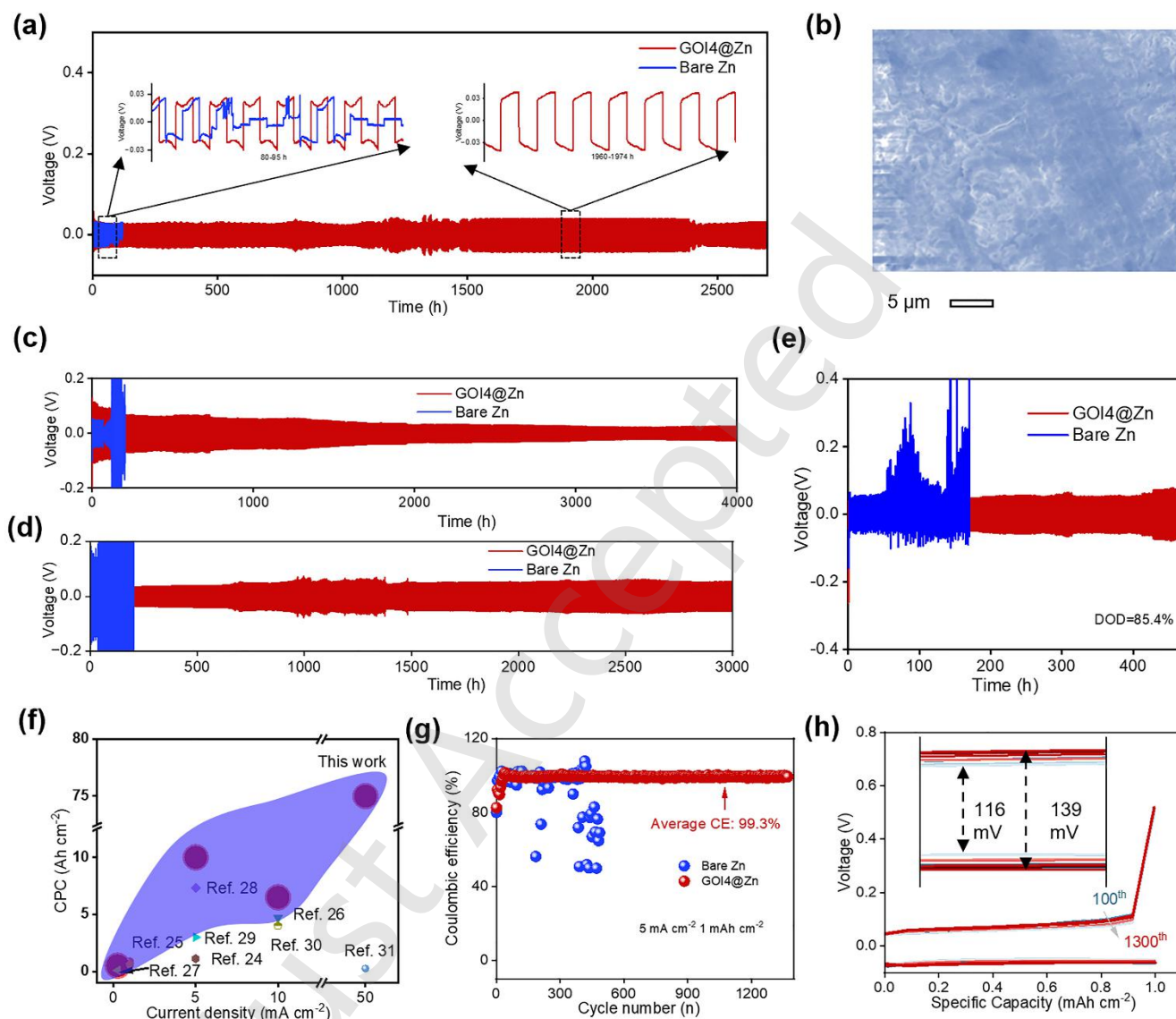


Figure 5 The electrochemical performances of symmetric and asymmetric batteries for bare Zn and GOI4@Zn. a) Cycle performances of symmetric batteries at $0.25 \text{ mA cm}^{-2}/0.25 \text{ mAh cm}^{-2}$ and corresponding charge/discharge curves. b) The SEM image of Zn under protection of GOI4 after 2500 h. c, d) Cycle performances of symmetric batteries at $5 \text{ mA cm}^{-2}/1 \text{ mAh cm}^{-2}$ and $50 \text{ mA cm}^{-2}/50 \text{ mAh cm}^{-2}$, respectively. e) The high DOD of 85.4%. f) The comparison of previous work and this work. g) The cycling performances of Cu||Zn asymmetrical cell. h) The plating/stripping curves of GOI4@Cu||Zn.

When Zn^{2+} penetrates interfacial layer (Fig. 4(i), 4k and 4m), transfer barrier of ZHS is 0.83 eV (Fig. 3j), which is higher than that (0.05 eV in Fig. 4(l)) of HGG and (0.21 eV in Fig. 4(n)) of Zn-MMT, further demonstrating fast electrochemical kinetics of GOI4 layer. These can be attributed to the sufficient Zn supplement and nanofluid as an electrokinetically driven dynamic concentration system fascinating the quick ion transport. In addition, since low crystallinity mismatch promotes the Zn^{2+} to deposit along customized-designed surface of substrate (Fig. S17). The calculated low lattice mismatch δ is 2%, indicating its coherent interface with Zn_{002} texture [33-35].

gradient soft-coupled organic-inorganic layer with superior mechanical strength can accommodate the volumetric change during the repeated depositing/stripping process.

2.5 Electrochemical Performance of symmetrical cells and asymmetrical cell

The uniform morphology coupling with suppression of HER during the electrochemical process, is expected to achieve excellent electrochemical performance of Zn anodes. The galvanostatic cyclic performances of symmetrical cells were measured at multiple current densities and areal capacities. In Fig. 5(a), the GOI4@Zn||GOI4@Zn symmetric

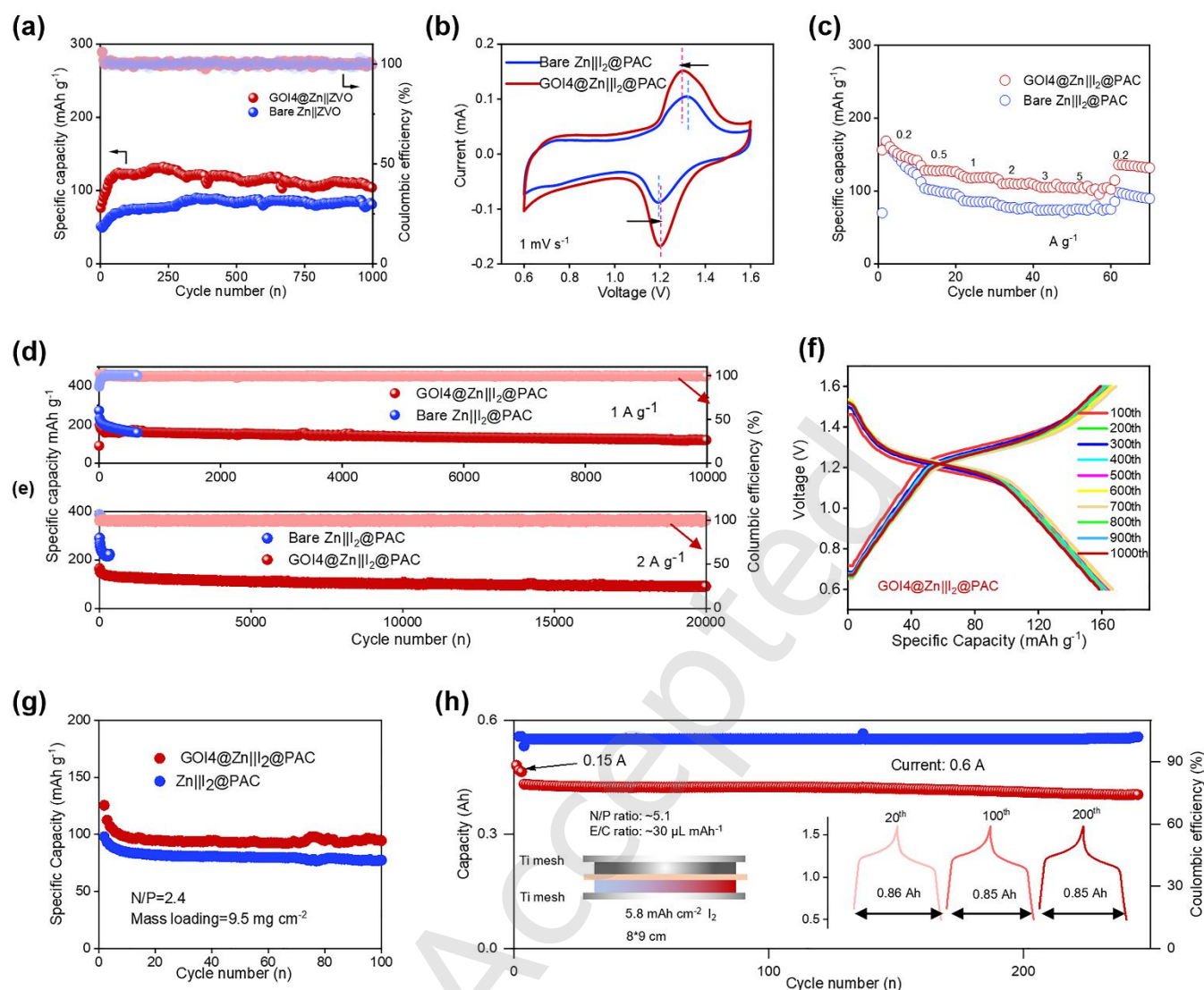


Figure 6 The electrochemical performance of full batteries and pouch cells. a) Cycling performances of Zn||ZVO and GOI4@Zn||ZVO at 1 A g⁻¹. b) The CV curve of GOI4@Zn||I₂@PAC and bare Zn||I₂@PAC at 1 mV s⁻¹. c) The rate performances of GOI4@Zn||I₂@PAC and Zn||I₂@PAC full cell. d, e) Cycling performances of Zn||I₂@PAC and GOI4@Zn||I₂@PAC at 1 A g⁻¹ and 2 A g⁻¹, respectively. f) Voltage profile of Zn||I₂@PAC and GOI4@Zn||I₂@PAC at 1 A g⁻¹. g) Cycling performances of Zn||I₂@PAC and GOI4@Zn||I₂@PAC at 0.1 A g⁻¹ based on low N:P and high loading. h) Cycling performances of pouch cell.

cell exhibits ultrastable cycling for 2700 h with smooth potential curves, while Zn||Zn symmetrical cell generates a sudden and irreversible voltage increase only after cycling for 80 h at a current density/capacity of 0.25 mA cm⁻²/0.25 mAh cm⁻². The SEM image of GOI4@Zn anode still exhibits relative smooth surface after 2700 h (Fig. 5(b)), proving the reversibility of oriented crystalline stacks during ultra-long stripping/plating process. When improving the current density (5 mA cm⁻²/1 mAh cm⁻²), GOI4@Zn can still deliver excellent reversible cycling behaviors (4000 h), as shown in Fig. 5(c). The superior results are attributed to fast ion conductivity given by protective layer enabling anode with remarkable kinetics, further demonstrated by rate performances (Fig. S18). Even at 50 mAh cm⁻²/50 mAh cm⁻², the longer cycling life with 3000 h is observed for GOI4@Zn, symmetrical cell compared to the pure Zn symmetrical cell (Fig 5(d)). If only using the HGG and MMT coating on the surface of Zn anode, the symmetrical batteries are failed at short time with large potential drift (Fig S19). In addition, to demonstrate the advantages of this structure, the

electrochemical performances of composite coatings with different inorganic/organic ratios are measured at 5 mA cm⁻²/1 mAh cm⁻² are presented in (Fig S20). Obviously, the Zn anode with composite coatings delivers inferior electrochemical performance. These results can be attributed to the fact that coating method is hardly binding the MMT and HGG, which suffers from weak tensile strength. In our work, the inner layer is MMT-dominated, but the less remained HHG in inner layer can act as binder to closely connect with MMT, contributing to strong flexible strength to accommodate the repeat volumetric change. The high energy density of batteries is associated with full use of metal anode, therefore, the reversibility test at high depth of discharge (DOD) of 85.4 % with 20 mAh cm⁻² was performed. As shown in Fig. 5(e), the GOI4@Zn anode stably cycles for over 400 h while pure Zn only operates for less 100 h, demonstrating its high feasibility for practical application. This achieved performance outperforms among state-of-art Zn-based batteries reported in previous works in Fig. 5(f) [36-43].

To illustrate the plating/stripping reversibility of Zn under SEI protection, coulombic efficiency (CE) measurements were performed by Zn||Cu asymmetric cells at a current density/capacity of $5 \text{ mA cm}^{-2}/1 \text{ mAh cm}^{-2}$. As shown in Fig. 5(g), the GOI4@Cu||Zn cell shows stable operation of 1375 cycles with an average CE of 99.3%, confirming its favorable durability and superior reversibility. However, the Zn||Cu cell only runs for 500 cycles with huge fluctuation of CE, indicating serious side reactions and dendrite growth. Since the inferior zincophilicity of Cu substrate, the total voltage hysteresis of GOI4@Cu is from 116 to 139 mV (Fig. 5(h)), which is much lower than those of bare Cu (from 400 to 800 mV) and maintains high reversibility (Fig. S21). Hence, the conclusion can be that the gradient organic-inorganic layer with Zn replenishment greatly regulates Zn deposition behavior, inhibits corrosion and accelerates Zn^{2+} transports responding to high-rate and stable GOI4@Zn anode.

2.6 Electrochemical Performances of Full Cells

To explore the practical application of GOI4@Zn anode, the full cells are assembled by coupling with ZVO and I_2 @PAC cathode. The SEM image and corresponding XRD patterns are shown in Fig. S22. The GOI4@Zn||ZVO full cell presents stable 1000 cycles with 110 mAh g^{-1} , while the Zn||ZVO presents lower capacity (80 mAh g^{-1}) (Fig. 6(a)). This trend is similar to the Zn|| MnO_2 full cell (23). To further evaluate the availability of GOI4@Zn, the full cell Zn|| I_2 @PAC was tested. From the CV curves at 1 mV s^{-1} , it can be seen that the GOI4@Zn|| I_2 @PAC cell exhibits higher current than that of I_2 @PAC||Zn full cell, indicative of enhanced interfacial reaction kinetic (Fig. 6(b)). The rate performances analysis was carried out from 0.2 A g^{-1} to 5 A g^{-1} (Fig. 6(c)). The specific SEI layer enables the full cell with 150 mAh g^{-1} at 0.2 A g^{-1} and 110 mAh g^{-1} at 5 A g^{-1} , whose superior results elucidate the fast ion transfer behaviors. When tested at 1 A g^{-1} , GOI4@Zn|| I_2 @PAC delivers a lifespan of 10000 cycles with a capacity of 123 mAh g^{-1} , while Zn|| I_2 @PAC cell fails quickly after 200 cycles, demonstrating that the GOI4 is responsible for the excellent cycling performance through suppressing the evolution of hydrogen and guiding the Zn^{2+} transfer process (Fig. 6(d)). The charge/discharge curves nearly are overlapped, indicative of the more excellent cycling performances compared to the fast fading of Zn|| I_2 @PAC (Fig. 6(f) and S24). To illustrate the feasibility of SEI advantages, the electrochemical performance of GOI4@Zn|| I_2 @PAC full battery was further evaluated at a higher current (Fig. 6(e)). The battery with GOI4@Zn as anode delivering an ultra-long life of 20000 cycles is realized for GOI4@Zn|| I_2 @PAC and its capacity still maintains 120 mAh g^{-1} with 87.5% capacity retention. The same trend is observed at 3 A g^{-1} , confirming the favorable merits promoting the stable Zn plating/stripping process (Fig. S25).

To further demonstrate practical application, we select I_2 @PAC as cathode with low N:P ratio and poor electrolyte, and then test the cycling stability of pouch cell. In $20 \mu\text{L}$ mAh^{-1} electrolyte (Fig. 6(g)), GOI4@Zn|| I_2 @PAC battery at low N:P (2.4:1) exhibits a long lifespan of 100 cycles with a high-capacity retention of 77.8%, while Zn|| I_2 @PAC suffers from lower capacity, demonstrating positive effect of protective layer on stability of anode. The pouch cell with a

capacity of $\sim 0.5 \text{ Ah}$ is measured at low current density of 0.15 A g^{-1} and still maintains a capacity of 0.43 Ah after 245 cycles with small capacity fading (Fig. 6(h)), which can light a LED (Fig. S26). Therefore, such thin SEI layer with gradient organic-inorganic to induce dense oriented crystalline Zn deposition bears practical potential and should be considered for the large-scale deployment of metal batteries.

3 Conclusion

In summary, a gradient layer with Zn^{2+} -rich replenishment was covered on the surface of Zn anode, where Zn-based MMT inorganic is mainly anchored below the organic HGG layer. This special configure can provide robust flexibility enabled by HGG and stiff strength gifted by MMT to improve volumetric change tolerance. The abundant Zn in GOI4 layer acts as nanofluidic concentrators for the efficient trapping and release of collected ions to inhibit concentration polarization, and its intrinsic -OH graft delivers rapid dynamic and adsorption sites. This design synergistically modulates the distribution of Zn^{2+} and sufficient ion supplement to ensure the uniformity of Zn^{2+}/Zn conversion. Leveraging these advantages, the GOI4@Zn||GOI4@Zn symmetric cell delivers an excellent cycling performance (3000 h) at an ultrahigh current density and capacity ($50 \text{ mAh cm}^{-2}/50 \text{ mA cm}^{-2}$). Additionally, the GOI4@Zn|| I_2 @PAC cell demonstrates stable cycling performance with a capacity retention rate of 87.5% after 20000 cycles at 2 A g^{-1} . The widespread production of GOI@Zn not only provides a convenient and cost-effective fabrication method but also ensures the stable deployment of the Zn anode.

Electronic Supplementary Material: Supplementary material (please provide the brief detail of the ESM) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94909106>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and/or the Electronic SupplementaryMaterial. Additional data related to this paper may be requested from the corresponding author upon request.

Acknowledgements

This work is funded by China Postdoctoral Science Foundation (2022TQ0285, 2023M733201), Modern Analysis and Gene Sequencing Center of Zhengzhou University and Southwest Jiaotong University. We thank Hongwei Tao for the SEM image characterization and Taeson for first principal calculation, and Yuxuan Yang for materials characterization.

Declaration of competing interest

There are no conflicts to declare.

Author contribution statement

We thank Hongwei Tao for the SEM image characterization and Taeson for first principal calculation, and Yuxuan Yang for materials characterization.

Use of AI statement

None.

References

- [1] Zhou, A.; Zhang, J.; Chen, M.; Li, X.; Li, S.; Ma, J.; Lv, T.; Zhu, X.; Feng, G.; Suo, L. Interface Preconstruction Enables Robust Passivation of the AhLevel Aqueous Li-ion Batteries. *J. Am. Chem. Soc.* **2025**, *147*, 11811-11820.
- [2] Wang, N.; Dong, X. L.; Wang, B. L.; Guo, Z. W.; Wang, Z.; Wang, R. H.; Qiu X.; Wang, Y. G.; Zinc-Organic Battery with a Wide Operation-Temperature Window from -70 to 150 °C. *Angew. Chem. Int. Ed.* **2020**, *59*, 14577-14583.
- [3] Cao, Z.; Zhuang, P.; Zhang, X.; Ye, M.; Shen J.; Ajayan, P. M. Strategies for Dendrite-Free Anode in Aqueous Rechargeable Zinc Ion Batteries. *Adv. Energy Mater.* **2020**, *10*, 2001599.
- [4] Cao, L.; Li, D.; Hu, E.; Xu, J.; Deng, T.; Ma, L.; Wang, Y.; Yang, X.-Q.; Wang, C. Solvation Structure Design for Aqueous Zn Metal Batteries. *J. Am. Chem. Soc.* **2020**, *142*, 21404-21409.
- [5] Cui, Y.; Zhao, Q.; Wu, X.; Chen, X.; Yang, J.; Wang, Y.; Qin, R.; Ding, S.; Song, Y.; Wu, J.; Yang, K.; Wang, Z.; Mei, Z.; Song, Z.; Wu, H.; Jiang, Z.; Qian, G.; Yang, L.; Pan, F. An Interface-Bridged Organic-Inorganic Layer that Suppresses Dendrite Formation and Side Reactions for Ultra-Long-Life Aqueous Zinc Metal Anodes. *Angew. Chem. Int. Ed.* **2020**, *59*, 16594-16601.
- [6] Hao, J.; Li, B.; Li, X.; Zeng, X.; Zhang, S.; Yang, F.; Liu, S.; Li, D.; Wu, C.; Guo, Z. An In-Depth Study of Zn Metal Surface Chemistry for Advanced Aqueous Zn-Ion Batteries. *Adv. Mater.* **2020**, *32*, 2003021.
- [7] Zheng, J.; Zhao, Q.; Tang, T.; Yin, J.; Quilty, C. D.; Renderos, G. D.; Liu, X.; Deng, Y.; Wang, L.; Bock, D. C.; Jaye, C.; Zhang, D.; Takeuchi, E. S.; Takeuchi, K. J.; Marschillok, A. C.; Archer, L. A. Reversible epitaxial electrodeposition of metals in battery anodes. *Science* **2019**, *366*, 645.
- [8] Qiu, H.; Du, X.; Zhao, J.; Wang, Y.; Ju, J.; Chen, Z.; Hu, Z.; Yan, D.; Zhou X.; Cui, G., *Nature Communications* **2019**, *10*, 5374.
- [9] Zhao, M.; Lv, Y.; Xu, Y.; Yang, H.; Bo Z.; Lu, J. Zinc anode-compatible in-situ solid electrolyte interphase via cation solvation modulation. *Nature Communications* **2025**, *16*, 2843.
- [10] Chen, H.; Zhang, W.; Yi, S.; Su, Z.; Zhao, Z.; Zhang, Y.; Niu B.; Long, D. Zinc iso-plating/stripping: toward a practical Zn powder anode with ultra-long life over 5600 h. *Energy Environ. Sci.* **2024**, *17*, 3146-3156.
- [11] Zhang, Y.; Wang, R.; Ao, H.; Ma, T.; Zhu, X.; Zhang, X.; Rong, J.; Zhou, Z.; Bai, Z.; Dou, S. X.; Wang, N.; Li, Z. Zn²⁺-Rich Chelate Layer Facilitates Ultrahigh-Rate Zinc Anodes Via Cation Compensation and Anion Repulsion. *Adv. Energy Mater.* **2025**, *15*, 2404203.
- [12] Wang, T.; Wang, Y.; Cui, Geng, P. H.; Wu, Y.; Hu, F.; You J.; Zhu, K. Constructing a gradient soft-coupled SEI film using a dilute ternary electrolyte system towards high-performance zinc-ion batteries with wide temperature stability. *Energy Environ. Sci.* **2025**, *18*, 2546-2558.
- [13] Li, A.; Hao, J.; Wu, K.; Chang, C.; Zhang, X.; Gan, H.; Tan, J.; Xie, T.; Zhou, F.; Wang, P.; Han, C.; Du, H.; Li, B.; Liu, Q. Turning Zn(PO₃)₂-Enriched Inorganic/Organic Hybrid Interfacial Chemistry with Chelating Ligands toward Robust Aqueous Zn Anodes. *ACS Nano* **2025**, *19*, 13016-13028.
- [14] Jiang, Z.; Fan, S.; Du, Z.; Zhang, W.; Chen, R.; Yang, H.; Chen, J.; Cui, Z.; Cui, F.; Zhang, G.; Zhu, C.; Lei, S.; He, G.; Yin, K.; Sun, L.; Gradient Interlayer Promotes Highly Stable Zn Metal Anodes for High-Performance Zn-Ion Batteries. *Adv. Funct. Mater.* **2026**, *36*, e24105.
- [15] Li, W.; Li, L.; Fu, X.; Hu, Y.; Deng, Y.; Innovative Design of a Double-Layer Gradient Coating for Dendrite-Free and Ultrastable Zinc Anodes. *Small* **2025**, *21*, 2411915.
- [16] Wang, Z.; Cao, J.; Yang, Z.; Cheng, J.; Liu, D.; Lei, W.; A Rigid-Soft Graded Organic-Inorganic Interlayer for Durable and Corrosion-Resistant Zinc Anodes. *Nano-Micro Let.* **2026**, *18*, 175.
- [17] Podsiadlo, P.; Kaushik, A. K.; Arruda, E. M.; Waas, A. M.; Shim, B. S.; Xu, J.; Nandivada, H.; Pumplun, B. G.; Lahann, J.; Ramamoorthy A.; Kotov, N. A. Ultrastrong and Stiff Layered Polymer Nanocomposites. *Science* **2007**, *318*, 80-83.
- [18] Gao, N.; Cui, M.; Xi, K.; Deng, T.; Yin, D.; He, J.; Cui, X.; Liu, L.; Li, W.; Ding, S.; Gao G.; Zhao, H. Elimination of Concentration Polarization Under Ultra-High Current Density Zinc Deposition by Nanofluid Self-Driven Ion Enrichment. *Adv. Mater.* **2025**, *37*, 2419034.
- [19] Wang, Y.; Chen, W.; Wang, F.; Li, X.; Zhang, Z.; Li W.; Wang, F. Covalent Anchoring of Mechanical Polymer for Highly Stable Zinc Metal Batteries. *Adv. Mater.* **2025**, *15*, 2500596.
- [20] Li, Y.; Zheng, X.; Carlson, E. Z.; Xiao, X.; Chi, X.; Cui, Y.; Greenburg, L. C.; Zhang, G.; Zhang, E.; Liu, C.; Yang, Y.; Kim, M. S.; Feng, G.; Zhang, P.; Su, H.; Guan, X.; Zhou, J.; Wu Y.; Xue, Z.; Li, W.; Bajdich M.; Cui, Y. In situ formation of liquid crystal interphase in electrolytes with soft templating effects for aqueous dual-electrode-free batteries. *Nature Energy* **2024**, *9*, 1350-1359.
- [21] Zeng, G.; Sun, Q.; Horta, S.; Martínez-Alanis, P. R.; Wu, P.; Li, J.; Wang, S.; Ibáñez, M.; Tian, Y.; Ci L.; Cabot, A. Modulating the solvation structure to enhance amorphous solid electrolyte interface formation for ultra-stable aqueous zinc anode. *Energy Environ. Sci.* **2025**, *18*, 1683-1695.
- [22] Wu, A.; Zhang, S.; Li, Q.; Xue, W.; Li, C.; Xi, B.; Mao, W.; Bao K.; Xiong, S. Multifunctional Crown Ether Additive Regulates Desolvation Process to Achieve Highly Reversible Zinc-Metal Batteries. *Adv. Energy Mater.* **2025**, *15*, 2404450.
- [23] Luo, J.; Xu, L.; Yang, Y.; Huang, S.; Zhou, Y.; Shao, Y.; Wang, T.; Tian, J.; Guo, S.; Zhao, J.; Zhao, X.; Cheng, T.; Shao Y.; Zhang, J. Stable zinc anode solid electrolyte interphase via inner Helmholtz plane engineering. *Nature Communications* **2024**, *15*, 6471.
- [24] Nian, Q.; Luo, X.; Ruan, D.; Li, Y.; Xiong, B.-Q.; Cui, Z.; Wang, Z.; Dong, Q.; Fan, J.; Jiang, J.; Ma, J.; Ma, Z.; Wang, D.; Ren, X. Highly reversible zinc metal anode enabled by strong Brønsted acid and hydrophobic interfacial chemistry. *Nature Communications*, **2024**, *15*, 4303.
- [25] Cheng, M.; Li, D.; Cao, J.; Sun, T.; Sun, Q.; Zhang, W.; Zha, Z.; Shi, M.; Zhang, K.; Tao, Z. Anions-in-Colloid” Hydrated Deep Eutectic Electrolyte for High Reversible Zinc Metal Anodes. *Angew. Chem. Int. Ed.* **2024**, *63*, e202410210.
- [26] Li, C.; Zhang, X.; Qu, G.; Zhao, S.; Qin, H.; Li, D.; Li, N.; Wang C.; Xu, X. Highly Reversible Zn Metal Anode Securing by Functional Electrolyte Modulation. *Adv. Energy Mater.* **2024**, *14*, 2400872.
- [27] Ma, W.; Wang, S.; Wu, X.; Liu, W.; Yang, F.; Liu, S.; Jun, S. C.; Dai, L.; He Z.; Zhang, Q. Tailoring desolvation strategies for aqueous zinc-ion batteries. *Energy Environ. Sci.* **2024**, *17*, 4819-4846.
- [28] Wang, C.; Gong, Z.; Yuwono, J. A.; Meng, Q.; Lyu, Y.; Zhang, S.; Xia, S.; Zeng, X.; Cullen, P. J.; Mao, J.; Guo, Z.; Pei, Z. Ligand-channel-induced ion liberation in crowded zwitterionic hydrogel electrolyte for efficient zinc metal batteries. *Nature Communications* **2025**, *16*, 11069.
- [29] Zhao, Y.; He, J.; Han, X.; Tian, X.; Deng, M.; Chen, W.; Jiang, B.; Modification of hydroxypropyl guar gum with ethanolamine. *Carbohydrate Polymers* **2012**, *90*, 988.
- [30] Wang, X.; Song, Y.; Wu, P.; Zhang, G.; Guo, J.; Li, Y. Rheological properties of hydroxypropyl guar gum fracturing fluids: Effects of cross-linking agents. *Carbohydrate Polymers* **2025**, *366*, 123837.
- [31] Zhang, F.; Liao, T.; Qi, D.-C.; Wang, T.; Xu, Y.; Luo, W.; Yan, C.; Jiang L.; Sun, Z. Zn-ion ultrafluidity via bioinspired ion channel for ultralong lifespan Zn-ion battery. *Natl Sci Rev* **2024**, *11*, nwae199.
- [32] Wang, L.; Zhang, B.; Zhou, W.; Zhao, Z.; Liu, X.; Zhao, R.; Sun, Z.; Li, H.; Wang, X.; Zhang, T.; Jin, H.; Li, W.; Elzatahry, A.; Hassan, Y.; Fan, H. J.; Zhao, D.; Chao, D.; Tandem Chemistry with Janus Mesopores Accelerator for Efficient Aqueous Batteries. *J. Am. Chem. Soc.* **2024**, *146*, 6199.
- [33] Zheng, Z.; Zhong, X.; Zhang, Q.; Zhang, M.; Dai, L.; Xiao, X.; Xu, J.; Jiao, M.; Wang, B.; Li, H.; Jia, Y.; Mao R.; Zhou, G. An extended substrate screening strategy enabling a low lattice mismatch for highly reversible zinc anodes. *Nature Communications* **2024**, *15*, 753.
- [34] Wu, Z.; Song, Y.; Guo, H.; Xie, F.; Cong, Y.; Kuang, M.; Yang, J. Tandem catalysis in electrocatalytic nitrate reduction: Unlocking efficiency and mechanism. *Interdisciplinary Materials* **2024**, *3* (2), 245-269.
- [35] Li, C.; Jia, K.; Liang, Q.; Li, Y.; He, S. Electrochemical biosensors and power supplies for wearable health-managing textile systems. *Interdisciplinary Materials* **2024**, *3* (2), 270-296.
- [36] Liu, H.; Li, Z.; Sui, B. B.; Bao, Q. P.; Wang, P. F.; Gong, Z.; Zhang,

Y. H.; Wu, Y. H.; Shi, F. N.; Zhou M. D.; Zhu, K. Calcium Alginate Hydrogel Coating Comprehensively Optimizes Zn Deposition Behavior of Aqueous Zinc-Ion Batteries Anode. *Industrial & Engineering Chemistry Research* **2024**, 63, 13611-13622.

[37] Yang, C.; Fang, Z. Y.; Wen, X. Y.; Zhong, C. A.; Ou, J. K. Nitrogen doped carbon nanotube interface modified coating provides stable zinc anode for aqueous zinc ions. *Journal of Alloys and Compounds* **2025**, 1016, 178959

[38] Li, X. W.; Ye, P.; Dou, A. C.; Jiang, Z. Y.; Naveed, A.; Zhou, Y.; Su, M. R.; Zhang P. P.; Liu, Y. J. Nanoporous Nb₂O₅ coatings enabled long-life and deeply rechargeable zinc anodes for aqueous zinc-ion batteries. *Journal of Energy Storage* **2024**, 76, 109874.

[39] Chen, X. J.; Li, W.; Hu, S. S.; Akhmedov, N. G.; Reed, D.; Li X. L.; Liu, X. B. Polyvinyl alcohol coating induced preferred crystallographic orientation in aqueous zinc battery anodes. *Nano Energy* **2022**, 98, 107269.

[40] Wan, Z. M.; Zhou, W. H.; Chen, Z.; Wang, J.; Feng, H. Y.; Sheng, L.; Feng, J. R.; Hao, Z. X., Construction of Metal-Organic Interface Layers via Highly Expandable Wet Etching for High Stability Zinc Anode. *Small* **2025**, 21, 2502128.

[41] Li, G. J.; Zhao, Z. H.; Zhang, S. L.; Sun, L.; Li, M. N.; Yuwono, J. A.; Mao, J. F.; Hao, J. N.; Vongsivut, J.; Xing, L. D.; Zhao C. X.; Guo, Z. P. A biocompatible electrolyte enables highly reversible Zn anode for zinc ion battery. *Nature Communications* **2023**, 14, 6526.

[42] Han, W. Y.; Tan, Y. H.; Ni, L. P.; Sun, X. M.; Li, K. Z.; Lu, L. L.; Zhang, H. Sn Penetrated Zincophilic Interface Design in Porous Zn Substrate for High Performance Zn-Ion Battery. *Small Methods* **2025**, 9, 2401499.

[43] Wang, H. N.; Wang, P. T.; Yu, K. F.; Wang, X. F.; Cao, J. P.; Jia, P. C.; Yuan Y. Z.; Liang, C. Constructing a rapid ion-transport anode interface protective layer for zinc ion batteries to suppress solvation and improve surface electronic structure. *Chemical Engineering Journal* **2024**, 485, 149544.

Electronic Supplementary Material

Zn-ion ultrafluidity by coupling ion-sieving and Zn ion replenishment for highly reversible Zn-metal anode chemistry

Taesoon Hwang^{2,§}, Hongwei Tao^{3,§}, Yuxuan Yang¹, and Qianzheng Jin¹  

¹ Zhengzhou University, Zhengzhou 450001, China

² Department of Materials Science and Engineering, University of Texas at Dallas, Richardson 75080, Texas, USA

³ Institute of Smart City and Intelligent Transportation, Southwest Jiaotong University, Chengdu 611756, China

[§] Taesoon Hwang and Hongwei Tao contributed equally to this work.

 Address correspondence to qzjin@zzu.edu.cn

Supporting information to <https://doi.org/10.26599/NR.2026.94909106>

Experiments:

Materials:

Zn(OTf)₂ (98%), hydroxymethyl guar gum (HGG, 98%), Glutaraldehyde (25%), CMC and PVDF (98%), purchased from Aladdin Ltd. V2O5 (99%) and iodide (I₂, >99.8%) were purchased from Shanghai Macklin Biochemical Technology Co., Ltd. The carbon papers were purchased from Nanjing XFNANO. Glass fibers were purchased from Whatman. Zn foil was purchased from Sinopharm Chemical Reagent Co., Ltd. Ketjen black, Ti foil (99.9%) were purchased from Canrud. Zn-based montmorillonitewere (98%) was purchased from Bidepharm Ltd. Porous activated carbon (PAC) was purchased from Sinopharm Chemical Reagent Co., Ltd.

The preparation of GOIs@Zn, HGG@Zn and MMT@Zn.

The GOIs@Zn electrode was synthesized by spinning the solution containing Zn-based MMT (Zn-MMT) and HGG on the surface of Zn foil and then dried at 60 °C for overnight. According to the weight ratio of HGG to MMT, the products are assigned as GOI2@Zn, GOI4@Zn and GOI6@Zn at 2:1, 4:1 and 6:1, respectively. The HGG@Zn and MMT@Zn are prepared using the same method.

The preparation of CCs@Zn.

The CCs@Zn electrode was synthesized by spinning the solution containing Zn-based MMT (Zn-MMT) and HGG on the surface of Zn foil through stepwise method, where Zn-based MMT is first spined and then dried at 60 °C for overnight, and then HGG is spined and dried. According to the weight ratio of HGG to MMT, the products are assigned as CC2@Zn, CC4@Zn and CC6@Zn at 2:1, 4:1 and 6:1, respectively.

The preparation of I₂@PAC

The loading of I₂ was conducted by the melt-diffusion method. First, I₂ was mixed with porous activated carbon (PAC) in a mass ratio of 2:1. After fully grinding, the mixture was transferred into the tube furnace and heated for 10 h at 115 °C in Ar atmosphere. Finally, the I₂@PAC was obtained. I₂ cathode contents is 67.2 wt%.

Materials characterization:

The surface morphologies of materials were observed by field emission scanning electron microscope (FESEM) with energy dispersive spectrometer (EDS). The crystal pattern was analyzed by X-ray diffraction (XRD). The chemical states and chemical compositions were characterized by X-ray photoelectron spectroscopy (XPS), Fourier Transform Infrared Spectrometer (FTIR). The mechanical properties and surface potential could be accurately analyzed using atom force microscopy (AFM) with Kelvin probe force microscopy model and Force modulation model. The HER activity of zinc anode is investigated by differential electrochemical mass spectrometry (DEMS). The wettability of materials is obtained by the contact angles measurements.

Electrochemical characterization:

The symmetric and asymmetric batteries were assembled by using Zn foil, glass fiber separator, and Ti foil to test the stability and morphologies using Land Battery Test System. The cathode was prepared by mixing active materials with Ketjen black and CMC in a fixed ratio of 70:20:10 coated on the carbon paper. The Zn_{0.25}V₂O₅ (ZVO) was prepared according to the previous

paper¹. Layered MnO₂ nanodots was prepared according to the previous paper². The active mass loadings of I₂@PAC and ZVO in button cell are 2-3 mg cm⁻², and electrolytes added to the cells is 60 μ L. For the pouch cell with 2 cm*3 cm, we selected thin Zn foil as anode, I₂@PAC cathode with 7.5 mAh was placed on either side with a fixed N/P ratio of 2.4 with 60 μ L the electrolytes, and the pouch cell was tested by galvanostatic charge/discharge method at 0.1 A g⁻¹. The corrosion potential and current were analyzed by conducting a linear polarization method from 0.2 V to -0.2 V with a scan rate of 1 mV s⁻¹ in symmetric Zn||Zn batteries. The EIS data were carried out at a frequency range from 100 kHz to 0.1 Hz. The active energy was obtained by fitting the interfacial impedances tested at different temperatures ranged from 10 °C to 60 °C. The voltage ranges are 0.3-1.5 V in Zn||ZVO batteries, and 0.5-1.6 V in Zn||I₂@PAC batteries.

The accurate Aurbach CE test was performed in Zn||Cu cells, which can avoid the influence of the Cu substrate on the result. Specifically, 2 mA h cm⁻² Zn was deposited onto the Cu foil at 0.5 mA cm⁻², and then fully stripped to 0.5 V. Subsequently, 2 mA h cm⁻² (Q_r) of Zn was plated onto the substrate, followed by repeated Zn stripping/plating cycles at a constant capacity of 0.5 mA h cm⁻² (Q_c) and current density of 0.5 mA cm⁻² for 20 cycles (n). Finally, the cells were charged to 0.5 V (Q_s). The Aurbach CE value can be calculated using eq 1.

$$\text{Average CE} = \frac{nQ_c + Q_s}{nQ_c + Q_r} \quad \text{eq 1}$$

In-situ electrochemical digital holography (EDH)

EDH was tested by using quartz colorimetric dishes to build symmetrical batteries, and the cells were charged at 10 mA cm⁻². The side where electrodeposition occurs was observed. The holographic monitoring system was employed to observe Zn deposition in a symmetric cell using a 2M ZnSO₄ electrolyte. The counter electrode was a bare Zn electrode, while the working electrode was different Zn plates. The digital holography method utilized a Mach-Zehnder interferometer optical setup and was explained in a previous publication. A charge coupled device (CCD) camera was utilized to document the dynamic processes. The zinc/solution interface holograms for various plating times were analyzed using numerical methods. when Zn is electrodeposited, the change of the ion concentration on the liquid side of the electrode/electrolyte interface results in changes in the refractive index of the electrolyte (Δn), and interference fringes will appear on the hologram when the following condition is satisfied:

$$\Delta n = (2i+1)\lambda/2d \quad \text{eq 2}$$

where i is an integer representing the order of the fringe, λ is the wavelength of the laser light, and d is the thickness of the solution layer in which the concentration changes in the direction of the optical axis. After the numerical reconstruction, the interference fringes are connected to the phase maps, which can visually and dynamically present the relevant ion concentration evolution of the diffusion layer during the deposition process. Chemical reactions may alter the concentration of certain species in the solution during deposition, deposit formation, and surface passivation film on the electrode surface. Such phase changes result in phase changes that can be numerically described. At this very moment, the relationships among the concentration change of the electrolyte (ΔC), the refractive index variation (Δn) and the phase difference ($\Delta\Phi$) at the electrode/electrolyte interface are as follows:

$$\Delta C = k\Delta n = k(\lambda/2\pi d) \Delta\Phi \quad \text{eq 3}$$

The theoretical calculation:

To investigate transition states and minimum-energy path-ways of atom transfer, we used the climbing-image nudged elastic band (CI-NEB) method. In particular, we used 7 images (including initial and final states) to model Zn atom transfer through PVA, Zn-MMT and OIS-SEI. The convergence parameters for the electronic and ionic relaxation during the CI-NEB calculation were 10⁻⁵ eV and -0.02 eV/Å, respectively. During a CI-NEB trajectory, we keep the volume and shape of the supercell fixed to that of the initial state (only atomic coordinates relaxed). The vacuum slab models are used to calculate the adsorption of different species on Zn (002), (101), and (100) planes. These Zn slabs comprise four layers Zn atoms in 3×3 super cell, and the top two-layer atoms are releasable during the geometry optimization. The adsorption energy (E_{abs}) is calculated using the following equation:

$$E_{abs} = E_{total} - (E_{surface} + E_{adsorbate})$$

where E_{total}, E_{surface}, and E_{adsorbate} represent the total energy of the Zn facets combined with different species, Zn facet, and electrolyte species, respectively.

The simulation of electrochemical behaviors:

Utilizing the COMSOL Multiphysics 6.3 software, the finite element analysis was conducted to scrutinize the ion flux, electrical field distribution and electrochemical behavior of Zn²⁺. In the two-dimensional geometric simulations model for Zn²⁺ deposition, to simulate the growth of dendrite, we use phase-field approach through solved the following equations based on general PDE and a time dependent solver.

$$\frac{\partial \xi_1}{\partial t} = -L_{\xi_1} * [g'(\xi_1) - k\nabla^2 \xi_1] - L_{\eta} * h'(\xi_1) * \left\{ \exp\left[\frac{(1-\alpha)nF\eta}{RT}\right] - \frac{c}{c_0} * \exp\left[\frac{-\alpha nF\eta}{RT}\right] \right\} \quad (1)$$

$$\frac{\partial \xi_2}{\partial t} = -L_{\xi_2} * [g'(\xi_2) - k\nabla^2 \xi_2] - \max\{-h'(\xi_1) * h'(\xi_2) * \left\{ \exp\left[\frac{(1-\alpha)nF\eta}{RT}\right] - \frac{c}{c_0} * \exp\left[\frac{-\alpha nF\eta}{RT}\right] \right\} * b * \frac{\partial \xi_2}{\partial x}\} \quad (2)$$

$$\frac{\partial c}{\partial t} = \nabla \left[D^{\text{eff}} \nabla c + \frac{D^{\text{eff}} c n F \varphi}{RT} \right] - c_s \frac{\partial \xi_1}{\partial t} \quad (3)$$

$$\nabla [\sigma^{\text{eff}} \nabla \varphi] = n F c_s \frac{\partial \xi_1}{\partial t} \quad (4)$$

The system size is chosen to be $6 \times 6 \mu\text{m}^2$. The mesh size is applied manually, and the maximum element size is set to be $0.05 \mu\text{m}$. Dirichlet boundary conditions are applied to solve the Zn^{2+} concentration ($C_{\text{Zn}^{2+}}$) and electric potential (φ), while zero flux boundary conditions are applied for order parameters ξ_1 and ξ_2 . The value of φ is set to be -0.2 V at the anode (left boundary) and 0 V at the right boundary of the half-cell, whereas the value of $C_{\text{Zn}^{2+}}$ is set to be 2 mol L^{-1} at the right boundary (Supplementary Fig.1). The initial value of the Zn^{2+} concentration in the electrolyte solution is assumed to be 2 mol L^{-1} . The temperature is 298 K .

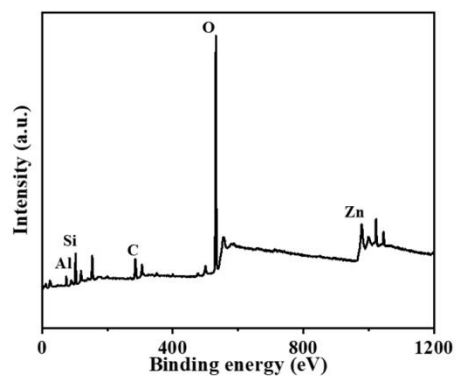


Fig. S1 The full XPS curve of Zn-MMT.

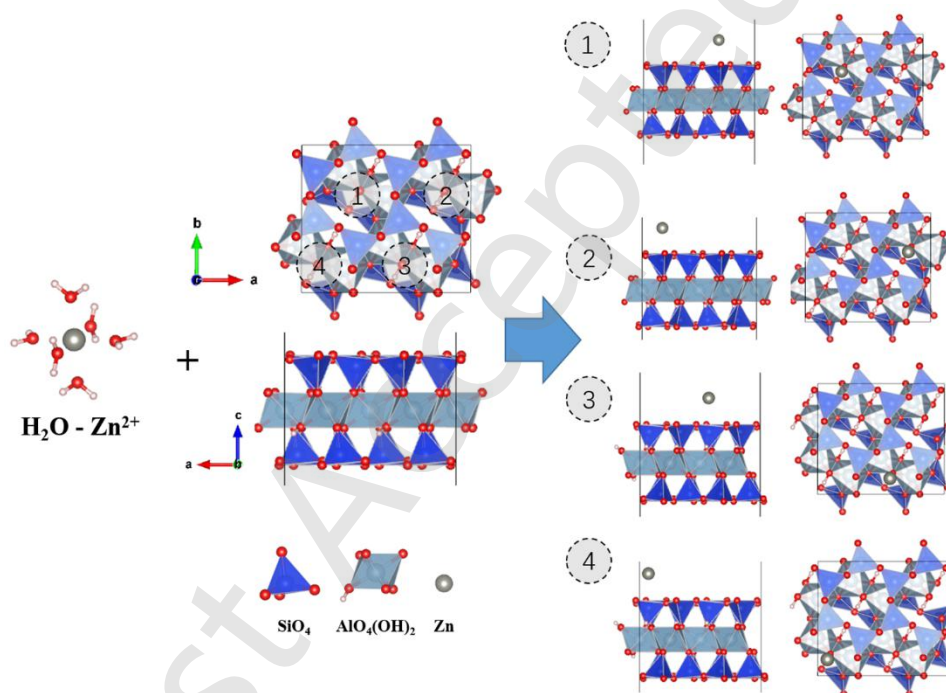


Fig. S2 The possible existing sites of Zn^{2+} in Zn-MMT.

Based on ELF, there are 4 sites for Zn adsorption. All cases are ~ -10.7 eV/f.u. Zn adsorption on MMT is very stable, and spontaneous reaction (promoted).

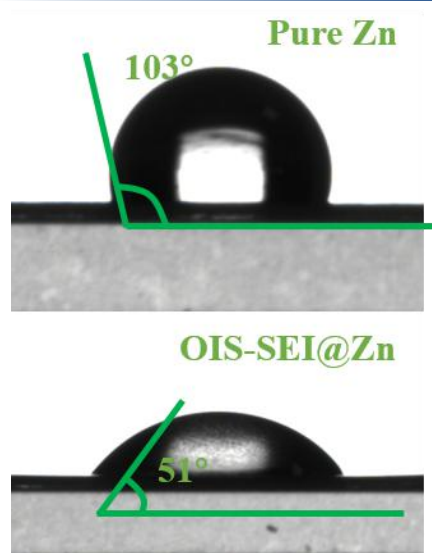


Fig. S3 The contact angles of OIS-SEI@Zn and bare Zn electrode.

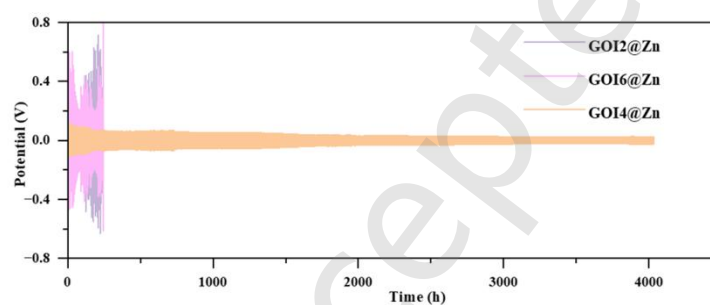


Fig. S4 The cycling performances of GOI2@Zn, GOI4@Zn, GOI6@Zn at $5 \text{ mA cm}^{-2} / 1 \text{ mAh cm}^{-2}$.

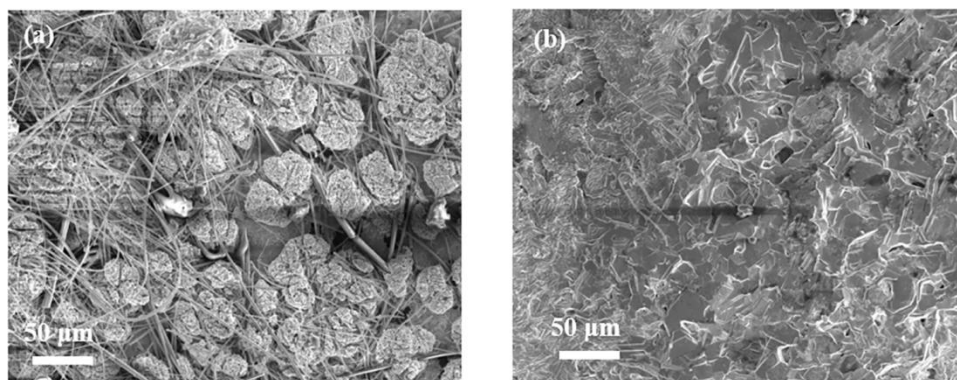


Fig. S5 The SEM images of bare Zn (a) and GOI4@Zn (b) after 400 h.

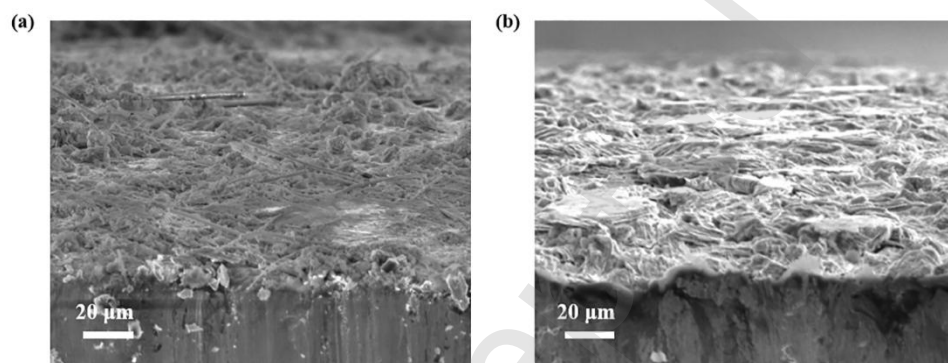


Fig. S6 The SEM images of bare Zn and Zn anode (a) after exploiting GOI4 layer (b) after 400 h.

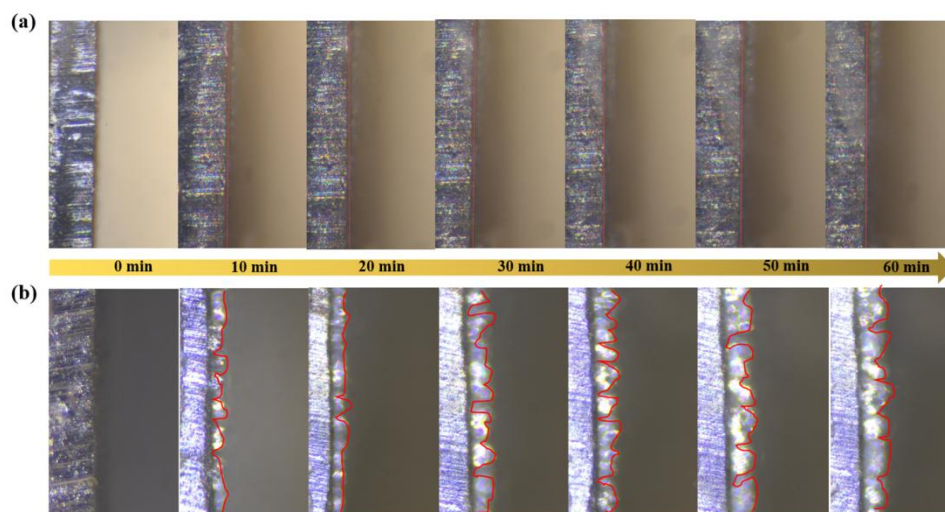


Fig. S7 The in-situ optical microscopy of GOI4@ Zn and bare Zn at 5 mA cm⁻².

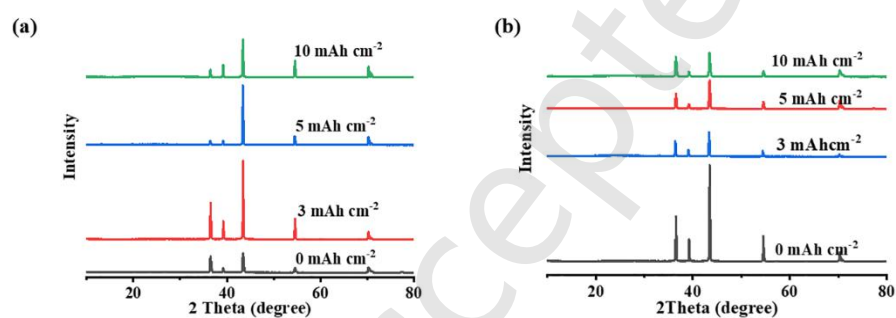


Fig. S8 The XRD patterns of bare Zn (a) and GOI4@Zn (b) at different deposition capacities.

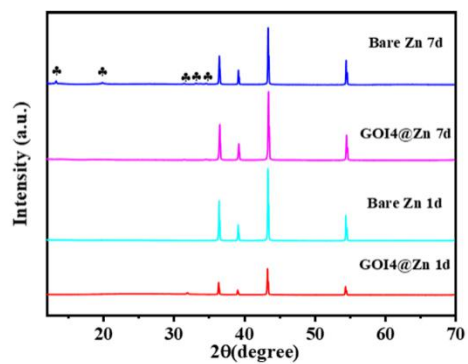


Fig. S9 The XRD patterns GOI4@Zn and Zn soaking in 2M $\text{Zn}(\text{OTf})_2$ electrolyte at different days.

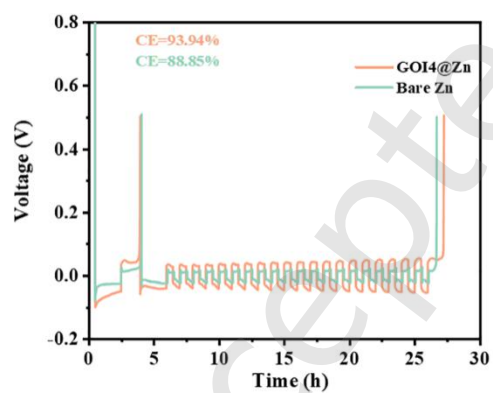


Fig. S10 Columbic efficiency of GOI4@Zn||Cu and Zn||Cu cells tested using the Aurbach method.

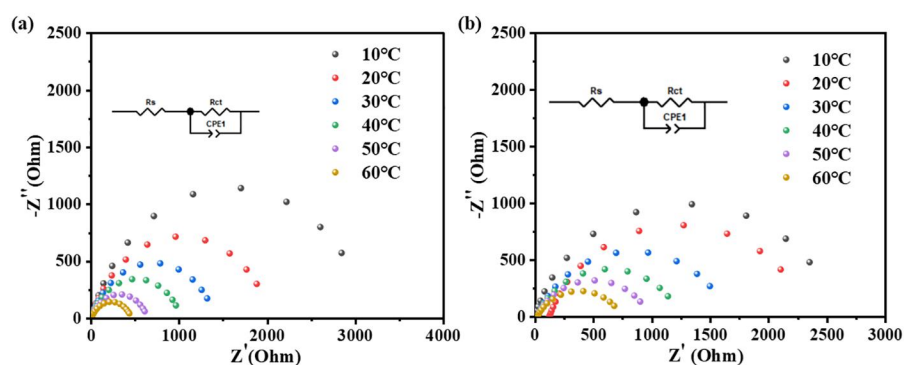


Fig. S11 The EIS curves at different temperatures for GOI4@Zn||GOI4@Zn (a) and Zn||Zn (b).

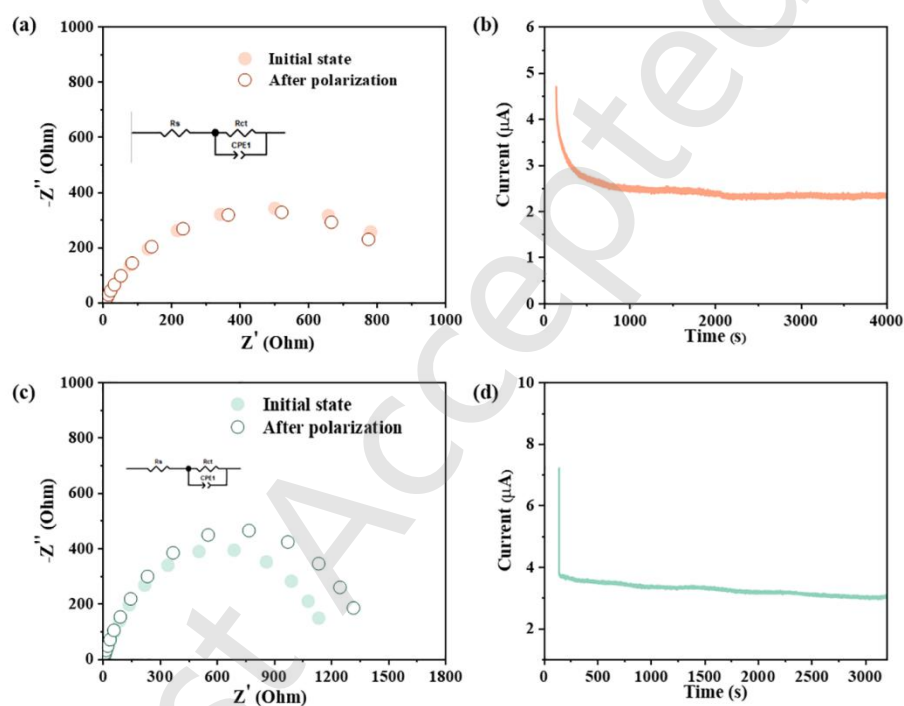


Fig. S12 The EIS curves of GOI4@Zn||GOI4@Zn (a) and Zn||Zn (c) after initial state and after polarization. The CA curves of GOI4@Zn||GOI4@Zn (b) and Zn||Zn (d) at 10 mV.

Note: The measured metal anode is soaked in electrolyte for several days.

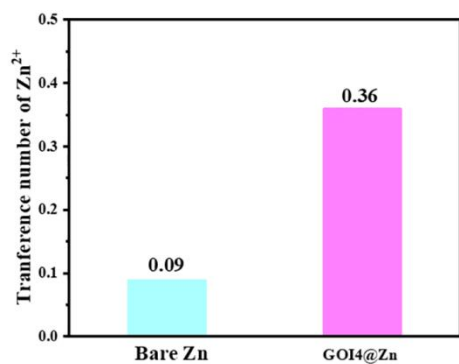


Fig. S13 The transfer numbers of GOI4@Zn||GOI4@Zn and Zn||Zn.

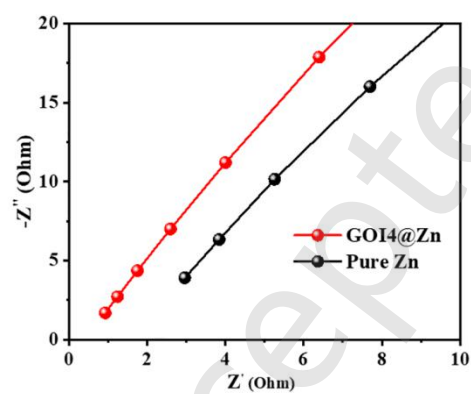


Fig. S14 The EIS curves of GOI4@Zn||stainless steel and Zn||stainless steel.

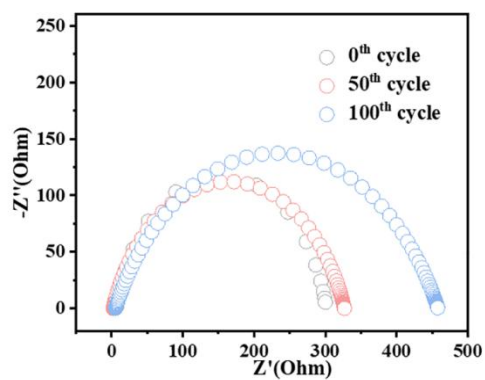


Fig. S15 The EIS curves of symmetrical cell Zn||Zn at different cycles.

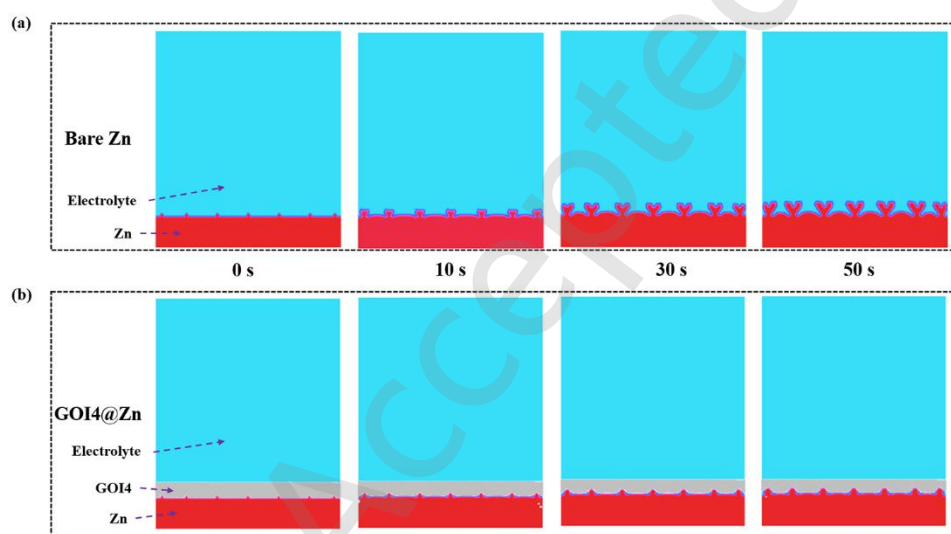


Fig. S16 The Comsol multiphysics is applied to simulate the deposition behaviors for bare Zn (a) and GOI4@Zn (b) symmetrical batteries.

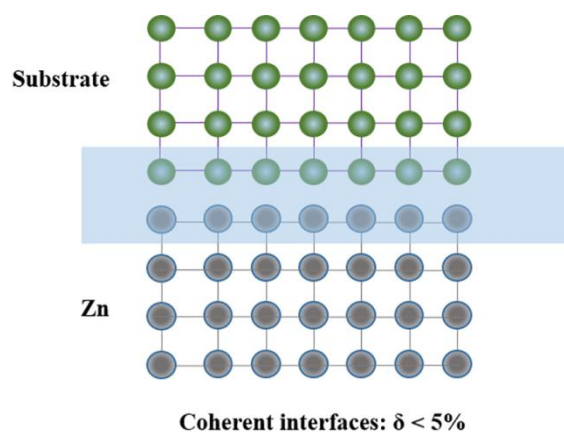


Fig. S17 The Low lattice mismatch δ of Zn and Zn-MMT.

Support notes 1

$$\text{Low lattice mismatch } \delta = \frac{d_{\text{substrate}} - d_{\text{epilayer}}}{d_{\text{epilayer}}} = \frac{d_{\text{substrate}} - d_{\text{zn(002)}}}{d_{\text{zn(002)}}}$$

If $d_{\text{substrate}}:d_{\text{zn(002)}} = 1$, the match of substrate to Zn(002) is perfect.

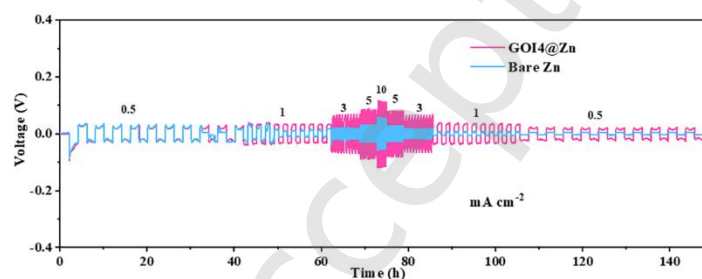


Fig. S18 The rate performances of symmetrical cell of GO14@Zn and bare Zn.

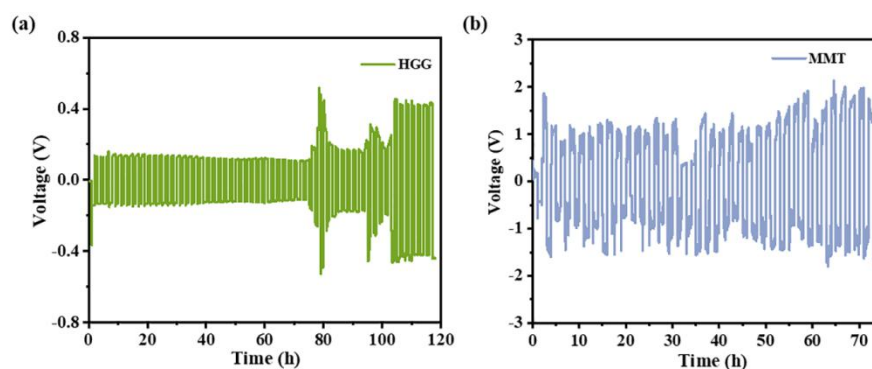


Fig. S19 The cycling performances of symmetrical cell HGG@Zn and MMT@Zn at $1 \text{ mA cm}^{-2}/1 \text{ mAh cm}^{-2}$.

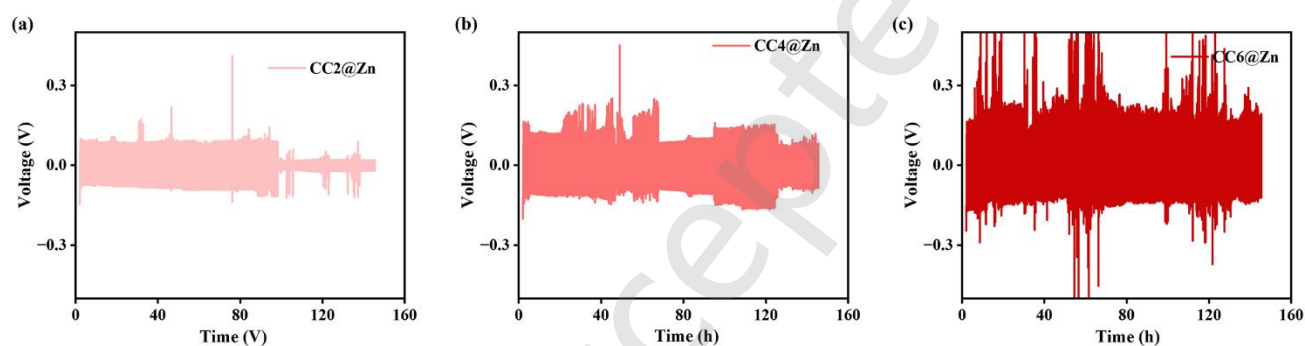


Fig. S20 The cycling performances of CC2@Zn, CC4@Zn, CC6@Zn at $5 \text{ mA cm}^{-2}/1 \text{ mAh cm}^{-2}$.

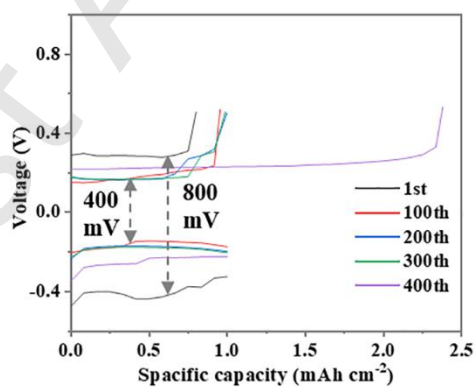


Fig. S21 The cycling performances of asymmetrical cell bare Zn||Cu at $5 \text{ mA cm}^{-2}/1 \text{ mAh cm}^{-2}$.

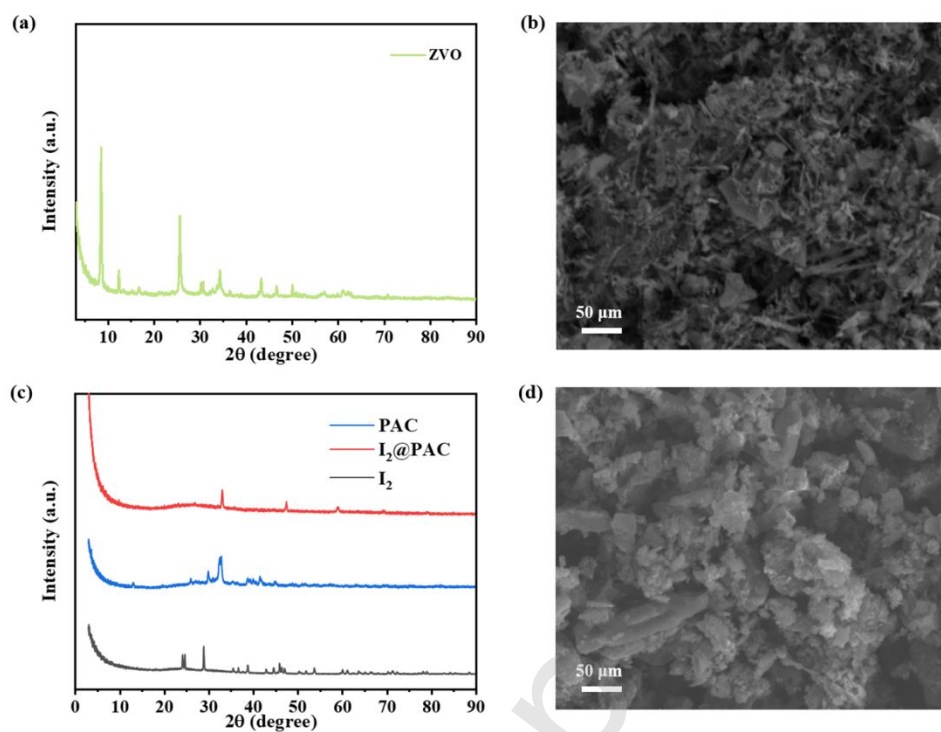


Fig. S22 The XRD patterns of ZVO (a), $I_2@PAC$, and I_2 , respectively (d). The SEM images of ZVO (c) and $I_2@PAC$ (d).

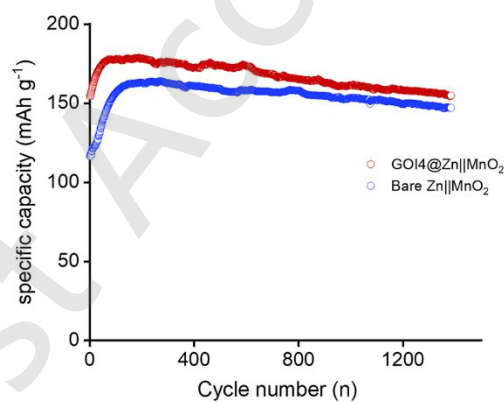


Fig. S23 The cycling performances of Bare Zn||MnO₂ and GOI4@Zn||MnO₂ at 1 A g⁻¹.

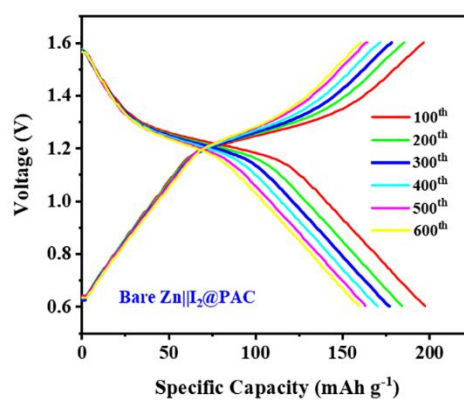


Fig. S24 The charge/discharge curves of GOI4@Zn||I₂@PAC full cell at 1 A g⁻¹.

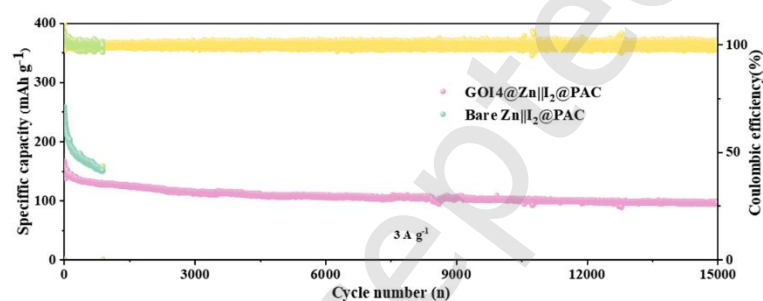


Fig. S25 The cycling performances of GOI4@Zn||I₂@PAC and bare Zn||I₂@PAC full cell at 3 A g⁻¹.

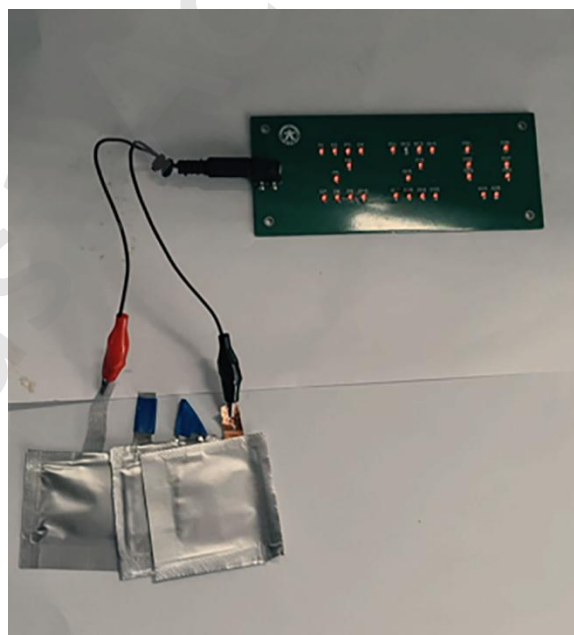


Fig. S26 The pouch cell can light a LED.

Table S1 The elemental content ratio of GOI4.

Elemental content				
	Zn	O	Si	Al
GOI4	5	57	16	21

Table S2 The ratio of Zn₀₀₂ to Zn₁₀₀ at different deposition capacities for GOI4@Zn and bare Zn.

Depositing capacity (mAh cm ⁻²)				
	0	3	5	10
GOI4@Zn	2.03	2.72	3.39	3.89
Zn	2.03	2.03	1.05	0.61

Reference

- [1] Z. Zhu, H. Lu, D. Zhang, X. Jiang, C. Duan, Y. Qin, X. Yuan, Y. Jin, Journal of Energy Storage 2024, 92, 112211.
- [2] Tang H, Chen W, Li N, Hu Z, Xiao L, Xie Y, et al. Layered MnO₂ nanodots as high-rate and stable cathode materials for aqueous zinc-ion storage. Energy Storage Materials 2022, 48: 335-343.