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Spontaneous passivation of selective Zn(101) plating via dangling bond saturation and electrostatic interaction regulation for high-utilization, fast-kinetics zinc anodes†

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Although Zn(101) exhibits faster Zn²⁺ plating/stripping kinetics and stronger bonding with Zn²⁺ compared to Zn(002), the application of Zn(101) in Zn batteries has been limited due to its higher reactivity with water. However, a novel approach utilizing spontaneous self-passivation of plated Zn(101) offers the potential to harness its favorable kinetics and stronger Zn-Zn bonding for battery applications. Here, we present a high-utilization and fast-kinetics Zn anode by promoting selective (101) facet growth and achieving spontaneous passivation of the underlying Zn plating. A non-stoichiometric Sn-O system is selected as the modification material because of its ability to engineer crystal structures (amorphous, rutile, and layered) and manipulate electrical polarity (n-type vs. p-type). The optimized p-type SnO_{1.17} saturates dangling bonds of Zn(101), benefiting the preferential growth of well-aligned Zn(101) planes. Besides, the Zn²⁺ plating location is altered underlying the interphase due to synergetic effects of lower Zn²⁺ migration barriers of the layered structure and electron-blocking properties of SnO_{1.17}. Consequently, a high Zn utilization ratio of over 91.5% is achieved in 800 hours, with an impressively low overpotential of 43 mV. Furthermore, an anode-free system combining a ZnMn₂O₄ cathode and a SnO_{1 17}@Cu anode retained 81.6% capacity after 200 cycles.

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Broader context

Inducing (002)-oriented Zn²⁺ plating has been widely explored as an effective strategy for achieving reversible Zn²⁺ plating/stripping, largely due to its resistance to water-triggered parasitic reactions. However, the weak bonding between Zn2+ and the Zn(002) plane often leads to lattice distortion at high Zn plating amounts. Furthermore, the slower mass transfer at Zn(002) can result in sluggish Zn²⁺ plating/stripping kinetics. In contrast, the Zn(101) plane offers faster mass transfer kinetics and stronger Zn²⁺ bonding; yet, its high reactivity towards water has limited its application. To leverage the advantages of Zn(101) while maintaining electrochemical stability, we constructed a SnO_{1.17} interphase on the anode. This interphase guided Zn²⁺ plating beneath its structure with a regulated (101) orientation, effectively isolating the (101)-oriented Zn from water molecules and eliminating water-triggered parasitic reactions. The SnO_{1,17} interphase further facilitates rapid Zn²⁺ transfer and provides low polarization, reducing voltage hysteresis during cycling. Additionally, the stronger interaction between Zn2+ and the Zn (101) plane prevents lattice distortion even at high Zn plating amounts, resulting in well-aligned Zn(101) planes. This study underscores the potential of oriented Zn²⁺ plating along the (101) facet to achieve a high Zn utilization ratio and superior Zn anode kinetics.

Introduction

Zn ion batteries (ZIBs) with mild aqueous electrolytes (i.e., ZnSO₄) have been considered grid-level energy storage solutions due to their high theoretical capacity (820 mA h g⁻¹), resource abundance, and eco-friendliness. 1-3

However, the uncontrollable Zn dendrite growth, hydrogen evolution reaction (HER), and corrosion severely limit the

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reversibility and lifespan of ZIBs.4,5 These issues are more detrimental to practical ZIBs, which require a negative/positive (N/P) capacity ratio lower than 1.08 (referenced to the commercialized lithium-ion batteries, LIBs).6,7 A Zn utilization ratio (ZUR) higher than 80% is the prerequisite to realize this low N/ P ratio. The low ZUR and poor reversibility significantly undermine the advantages of ZIBs compared to alternative technologies such as lithium-ion and sodium-ion batteries. The characteristics of plated Zn, which are normally dominated by the crystallographic (002), (100), and (101) facets of hexagonal close-packed Zn, are highly correlated to the Zn stripping/ plating behaviors and concomitant side reactions. 9-11 According to the Gibbs-Curie-Wulff theorem, the (002) facet of Zn metal has a lower reactivity towards water and a slower growth rate due to the lower surface energy compared to that of the (001) and (101) facets. 12,13 Therefore, attention has been focused on inducing the crystalline orientation of plated Zn along the (002) plane, which may reduce dendritic growth, HER, and corrosion. 14-16 Archer et al. employed graphene as the anode to induce the (002) oriented growth of Zn²⁺ plating, leading to enhanced Zn²⁺ stripping/plating reversibility.¹⁷ Subsequently, a series of materials such as metallic sulfides, MXenes, and metal-organic frameworks followed the work to modulate the orientation of plated Zn along the (002) facet, which suppressed the formation of dendrites to some extent. 18-20 In addition to the anode modifications, separator alterations (e.g., by sulfonic cellulose coating) and the adoption of electrolyte additives (e.g., anionic surfactants) have also been demonstrated to regulate Zn²⁺ plating along the (002) facet.^{21,22}

Despite the effect being somewhat demonstrated, the slower growth rate of Zn(002) compared to Zn(100) and (101) results in a larger polarization during Zn stripping/plating, which negatively impacts battery performance. 23-25 In addition, as research into Zn(002) has progressed, it has been verified that the plated Zn orientation easily deviates from the intended (002) facet, resulting in significant lattice distortion and irreversible Zn2+ plating/stripping, due to the weak bonding between the (002) facet and the plated Zn atoms, further compromising structural integrity and efficiency. 9,26 It is urgent to establish an alternative solution to achieve a high ZUR and kinetically favorable Zn²⁺ plating/stripping process.

Although vulnerable to HER and corrosion reactions, Zn(101) has garnered increasing attention from researchers due to its faster growth rates compared to other major facets and stronger Zn-Zn bonding to maintain the desired facet, which shows feasibility to address issues associated with Zn(002). For example, Liu et al. demonstrated that the epitaxial growth of the Zn(101) facet can be achieved by constructing a highly oriented Zn(101) substrate, resulting in exceptional Zn²⁺ plating kinetics.²⁴ Electrolyte additives such as theophylline and dextrin have also been shown to promote the preferential growth of the Zn(101) facet, where the additives are selectively adsorbed onto Zn(002) and Zn(100) facets, directing Zn²⁺ to migrate to and deposit along the (101) facet. 25,27 However, in these studies, the plated Zn(101) is directly exposed to water molecules, leading to inevitable HERs, corrosion reactions, and

dendrite growth-issues that will be drastically exaggerated with increased Zn²⁺ plating/stripping amounts. Consequently, the ZUR is critically limited to below 40%, compromising reversibility and energy density. 24,25,27-29

The primary goal of this study is to harness the favorable kinetics and stronger Zn-Zn bonding strength of Zn(101) towards sustainable Zn anode applications, particularly featuring a high ZUR (> 80%). To this end, the following hypotheses were established: (a) selective Zn orientation (in this study (101)) may be achieved by saturating the Zn dangling bonds of the selected (101) facet of Zn. (b) The highly reactive Zn(101) can be spontaneously passivated by an artificial interphase that can shield Zn^{2+} from electrons and rapidly transport Zn^{2+} throughout the interphase. (c) The formation of Zn dendrites can be restricted by an artificial interphase with a high Young's modulus (>100 GPa).

These hypotheses were formulated from the well-known facts that (1) the existence of dangling bonds is directly associated with surface energy, which raises the nucleation energy barrier and consequently limits the growth of crystalline phases; 12,30 (2) the Zn²⁺ plating location is governed by Zn²⁺ diffusion and electron reduction. The rapid diffusion of Zn²⁺, coupled with limited electron availability within the material, may prevent the reduction of Zn2+ upon coming into contact with the interphase. This allows Zn²⁺ to migrate through the interphase until the ions reach its end, where Zn begins plating beneath the interphase upon encountering an electron source (i.e., Zn electrode), immediately being isolated from water/ electrolyte;31,32 and (3) Zn dendrites, whose Young's modulus is as high as ~ 100 GPa, have been reported to penetrate the artificial interphase of low mechanical strength and cause an internal short circuit. 17,33 Therefore, the mechanical properties of the implemented artificial interphases need to be greater than those of Zn dendrites.

To identify optimal materials for constructing an artificial interphase for the Zn anode, the candidate materials were divided into five main categories: carbon composites, polymers, metal alloys, fluoride materials, and oxide materials, as presented in Fig. 1(a). Among these, carbon composites, metal alloys, and oxide materials demonstrated Young's modulus higher than 100 GPa, which is crucial for inhibiting Zn dendrite formation and thereby preventing battery short circuits. The selected interphase material must also possess electron shielding capabilities, making metal alloys and carbon composites unsuitable due to their electron-conducting nature. Both dielectric and p-type oxide materials meet the electron shielding criterion, creating an electron transfer barrier with the Zn electrode. However, p-type oxide materials may present a distinct advantage over dielectric materials due to their tunable doping and hence the work function energy level to tune the barrier height. 34,35 The tunable barrier height may be of significant advantage for long term sustainability of batteries since dynamic changes in the barrier height (E_b) promote reversible charge (with reduced E_b) and discharge (with increased E_b) processes, which decrease the Zn^{2+} concentration polarization and benefit uniform Zn²⁺ stripping/plating.^{36,37}

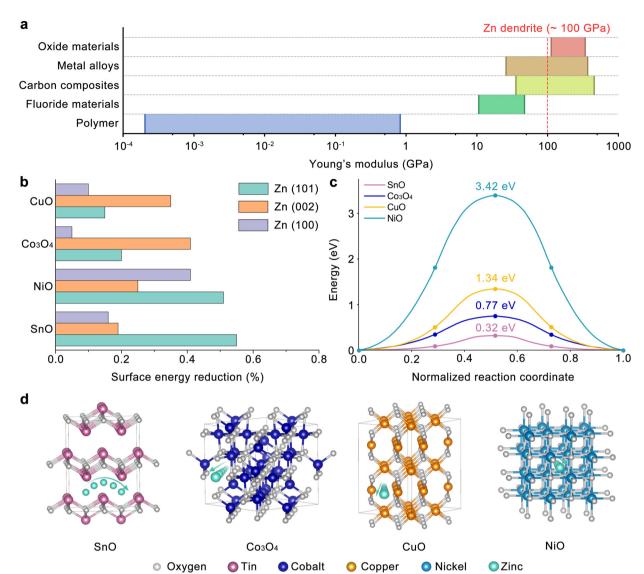


Fig. 1 (a) Overview of Young's moduli of oxide materials, metal alloys, carbon composites, fluoride materials, and polymers. (b) Surface energy variation of Zn(002), (100), and (101) applied with different oxide interphases. (c) Migration energy barrier and (d) the corresponding paths of Zn^{2+} in different oxide materials.

Based on these selection criteria, we narrowed our options to ptype metal oxides such as CuO, NiO, SnO, and Co₃O₄ for further evaluation, specifically focusing on their capabilities to selectively saturate dangling bonds at the Zn(101) surface and promote Zn²⁺ transfer kinetics. According to the calculation results in Fig. 1(b), the surface energy of Zn(101) can be most selectively reduced with SnO, while NiO non-selectively reduces the surface energy of both Zn(101) and (100). The surface energy reduction capability of these p-type oxides was estimated by the overlaps of the projected density of states (pDOS) between the Zn 4s orbital of the Zn facet and O 2p orbital of the oxide. The pDOS calculations are presented in Fig. S1 (ESI†) as a function of Zn orientation and p-type oxide, where the higher overlap of O 2p and Zn 4s orbitals indicates the stronger interactions between the O and Zn dangling bonds, leading to their saturation. The selective reduction in the surface energy

of the Zn(101) facet by the implementation of SnO is attributed to these stronger interactions between O and Zn (orbital overlaps) estimated in Fig. S1a (ESI †), resulting in the saturation of Zn dangling bonds.

Furthermore, taking the Zn^{2+} transfer kinetics into consideration, SnO, whose layered structure favors Zn^{2+} transport with the lowest migration energy (~ 0.32 eV), compared to Co_3O_4 , CuO and NiO where Zn^{2+} transfer is limited with much higher migration energies (0.77–3.42 eV), is selected as the ideal candidate for the artificial interphase in the current Zn battery study as shown in Fig. 1(c) and (d).

Herein, we demonstrate reversible Zn^{2+} plating along (101) orientation beneath the $\mathrm{SnO}_{1.17}$ interphase by precisely controlling the O ratio in the Sn–O system, which selectively saturates the dangling bonds of $\mathrm{Zn}(101)$ and ensures built-in electrostatic interactions and low Zn^{2+} migration barrier.

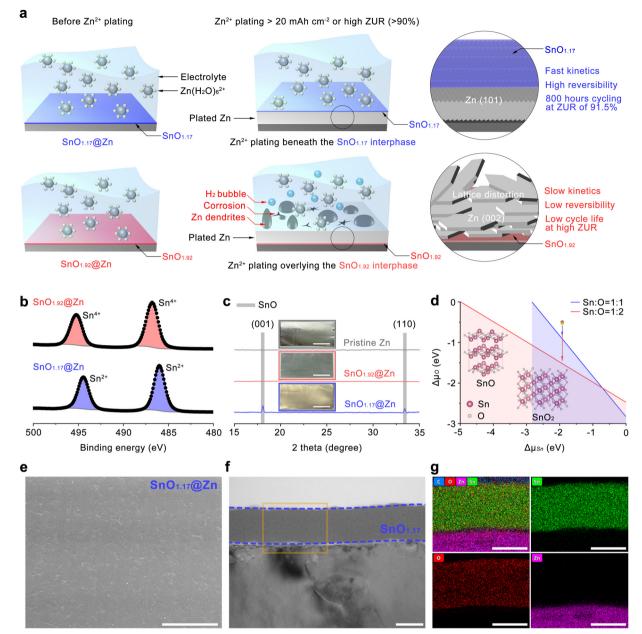


Fig. 2 Mechanism of the two different Zn²⁺ plating behaviors and properties of SnO_{1,17}@Zn. (a) Schematic illustration of the underlying Zn(101) plating and overlying Zn(002) plating relative to the interphase. (b) HR-XPS of Sn 3d for SnO₁₉₂@Zn and SnO₁₁₇@Zn. (c) XRD patterns of pristine Zn, SnO₁₉₂@Zn, and SnO_{1.17}@Zn with insets showing digital photos of the specimens (scale bar, 4 cm). (d) The chemical potential of Sn and O for crystalline SnO and SnO₂ with insets showing the crystalline atomic structures of the two Sn-O phases. (e) A plane-view SEM image of SnO₁₁₇@Zn (scale bar, 100 μm). TEM images of (f) a cross-sectional view and (g) the corresponding elemental mapping micrographs of $SnO_{1.17}$ @Zn (scale bar, 50 nm).

Consequently, the preferential growth of the well-aligned Zn(101) facets is facilitated due to the decreased surface energy of Zn(101). Different from the previously reported Zn(101) facet exposed to water, it should be noted that our study first demonstrates simultaneous passivation of the selectively grown Zn(101) facet, preventing direct contacts between the plated Zn(101) and water molecules since Zn(101) is plated underlying the $SnO_{1.17}$ interphase, as shown in Fig. 2(a). The higher growth rate of the (101) facet promotes faster mass transfer, leading to a lower overpotential in the Zn²⁺ plating/stripping process

compared to that of the (002) facet. 10,23 In addition, the manipulated Zn^{2+} plating beneath $SnO_{1,17}$ spontaneously eliminates the HER and corrosion by isolating the highly reactive Zn(101) from water, which enables sustainable Zn²⁺ plating/ stripping, therefore ensuring superior reversibility under high current density and high ZUR conditions. The SnO_{1.17} interphase characterization and the comparison with SnO_{1,92} validate our hypotheses, which helps to develop an engineering approach to achieve enhanced reversibility and kinetics for Zn anode applications. The Zn anode modified with the SnO_{1.17}

interphase demonstrates outstanding electrochemical performance in the half-cell tests, allowing for stable cycling for more than 600 hours (20 mA cm⁻², 20 mA h cm⁻²) with a nucleation overpotential of 72 mV and 800 hours at a high ZUR of 91.5% with a nucleation overpotential of 43 mV. This performance is significantly enhanced, compared to the SnO_{1 92} counterpart, which deposits Zn overlying the artificial interphase (i.e., SnO_{1 92}) along the (002) facet. The SnO_{1 92}-modified anode sustained cycling for only 140 hours (at 20 mA h cm⁻²) with an overpotential of 124 mV and 350 hours (a high ZUR of 91.5%) with a polarization voltage of 68 mV. The sulfur cathode, MnO2 cathode, and ZnMn2O4 cathode were selected to pair with (i) commercial Zn foil (40 μm) for the full-cell performance evaluation under high plating/stripping, (ii) ultrathin Zn foil (2.8 µm) at low N/P ratios, and (iii) Cu foil under anode-free conditions. The anode modified with the SnO_{1,17} interphase demonstrated capacity retention values of 95.2% and 77.4% when paired with PEDOT@S and MnO₂ cathodes after 600 and 400 cycles, respectively. Noteworthily, in an anode-free system, the anode modified with the SnO_{1.17} interphase retained capacity as high as 81.6%, compared to its original capacity after 200 cycles in a configuration of ZnMn₂O₄||SnO_{1.17}@Cu, which far surpasses 30.9% for the ZnMn₂O₄||SnO_{1.92}@Cu cell after 200 cycles.

Results and discussion

X-ray photoelectron spectroscopy (XPS) surveys (Fig. S2, ESI†) with binding energies (BE) ranging from 0 to 900 eV show similar spectra to each other, in which Sn 3d and O 1s peaks are observed with other Sn-related peaks from Sn 3s, 3p, 4s, and 4d excitations. High-resolution XPS (HR-XPS) investigations were performed to analyze the elemental compositions and the valence state of major elements in both SnO_{1,92} and SnO_{1,17} artificial interphases. SnO_{1.17} exhibits two major spin-orbit split pairs of Sn $3d_{5/2}$ at 486.0 eV and Sn $3d_{3/2}$ at 494.4 eV, resulting from the Sn²⁺ state in SnO (Fig. 2(b)). In contrast, the overall peak location of Sn 3d in SnO_{1,92} shifted toward higher binding energy by approximately 0.8 eV, which is attributed to Sn⁴⁺ in SnO₂.³⁸ Moreover, the main peak of O 1s in SnO_{1,92} is located at higher binding energies ($\Delta B_{\rm E} \sim 1.6$ eV) compared to that in SnO_{1.17} (Fig. S3, ESI†), suggesting a higher oxidation state. The Sn to O elemental ratios of the two distinct tin oxide films are estimated to be 1:1.92 for the higher oxygen species $(SnO_{1.92})$ and 1:1.17 for the lower oxygen phase $(SnO_{1.17})$, respectively through peak area analysis of the HR XPS spectra, indicating slight non-stoichiometric compositions of both phases.

Digital photographs show that the pristine Zn foil turns from shiny silvery to blueish-grey and to pale gold after applying $SnO_{1.92}$ and $SnO_{1.17}$ interphases, respectively (the inset of Fig. 2(c)). Homogeneous films were achieved over a large area $(12 \times 5.5 \text{ cm})$ for both $SnO_{1.92}$ @Zn and $SnO_{1.17}$ @Zn samples, suggesting the viability of mass production for practical applications. The X-ray diffraction (XRD) spectra show that the two

modified Zn samples (SnO_{1.92}@Zn and SnO_{1.17}@Zn) well preserve typical metallic Zn, compared to pristine Zn as illustrated in Fig. S4 (ESI†). Noteworthily, two crystalline peaks at the diffraction angles of near 18.1 and 33.4° are observed for SnO_{1.17}@Zn (Fig. 2(c) and Fig. S4, ESI†), which correspond to the (001) and (110) planes of the SnO crystal structure (JCPDS no. 06-0395). In contrast, no significant diffraction peaks are observed for SnO_{1.92}@Zn, suggesting the amorphous state of the SnO_{1.92} interphase.

To understand the mechanism of crystallinity of Sn–O compounds with different stoichiometries, the chemical potential of the Sn–O system was investigated. The growth conditions of the crystalline phases of SnO and SnO₂ of each element should satisfy the following thermodynamic conditions (eqn (1) and (2)).

$$\Delta \mu_{\rm Sn} + \Delta \mu_0 = \Delta H_{\rm f,SnO} = -2.827 \text{ eV}$$
 (1)

$$\Delta\mu_{\rm Sn} + 2\Delta\mu_0 = \Delta H_{\rm f,SnO_2} = -4.923 \text{ eV}$$
 (2)

where $\Delta H_{\rm f,SnO}$ and $\Delta H_{\rm f,SnO_2}$ represent the formation enthalpies of SnO and SnO₂ calculated for bulk Sn and molecular O₂. The crystalline phases of SnO and SnO2 will be formed when the chemical potential of Sn and O lies within the blue and red regions, respectively in Fig. 2(d). The chemical potentials of Sn and O for the synthesis of Sn-O phases in our experiment are calculated based on ideal gas assumption and marked as a grey dot for SnO ($\Delta\mu_0$ = -0.509 eV, $\Delta\mu_{\rm Sn}$ = -1.914) and a yellow dot for SnO₂ ($\Delta \mu_0 = -0.522$ eV, $\Delta \mu_{Sn} = -1.909$ eV) in Fig. 2(d), which are located near each other and closer to the blue line (i.e., crystallization of SnO).40,41 This comparison suggests that lower energy (i.e., annealing in this study) is required to achieve the crystalline structure of SnO compared to the crystalline structure of SnO2, leading to the formation of crystalline SnO_{1,17}, while SnO_{1,92} remains amorphous. In addition, nanoindentation measurements reveal that the Young's moduli of SnO_{1,17}@Zn and SnO_{1,92}@Zn are determined to be \sim 152 GPa and \sim 207 GPa, both exceeding the \sim 95 GPa of pristine Zn as indicated in Fig. S5 (ESI†). This enhanced mechanical strength is expected to effectively restrain Zn dendrite formation. Furthermore, the elastic deformation energy densities (U_e) of SnO_{1 17}(a)Zn and SnO_{1 92}(a)Zn, representing the amount of mechanical energy sustained per unit volume when a material undergoes elastic deformation, were calculated to be 1.87 J cm⁻³ and 2.32 J cm⁻³, respectively (Table S3, ESI†), which are higher than $0.64 \, \mathrm{J \, cm^{-3}}$ for pristine Zn. The higher U_{e} of the artificial interphase enables effective sustainment of substantial volume variations in the anode during Zn2+ plating/stripping, thereby enhancing structural stability. 42 Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analyses were carried out to investigate the characteristics of surface structures of SnO_{1,17} and SnO_{1,92} interphases. The SEM images in Fig. 2(e) and Fig. S6 (ESI†) show the shallow flexures originating from the Zn foil of both SnO_{1.17}@Zn and SnO_{1.92}@Zn, suggesting the well-maintained surface morphologies of Zn foil due to the thin thickness $(\sim 70 \text{ nm})$ of Sn-O interphases. It should be noted that artificial

interphases less than 100 nm thick (considering the thickness (~100 nm) of the solid electrolyte interphase in lithium-ion batteries) are more practical, given that the theoretically required thickness of the Zn foil for ZIBs is approximately 7.4 µm (Note S1 in the ESI†). Uniform interphase coating and the thickness are verified from TEM micrographs of both SnO_{1,17}@Zn and SnO_{1,92}@Zn in Fig. 2(f) and Fig. S7a (ESI†). Energy dispersive X-ray (EDX) mapping analysis of the selected regions (marked by a yellow rectangle in Fig. 2(f) and Fig. S7, ESI†) unveils that the SnO_{1.17} and SnO_{1.92} layers compactly and uniformly cover the Zn surface as shown in Fig. 2(g) and Fig. S7b (ESI†). The contact angle was tested to evaluate the hydrophobicity of the Sn-O compound layers. SnO_{1,17} and SnO_{1.92} exhibit a higher hydrophobicity as confirmed by larger contact angle values (116.5° and 108.6°) than that of pristine Zn (91.3°) as indicated in Fig. S8 (ESI†), which may be attributed to the lower surface energy of oxide compounds compared to pure metal.43,44 The strong hydrophobicity of Sn-O compound

interphases enables the isolation of the active Zn from the bulk electrolyte, thereby inhibiting water-induced erosion.

Linear sweep voltammetry (LSV) at 5 mV s⁻¹ in 2 M Na₂SO₄ aqueous electrolyte based on a three-electrode system was employed to characterize the polarization behaviors of pristine and modified Zn anodes to evaluate the efficacy of the stoichiometrically different Sn-O interphases in HER inhibition. The Zn foil, Pt foil, and Ag/AgCl acted as the working electrode, the counter electrode, and the reference electrode, respectively. Without the Zn²⁺ deposition, the current responses in LSV directly account for HER. The presence of Sn-O compounds decreases the cathodic current density and shifts the potential of the HER at -2 mA cm^{-2} from -1.30 V on pristine Zn to -1.57 V on SnO_{1.92}@Zn and −1.78 V on SnO_{1.17}@Zn (vs. Ag/ AgCl) as indicated by the dashed lines in Fig. 3(a). This confirms the stronger resistance of SnO_{1.17} to the HER. Cyclic voltammetry (CV) was used to verify the compatibility and effect of the Sn-O interphase on the electrochemical deposition of

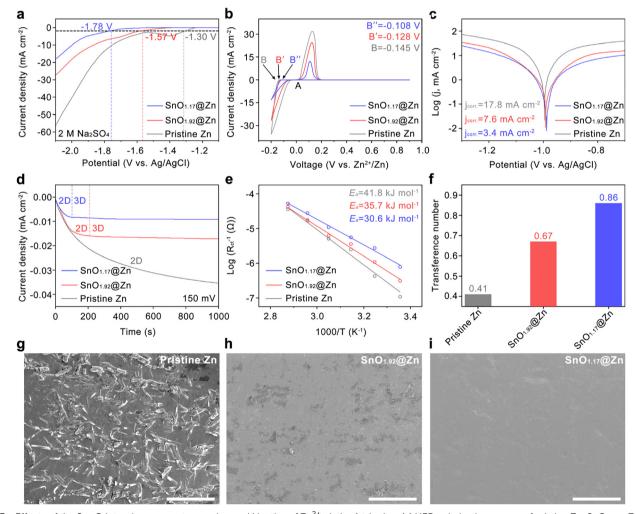


Fig. 3 Effects of the Sn-O interphase on water erosion and kinetics of Zn²⁺ plating/stripping. (a) HER polarization curves of pristine Zn, SnO_{1.92}@Zn, and $SnO_{1.17}$ @Zn in 2 M Na_2SO_4 aqueous electrolyte at 5 mV s⁻¹. (b) CV of Zn nucleation on pristine Zn, $SnO_{1.92}$ @Zn, and $SnO_{1.17}$ @Zn at the scan rate of 10 mV s $^{-1}$. (c) Tafel plots of pristine Zn, SnO_{1,92}@Zn, and SnO_{1,17}@Zn. (d) Chronoamperograms of pristine Zn, SnO_{1,92}@Zn, and SnO_{1,17}@Zn anodes. (e) Arrhenius curves of pristine Zn, $SnO_{1.92}$ @Zn, and $SnO_{1.92}$ @Zn anodes. (f) Zn^{2+} transference numbers of pristine Zn, $SnO_{1.92}$ @Zn, and $SnO_{1.17}$ @Zn. SEM images of (g) pristine Zn, (h) SnO_{1.92}@Zn, and (i) SnO_{1.17}@Zn anodes soaked in 2 M ZnSO₄ aqueous electrolyte for 5 days (scale bar, 20 µm).

Zn²⁺. As shown in Fig. 3(b), the oxidation and reduction peaks of Zn||Ti cells appear only when Zn²⁺ stripping/plating occurs, which suggests the electrochemical activity of Zn²⁺ through the Sn-O interphase. The reduction potential increased from B (pristine) to B' (with SnO_{1.92}) and B" (with SnO_{1.17}), signifying that SnO_{1 17} has a better ability to enable the rapid transfer of Zn²⁺ and to alleviate the concentration polarization during Zn²⁺ plating. The higher current densities observed in the SnO_{1,92}@Zn and pristine Zn anodes are attributed to parasitic reactions, such as the HER and corrosion, which contribute to the overall reaction current densities. ^{24,45} Tafel plots in Fig. 3(c) confirm a decreased corrosion current of 3.4 mAcm⁻² on SnO_{1,17}@Zn, which is much lower than that of pristine Zn $(17.8 \text{ mA cm}^{-2})$ and $SnO_{1.92}$ (2.6 mA cm⁻²). These results demonstrate that the SnO_{1,17} interphase shows a stronger resistance to the HER and Zn corrosion than SnO_{1.92}. The chronoamperometry (CA) investigations in Fig. 3(d) provide insights into the Zn²⁺ plating mechanisms of the pristine and modified anodes. The current density with the pristine Zn continuously increases, suggesting a long rampant 2D Zn diffusion process, during which Zn²⁺ tends to accumulate at the tip of the Zn anode and generate dendrites. 46,47 In contrast, the current reaches a steady state after about 100 s for SnO_{1.17}@Zn and 200 s for SnO_{1.92}@Zn, which indicates that the Zn²⁺ diffusion shifts to stable 3D diffusion after a short 2D diffusion, resulting in dense Zn nucleation sites and smooth deposition morphology. This result suggests that the SnO_{1.17} interphase establishes the rapid stabilization of the Zn²⁺ diffusion process more effectively than SnO_{1.92}. In addition, the activation energy (E_a) for charge transfer resistance (R_{ct}) estimated from the Arrhenius equation (Fig. 2(e) and Fig. S9, ESI†) allows for the identification of the de-solvation capability of each electrode. Notably, SnO_{1,17}@Zn exhibits a significantly lower E_a of 30.6 kJ mol⁻¹ compared to 41.8 kJ mol⁻¹ for pristine Zn and 35.7 kJ mol⁻¹ for SnO_{1.92}@Zn. These results indicate that the de-solvation process of Zn²⁺ is more facile on SnO_{1.17} than on SnO_{1,92} and pristine Zn, resulting in improved kinetic conditions. The Zn^{2+} transference number $(t_{Zn^{2+}})$ is measured to evaluate the Zn²⁺ diffusion ability of the Sn-O interphase (Fig. 3(f)). Based on the CA and electrochemical impedance spectroscopy (EIS) tests (Fig. S10, ESI†), SnO_{1 17}(a)Zn exhibits a $t_{\rm Zn^{2+}}$ of 0.86 in Fig. 3(f), which significantly surpasses those of pristine Zn $(t_{Zn^{2+}} = 0.41)$ and SnO_{1.92}@Zn $(t_{Zn^{2+}} = 0.67)$, The higher $t_{\text{Zn}^{2+}}$ ensures a more efficient transfer of Zn^{2+} while restricting the migration of SO42- anions, ultimately contributing to uniform Zn²⁺ plating due to the mitigated concentration polarization.48

In addition to the contact angle hydrophobicity measurements shown in Fig. S8 (ESI †), the endurance of the SnO_{1.17} interphase to water-induced erosion was further investigated. Pristine Zn, SnO_{1.92}@Zn, and SnO_{1.17}@Zn anodes were soaked in 2 M ZnSO₄ aqueous electrolyte for 5 days. As shown in a SEM microstructure, Fig. 3(g), numerous rod-like products accumulated on the surface of the pristine Zn anode, identified as Zn₄SO₄(OH)₆·5H₂O based on XRD results (Fig. S11, ESI †). The formation of Zn₄SO₄(OH)₆·5H₂O is known to be induced by the

HER on Zn, which elevates the local pH near Zn, thereby triggering the precipitation of by-products. ⁴⁹ In contrast, minor $Zn_4SO_4(OH)_6\cdot 5H_2O$ peaks are observed in $SnO_{1.92}$ @Zn, while they are entirely absent in $SnO_{1.17}$ @Zn as shown in Fig. S11 (ESI†). The SEM microstructure of $SnO_{1.92}$ @Zn (Fig. 3(h)) reveals identifiable by-products on the surface, whereas the $SnO_{1.17}$ @Zn surface (Fig. 3(i)) remains compact and uniform without any by-products, consistent with the XRD results (Fig. S11, ESI†), suggesting the effective inhibition of water erosion on $SnO_{1.17}$ @Zn.

The effect of the SnO_{1.17} and SnO_{1.92} interphases on the electrochemical performance of the Zn anode was investigated using symmetric Zn cells. As shown in Fig. 4(a), the SnO_{1.17}@Zn symmetric cell exhibits cycling stability over 3000 h at 1 mA cm⁻² and 1 mA h cm⁻² with a much lower overpotential of 33 mV, which is about 2 and 11 times longer lifespan compared to SnO_{1,92}@Zn (overpotential: 54 mV) and pristine Zn (overpotential: 58 mV), respectively. Optical images of symmetric cells after cycling demonstrate a significant reduction in HER activity during long-term cycling (>3000 h) due to the presence of the SnO_{1.17} interphase (Fig. S12, ESI†). In addition, at 5 mA cm⁻² and 5 mA h cm⁻² (Fig. S13, ESI \dagger), the SnO_{1.17}@Zn symmetric cell showed high stability over 1500 h and a lower overpotential of 61 mV, which surpasses the pristine Zn (~190 h, 128 mV) and SnO_{1.92}@Zn (~700 h, 92 mV) cells. Additionally, SEM images of the cycled electrodes (Fig. S14, ESI†) show that the SnO_{1.17}@Zn electrode maintains a compact and uniform surface, in contrast to the higher roughness and by-products formed on SnO_{1.92}@Zn and pristine Zn. These microstructure comparisons suggest that SnO_{1,17}, as the anode interface modifier, exhibits a strong capability to restrict the dendrite formation during the Zn²⁺ plating/stripping process. Notably, even at the high current density of 20 mA cm⁻² with 20 mA h cm⁻² (Fig. 4(b)), the SnO_{1.17}@Zn symmetric cell still sustains stable cycling over 600 h with a relatively low overpotential of 72 mV, which corresponds to a ZUR as high as 85.72%. In contrast, the SnO_{1.92}@Zn symmetric cell retained stable cycling only for approximately 140 hours with a larger overpotential of 124 mV, while the pristine Zn cell experienced a short circuit after only about 40 hours. To realize the low N/P ratio for practical applications, an ultrathin Zn (UT Zn) anode with a thickness of around 2.8 µm, which corresponds to an areal capacity of 1.63 mA h cm⁻², was made by thermal evaporation. The UT Zn anodes were cycled at 1.5 mA cm⁻² with 1.5 mA h cm⁻², equivalent to a ZUR of $\sim 91.5\%$ as indicated in Fig. S14 (ESI†). The SnO_{1.17}@UT Zn symmetric cell stably cycled for 800 h with a low overpotential of 43 mV compared to the ~350 h for the SnO_{1.92}@UT Zn (68 mV) and the \sim 70 h for the pristine UT Zn anodes (76 mV), respectively. This confirms that SnO_{1.17} could promote Zn²⁺ transfer kinetics and enhance cycling stability even at large current densities and high ZURs. Zn||Cu asymmetric cells were adopted to evaluate the Zn²⁺ plating/striping reversibility. The lower nucleation overpotential of SnO_{1.17}@Zn at the initial cycle indicates the promoted Zn reaction kinetics (Fig. S16, ESI†). As shown in Fig. 4(c), the $SnO_{1.17}$ @Zn cell exhibits a higher

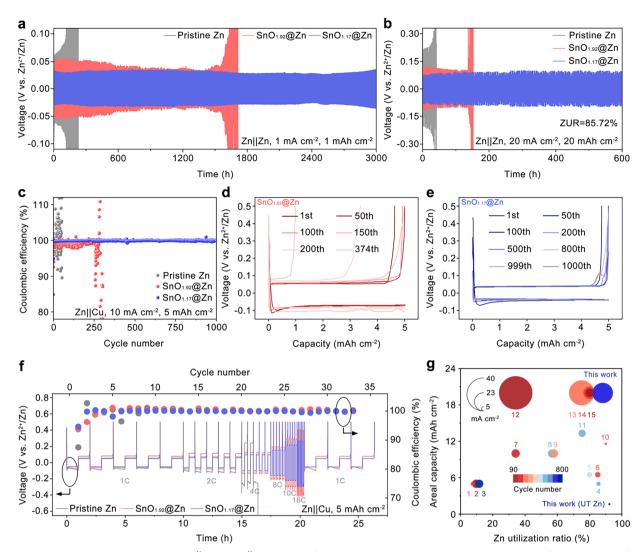


Fig. 4 Electrochemical performance of the Zn||Zn and Zn||Cu half cells. Galvanostatic cycling performance of pristine Zn, $SnO_{1.92}$ @Zn, and $SnO_{1.17}$ @Zn based on symmetric Zn||Zn| cells at (a) 1 mA cm⁻², 1 mA h cm⁻² and (b) 20 mA cm⁻², 20 mA h cm⁻². (c) Galvanostatic cycling performance of pristine Cu, SnO_{1.92}@Cu, and SnO_{1.17}@Cu based on asymmetric Zn||Cu cells at 10 mA cm⁻² and 5 mA h cm⁻². Voltage-capacity curves at different cycles of asymmetric Zn||Cu cells with (d) the $SnO_{1.92}$ interphase and (e) the $SnO_{1.17}$ interphase. (f) Rate capacities of asymmetric Zn||Cu cells at an areal capacity of 5 mA h cm⁻² and current densities from 5 to 80 mA cm⁻². (g) Comprehensive comparison of the SnO_{1.17}@Zn anode with recently reported Zn anodes.

initial coulombic efficiency (CE) of 96.38% and a higher average CE of 99.87%, compared to the pristine Zn (initial CE: 85.47%, average CE: 90.46%) and SnO_{1.92}@Zn (initial CE: 93.52%, average CE: 99.66%). The average CE of 99.87% measured at 5 mA cm⁻² is comparable to 99.83% obtained at 0.1 mA cm⁻², indicating the high reversibility of the SnO_{1,17}@Zn anode as indicated in Fig. S17a (ESI†). Additionally, the Aurbach method was employed to eliminate the influence of conversion reactions between Zn metal and the Cu substrate surface, ensuring a more precise determination of the CE. Using this method, the average CE of SnO_{1.17}@Zn was determined to be 99.89%, as shown in Fig. S17b (ESI†), further confirming the highly reversible Zn plating/stripping process. The selected voltage profiles of SnO_{1,92}@Zn (Fig. 4(d)) show the larger polarization potential between each charge and discharge process compared to those of SnO_{1.17}@Zn (Fig. 4(e)), which suggests a facilitated

Zn plating process in SnO_{1 17}@Zn. Fig. S18 (ESI†) shows that the pristine Zn cell displays unstable cycling behavior after only 50 cycles, with fluctuating voltage profiles attributed to severe water erosion and dendrite growth on the pristine Zn anode. Fig. 4(f) demonstrates the rate capacities of Zn||Cu asymmetric cells. SnO_{1,17}@Zn displays a higher average CE of over 99.50% with an areal capacity of 5 mA h cm⁻² compared to 99.23% for SnO_{1.92}@Zn. The pristine Zn cell experienced a short circuit after only 12 cycles, indicating severe non-uniform Zn plating behavior on the surface of bare Zn. These results confirm that the capability of SnO_{1,17} to stabilize the electrodeposition of Zn²⁺ is not limited to low current densities but extended to a much higher density, particularly promising for high-power Zn batteries. Fig. 4(g) presents a comprehensive comparison between this work and reported Zn electrodes with various artificial protection layers in terms of four key parameters (i.e.,

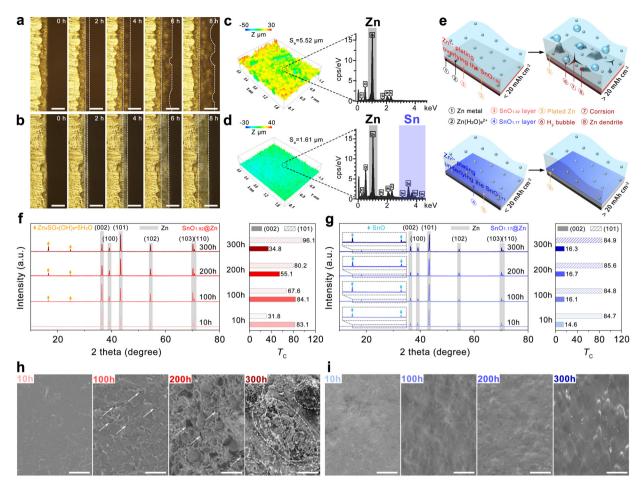


Fig. 5 Comparison of Zn²⁺ plating behavior between SnO_{1.92}@Zn and SnO_{1.17}@Zn. In situ optical microscopy visualization of Zn²⁺ plating on (a) SnO_{1.92}@Zn and (b) SnO_{1.17}@Zn at 5 mA cm⁻² (scale bar, 100 μ m). Three-dimensional confocal laser microscopy images and EDX analysis of Zn²⁺ plating on (c) SnO_{1.92}@Zn and (d) SnO_{1.17}@Zn for 8 h. (e) Schematic illustration of the overlying and underlying Zn²⁺ plating of the Sn-O interphase. XRD patterns with the corresponding texture coefficients of (f) SnO_{1.92}@UT Zn and (g) SnO_{1.17}@UT Zn cycled at 1.5 mA cm⁻² and 1.5 mA h cm⁻² for different times. SEM images of (h) SnO_{1.92}@UT Zn and (i) SnO_{1.17}@UT Zn cycled at 1.5 mA h cm⁻² for different times (scale bar, 10 μ m).

areal capacity, ZUR, cycle number, and current density). Notably, this work leveraging the anti-corrosion ability and favorable $\rm Zn^{2^+}$ transfer kinetics of $\rm SnO_{1.17}$ contributed to the significantly extended cycle lives at a 85.7% ZUR for 600 hours at 20 mA cm⁻² and 20 mA h cm⁻² as well as at a 91.5% ZUR for 800 hours, outperforming previously reported results with generally less than 500 hours, as indicated in Table S4 (ESI†).

The electrodeposition behavior of Zn²⁺ was characterized to identify the mechanism responsible for the stability difference between SnO_{1.17}@Zn and SnO_{1.92}@Zn during electrochemical testing. An optical microscopy system was developed to monitor the behavior of substantial Zn²⁺ plating (>20 mA h cm⁻²) in transparent Zn||Zn cells at a current density of 5 mA cm⁻² *in situ*. Uneven Zn nucleation sites emerge only after 15 min in pristine Zn and gradually develop into dendritic and Zn protrusions (white circles in Fig. S19, ESI†) on the electrode surface with further plating. In contrast, the *in situ* optical images in Fig. 5(a) (SnO_{1.92}@Zn) and 5(b) (SnO_{1.17}@Zn) show that the plated Zn (marked with a white dashed line) was uniformly distributed in the initial 4 hours. However, after 4 hours, the

Zn²⁺ plating layer in SnO_{1.92}@Zn becomes thicker (\sim 48 μm) than the 38 μm-thick layer in SnO_{1.17}@Zn. This thickness difference may be attributed to the growth of uneven and random Zn protrusion, resulting in looser Zn²⁺ plating in SnO_{1.92}@Zn. Moreover, the thickness of the Zn²⁺ plating layer in SnO_{1.92}@Zn is close to the theoretical thickness of Zn²⁺ plating at 5 mA cm⁻² for 4 hours (\sim 34 μm; Note S1 in the ESI†), suggesting a highly dense Zn²⁺ plating layer formed with SnO_{1.17}@Zn. Subsequent Zn²⁺ plating (after 6 hours and 8 hours) in SnO_{1.92}@Zn further increased the surface roughness, resulting in the formation of Zn protrusions. In contrast, the SnO_{1.17}@Zn interphase layer ensures homogeneous and more compact Zn²⁺ plating throughout the entire 8-hour plating process.

Moreover, the confocal laser microscope was employed to quantitively estimate the topological morphology and roughness of the Zn^{2+} plating layer. Fig. 4(c) and (d) reveal a significant difference in surface roughness (arithmetic mean height, abbreviated as S_a) between $SnO_{1.92}$ @Zn and $SnO_{1.17}$ @Zn after 8 hours. $SnO_{1.92}$ @Zn exhibits a S_a of

5.52 µm, which is more than three times the value of 1.61 µm obtained for SnO_{1.17}@Zn, indicating the uneven Zn²⁺ plating at a high Zn^{2+} plating amount (>20 mA h cm⁻²) in $SnO_{1.92}$ @Zn. The surface roughness of pristine Zn after 1 hour Zn plating is 10.02 μm (Fig. S20, ESI†), critically rougher than those of the modified anodes with a longer duration.

Optical photographs in Fig. S21a-c (ESI†) show different colors of the Zn-plated regions of pristine Zn, SnO_{1 92}@Zn, and SnO_{1.17}@Zn. For the pristine Zn, the apparent color of plated Zn is different from that of pure metallic Zn (initial, not plated). This difference is attributed to the fact that the plated Zn has not undergone polishing, resulting in the absence of metallic shine. Notably, the SnO_{1,17} interphase exhibits a visible transparency of approximately 50%, as demonstrated by the clear visibility of the "Purdue" logo (Fig. S21d and inset, ESI†), which allows the Zn²⁺-plated region to remain observable even when located underlying the SnO_{1.17}-coated glass coverslip. EDX was conducted to further analyze the elemental compositions of coated layers. In the EDX spectrum of SnO_{1,17}@Zn (Fig. 5(d)), the characteristic peaks of the element Sn were detected as well as the Zn peaks, whereas no Sn-related peaks were observed in the EDX spectrum of the SnO_{1.92}@Zn sample (Fig. 5(c)), confirming the Zn²⁺ plating underlying the SnO_{1.17} interphase, while overlying the SnO_{1.92} interphase of each modification layer. From further analysis of the elemental weight ratio obtained from EDX (Fig. S22 (ESI†)), the ratio of Sn to O in the SnO_{1.17}@Zn sample was estimated to be 1:1.22, which is close to 1:1.17 for the SnO_{1.17} interphase. The slightly higher O content may be attributed to the residual of $SO_4^{\ 2-}$ in the electrolyte and the adsorbed O2 from the air or detection resolution differences between EDX and XPS. The crosssectional SEM images and EDX elemental mapping of Sn and Zn for the SnO_{1.17}@Zn anode, after Zn²⁺ plating at ~ 2 mA h cm⁻², directly confirm that the plated Zn is located beneath the $SnO_{1.17}$ interphase, as shown in Fig. S23 (ESI†). XRD was employed to further analyze the amorphous/crystalline structure of these Sn-O layers after plating. Two peaks are observed at identical diffraction angles of around 18.1 and 33.4° for plated SnO_{1.17}@Zn as shown in Fig. S24 (ESI†), which correspond to SnO(001) and (110) as discussed in Fig. 2(c), further validating Zn plating beneath SnO_{1 17} as shown in Fig. 5(e). The in situ observations combined with EDX and XRD also provide strong evidence of both Sn-O interphases controlling the Zn nucleation and growth when the Zn²⁺ plating amount is below 20 mA h cm⁻² (from 0 to 4 hours). Noteworthily, only the SnO_{1,17} interphase layer can facilitate the formation of a compact and uniform Zn-plated layer from 4 to 8 hours of Zn^{2+} plating (>20 mA h cm⁻²). Unlike the $SnO_{1.17}$ interphase, the SnO_{1.92} interphase, despite its higher Young's modulus of 207 GPa, does not play any role in suppressing Zn dendrite formation since Zn²⁺ is plated above the SnO_{1,92} interphase. This reveals the limitations of $\mathrm{SnO}_{1.92}$ in managing dendrite growth. These results explain the failure process of $SnO_{1.92}$ (a) Zn at a high plating amount with a low ZUR of ~30%.

Furthermore, $SnO_{1.17}$ @UT Zn and $SnO_{1.92}$ @UT Zn anodes in symmetric Zn||Zn cells at different cycling times were

characterized by XRD (Fig. 5(f) and (g)), with aim of understanding the failure mechanism of the SnO_{1.92}@UT Zn anode at a high ZUR of 91.5% with a low Zn plating amount of 1.5 mA h cm⁻² presented earlier in Fig. S15 (ESI†). Peaks at 36.3, 38.9, 43.2, 54.3, 70.1, and 70.7° are observed for both SnO_{1 92}@Zn and SnO_{1 17}@Zn, which are attributed to the plated Zn. The relative texture coefficient of each plane $(T_c,$ Note 2 in ESI†), representing the preferential growth of a particular plane, was calculated to quantify the phase evolution of the plated Zn. As shown in the right of Fig. 5(f) for $SnO_{1.92}$ (a) Zn, the T_c of the Zn (002) plane at 10 and 100 hours is 83.1 and 84.1 respectively, which is higher than 31.8 and 67.6 for the (101) plane. The T_c comparison indicates that a higher amount of (002)-oriented Zn is plated on the SnO_{1.92} interphase during the initial cycling. Note that, however, the still exposed Zn(101) in the electrolyte continuously reacts with water due to its higher reactivity than Zn (002), which aggravated the HER and corrosion reactions, contributing to the accumulation of Zn₄SO₄(OH)₆·5H₂O (marked as yellow diamonds in Fig. 5(f)). The accumulation of by-products deactivates the ability of the SnO_{1.92} interphase to induce Zn(002) plating. Subsequently, the T_c of Zn(002) decreased to 55.1 after 200 hours and to even 34.8 after 300 hours, while the T_c of Zn(101) increased to 80.2 and 96.1 after 200 and 300 hours respectively, due to the faster growth rate of Zn(101) than (002). Consequently, the inevitable HER and corrosion reactions with the exposed Zn(101) in $SnO_{1.92}$ (a) Zn lead to anode failure. In contrast, the T_c of Zn(002) and T_c of Zn(101) in $SnO_{1.17}$ @Zn in Fig. 5(g) (right) were retained until 300 hours, suggesting a highly reversible Zn²⁺ plating/stripping process at a high ZUR of 91.5%. Noteworthily, the T_c of Zn(101) plated under the SnO_{1.17} interphase is significantly higher than the T_c of Zn(002) in the entire cycling, indicating the Zn2+ plating preferentially along the (101) plane. The faster mass (Zn^{2+}) transfer of the Zn(101) plane contributes to a lower overpotential during the Zn²⁺ plating, compared to the (002)-oriented growth of Zn in SnO_{1,92}@Zn.

Fig. 5(h) shows the evolution of the surface morphology of SnO_{1.92}@Zn at different cycling times. Initially, a smooth and compact surface was preserved, as observed at 10 hours of cycling, where the SnO_{1.92} interphase benefits uniform Zn²⁺ plating and inhibits the parasitic reactions within the initial 10 hours. However, it is noticed that the surface roughness increased at 100 hours of cycles with several pores (marked with white arrows) generated, which may reduce the compactness of the Zn²⁺ plating layer and lead to the penetration of the water, triggering the mechanical failure and the water corrosion of SnO_{1.92}@Zn. As the cycling further proceeded for 200 hours, the roughness of the surface regions of SnO_{1,92}@Zn increased drastically with the protrusions and cavities (marked with white arrows). Besides, the pore size increased from hundreds of nanometers to several micrometers, which would lead to a more severe HER and corrosion reaction, which was further confirmed by the SEM image of SnO_{1.92}@Zn cycled for 300 hours. A lot of by-products (marked with white dashed lines) derived from the water corrosion process can be identified, resulting in the rapid failure of electrochemical

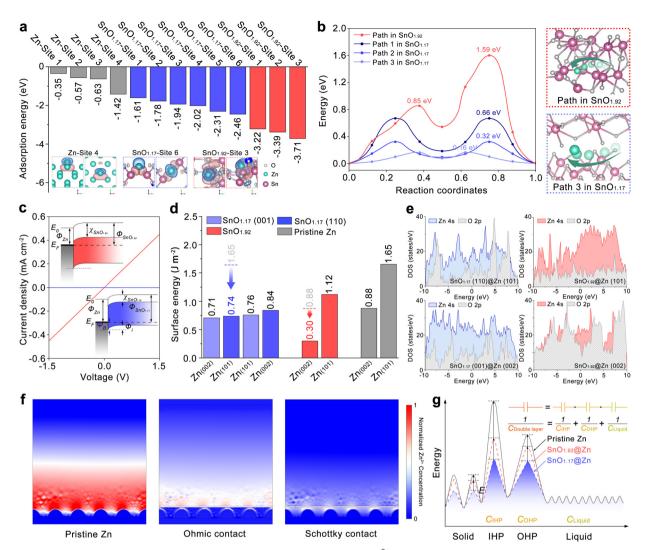


Fig. 6 Mechanistic understanding of the effect of SnO_{1,17} and SnO_{1,92} interphases on Zn²⁺ plating. (a) Adsorption energy of the Zn atoms on Zn, SnO_{1,17}. and SnO_{1,92}. Insets show the charge density differences of Zn-site 4, SnO_{1,17}-site 6, and SnO_{1,92}-site 3. (b) MEPs (right) obtained from NEB calculations and the corresponding diffusion energy barrier (left) for Zn²⁺ diffusion through SnO₁₉₂ and SnO₁₁₇. (c) I–V curves of SnO₁₉₂@Zn (red) and SnO₁₁₇@Zn (blue). Insets show schematic illustration of the band diagrams of $SnO_{1.92}/Zn$ (top) and $SnO_{1.17}/Zn$ (bottom). (d) Surface energies of Zn(0.02) and Zn(1.01)with SnO_{1.17} and SnO_{1.92} interphases. (e) The pDOS of Zn 4s and O 2p orbitals of SnO_{1.17}@Zn and SnO_{1.92}@Zn. (f) Simulated results of Zn²⁺ concentration of pristine Zn, Ohmic contact of SnO_{1.92} α Zn, and Schottky contact of SnO_{1.17} α Zn. (g) Schematic of the correlation between the energy barrier of Zn²⁺ and the specific diffusion in the OHP, IHP, and solid phase of pristine Zn, SnO_{1.92}@Zn, and SnO_{1.17}@Zn.

performance. In contrast, the surface morphology of SnO_{1,17}@Zn remained compact and smooth throughout the entire process. The (101)-oriented Zn plated underlying SnO_{1.17} was shielded from direct exposure to water molecules by the SnO_{1.17} interphase, protecting it from corrosion and the HER, resulting in a fast and reversible Zn²⁺ plating/stripping process.

Additionally, a combination of experimental and theoretical methods was employed to further understand the Zn²⁺ plating behaviors (position and crystalline orientation) as a function of Sn-O phases. According to the widely accepted ion deposition mechanism, the Zn²⁺ plating process is generally understood to involve three steps: Zn²⁺ adsorption, Zn²⁺ diffusion, and Zn²⁺ reduction. 50 Density functional theory (DFT) was employed to

evaluate the adsorption capabilities of the Zn atom by calculating the selected sites on pristine Zn, SnO_{1,17}, and SnO_{1,92} as shown in Fig. S25 and Table S5 (ESI†).

As indicated in Fig. 6(a), the Zn atom tends to adsorb on the hollow site on the (101) plane (site 4) with the lowest adsorption energy of -1.42 eV in pristine Zn. For $SnO_{1.17}$, the Zn atom thermodynamically prefers adsorption on the hollow site between two O atoms on the (101) plane (site 6) owing to the lower energy of -2.48 eV. $SnO_{1.92}$ shows an overall stronger adsorption tendency (-3.22 to -3.71 eV) towards the Zn atom with the most preferable Zn adsorption on top of the O atom (site 3; -3.71 eV). The insets show the charge density difference of Zn-site 4, SnO_{1.17}-site 6, and SnO_{1.92}-site 3. Among the three anode systems, Zn metal shows the least tendency to adsorb Zn

ions (-1.42 eV), which is accounted for by the weakest (the smallest size of the charge difference density region) charge accumulation (red) and depletion (blue) between the Zn and Zn atoms. In SnO_{1.17}-site 6 and SnO_{1.92}-site 3, the electrons are strongly depleted around the Zn atom, while electrons accumulate around the O adjunct of the Zn atom, suggesting a strong tendency of the Zn atom to donate electrons. Noteworthily, the charge accumulation and depletion regions in SnO_{1 92}site 3 are more prominent than those in SnO_{1,17}-site 6, resulting in stronger adsorption. It should be noted that strong adsorption may reduce the Zn nucleation overpotential and improve the uniform Zn deposition but may not lead to the facilitated Zn transport on the anode surface. However, weak adsorption is not beneficial for promoting uniform nucleation and deposition but is always accompanied by a low migration energy barrier, which can achieve fast Zn transport. SnO_{1.17} with moderate adsorption capabilities may achieve an optimization between the Zn nucleation overpotential and Zn transport kinetics compared to metallic Zn and the one with the SnO_{1.92} interphase. An optimal Zn²⁺ adsorption strength of SnO_{1.17} secures both uniform Zn²⁺ plating and fast ion transport on the anode, as proved by electrochemical analysis in Fig. 3 and 4.

The migration energy barriers for Zn²⁺ near the most stable adsorption sites of SnO_{1.17} and SnO_{1.92} were calculated using the climbing image nudged elastic band (NEB) method. 51,52 Fig. 6(b) shows that the migration energy barrier of Zn²⁺ in SnO_{1.92} is about 1.59 eV, and this high energy barrier indicates a slow transport of Zn²⁺, leading to the sluggish Zn²⁺ plating/ stripping behavior. However, Zn2+ is able to more easily migrate along the (110) and (001) planes of SnO_{1.17} due to the significantly lower energy barriers of 0.66 and 0.32 eV. The Zn²⁺ migration along the interface of the (110) and (001) planes needs to be considered as well due to the fast kinetics of Zn^{2+} .⁵³ It should be noted that the grain boundary between (101) and (001) planes (path 3 in SnO_{1.17}) is identified to be the fastest Zn²⁺ transport path with the lowest barrier energy of 0.16 eV. Fig. 6(b) and Fig. S26 (ESI†) illustrate the minimum energy path (MEP) of Zn²⁺ connecting the initial and final states of SnO_{1.17} and SnO_{1.92}. SnO_{1.92} shows a much narrower Zn²⁺ transport channel with an average distance of 1.62 Å between Zn and O, which contributes to stronger Zn-O interactions and a resultant higher migration energy barrier, compared to 1.78 Å for path 1, 1.91 Å for path 2, and 2.23 Å for path 3 in $SnO_{1.17}$. Additionally, the MEP of SnO_{1.92} that involves seven O atoms experiences more interactions between Zn and O during the Zn²⁺ migration, which hence results in slow Zn²⁺ transport. In contrast, SnO_{1.17} engaging less O atoms (four in path 1, six in path 2, and five in path 3) facilitates the Zn²⁺ migration with a higher ionic conductivity of 1.36 \times 10⁻⁴ mS cm⁻¹, compared to 8.72 \times 10^{-7} mS cm⁻¹ for SnO_{1.92}, as measured in Fig. S27 (ESI†). Consequently, excessively strong adsorption and a large migration energy barrier of SnO_{1.92} may impede the diffusion of Zn²⁺ into the bulk Zn. However, SnO_{1.17} is considered to be more suitable for Zn²⁺ diffusion due to the favorable kinetics, which is a prerequisite for Zn²⁺ plating underlying the SnO_{1.17} interphase.

The electrostatic interaction between the Sn-O interphase and the Zn foil was investigated to unveil the effect of Sn-O interphases on the inner Helmholtz plane (IHP), which is crucial for determining the morphology of Zn plating and parasitic reactions. Current-voltage (I-V) behaviors of the symmetric cells of Zn|SnO_{1 17}|Zn and Zn|SnO_{1 92}|Zn (without electrolyte) were characterized to verify the electrostatic interactions at the interface between each Sn-O interphase and the Zn metal, and the results are shown in Fig. 6(c). A linear increased *I–V* curve of the SnO_{1,92}/Zn contact implies an Ohmic behavior and a continuous electron transfer across the interface within the applied voltage range from -1.5 to 1.5 V, leading to an areal current density higher than 0.4 mA cm⁻². In contrast, the absolute value of the current density of $Zn|SnO_{1.17}|Zn$ is lower than 5 μ A cm⁻² within -1.5 and 1.5 V, which suggests that electron transport is significantly limited at the SnO_{1.17}/Zn interface. Besides, the measured *I-V* characteristic indicates the non-linear behavior at the SnO_{1.17}/Zn interface (Fig. S28, ESI†). The different electrostatic behaviors at the interface are attributed to the distinct band alignments at the Sn-O phase-dominated interface and the types of majority carriers. The majority carrier of SnO_{1.17} has been identified as holes (i.e., p-type) with a work function of 5.42 eV, as shown in Fig. S29 (ESI†).³⁹ SnO_{1.17} forms a Schottky contact with Zn metal ($\Phi_{\rm Zn}$: ~4.3 eV) with a Schottky energy barrier ($\Phi_{\rm B}$), which is the required energy for carrier conduction and estimated to be 1.1 eV from the difference between the work functions (i.e., $\Phi_{\text{SnO1.17}} - \Phi_{\text{Zn}}$). This non-Ohmic contact would create a charge depletion region in SnO_{1.17} near the interface, limiting the charge carrier transport within the Zn metal during the Zn²⁺ plating/stripping process. Besides, the p-type SnO_{1,17} has a positively charged environment, which delays the electron reception of Zn²⁺ within the SnO_{1.17} interphase until the Zn²⁺ reaches the Zn anode (i.e., at the $SnO_{1,17}/Zn$ interface), enabling the Zn²⁺ reduction beneath the SnO_{1.17} interphase.⁵⁴ Conversely, electrons work as the majority carriers (i.e., n-type) in SnO_{1.92} with a work function of 4.53 eV.55 The contact of SnO_{1.92} and Zn metal could facilitate electron transfer since there is no energy barrier for electron flow between SnO_{1.92} and Zn metal, which induces electron accumulation at the surface of SnO_{1 92} in the Zn²⁺ plating process. The electrostatic interaction between Sn and O interphases and Cu foil was also tested to understand the origin of the compelling performance of the SnO_{1.17}@Cu anode in Zn||Cu asymmetric cells (Fig. S30, ESI†). Similar to the contacts with Zn, Schottky behavior was also observed when SnO_{1.17} was in contact with Cu metal, while Ohmic behavior occurred in SnO_{1.92} with Cu metal. Consequently, charge carrier transport is restricted to the Cu metal in $SnO_{1.17}$ (a) Cu during Zn^{2+} stripping/plating, by which the reduction location for Zn2+ was altered underlying the SnO1.17 interphase. However, the electron transfer at the SnO_{1.92}/Cu interface was facilitated by the Ohmic contact.

The capacitance of the non-faradaic electric double layer (EDL) was measured via alternating current (AC) voltammetry to quantify the effect of SnO_{1.17} and SnO_{1.92} on the ion distribution in IHP. The voltage range of the non-faradaic

region was identified as 0.6-0.9 V (vs. Zn2+/Zn) according to the CV measurement (Fig. S31, ESI†). As shown in Fig. S32 (ESI†), the capacitance value of 7.23 μF of the cell with $SnO_{1.17}$ is lower than 12.32 μF for the cell with SnO_{1.92} and 14.42 μF for the pristine sample, which was ascribed to the weaker EDL with the increased distance between the negatively charged surface and IHP. These results suggest that appropriate band alignment through work function engineering may promote the Zn²⁺ migration within IHP as demonstrated in the modified Zn anode surface, i.e., SnO_{1.17}/Zn metal. As a result, the Zn²⁺ migrates through the SnO_{1,17} interphase and is reduced to Zn⁰ when receiving electrons from Zn metal, inducing the Zn^{2+} plating beneath $SnO_{1.17}$. In contrast, with the high Zn^{2+} migration barrier for SnO_{1.92} and the sufficient electrons supplied by the Ohmic SnO_{1,92}/Zn contact, Zn²⁺ tends to be plated on top of the SnO_{1.92} surface.

To further identify the underlying mechanism of the preferential crystalline orientation of Zn electroplating and morphology regulation by Sn-O interphases, the variation of the surface energy of the (002) and (101) planes before and after integrating with Sn-O interphases has been calculated (Fig. 6(d)). The Zn(101) plane exhibited a high surface energy of 1.65 J m⁻² due to the presence of Zn dangling bonds at the surface, making it challenging to achieve well-aligned Zn(101) plating. The surface energy of the Zn(101) plane decreased from 1.65 J m⁻² (in pristine Zn) to 0.74 J m⁻² when the $SnO_{1.17}$ interphase was applied, resulting in reduced Zn(101) nucleation resistance. Even the Zn(002) and (101) planes have similar surface energy after applying the SnO_{1.17} interphase; the Zn(101) plane will cover the (002) plane due to the faster growth rate, leading to the high ratio of the well-aligned Zn (101) plane. The SnO_{1,92} interphase drastically reduces the surface energy of Zn(002) from 0.88 J m⁻² (in pristine Zn) to 0.30 J m⁻², promoting the preferential growth of the Zn(002) plane. The projected density of states (pDOS) was calculated to elucidate why SnO_{1.17} and SnO_{1.92} have different effects on reducing surface energy. As shown in Fig. 6(e), $SnO_{1.17}$ exhibits strong affinity towards the Zn atoms of the (101) plane due to the obvious overlap between the O 2p orbital and the Zn 4s orbital, while only weak pDOS overlap between Zn 4s of the (002) plane and O 2p. In contrast, a strong pDOS overlap between Zn 4s of the Zn (002) plane and O 2p is observed when the SnO_{1,92} interphase is applied, as illustrated in Fig. 6(e), indicating a prominent interaction between $SnO_{1.92}$ and the Zn(002) plane. Besides, only faint pDOS overlaps were observed between O 2p and Zn 4s of Zn(101), suggesting a much weaker interaction between SnO_{1.92} and the Zn(101) plane. In summary, the SnO_{1.17} interphase could saturate the Zn dangling bonds on the surface of Zn(101), resulting in the formation of dative bonds, thus significantly reducing the surface energy of the Zn(101) plane and hence leading to the preferential growth of Zn(101). However, the SnO_{1.92} interphase decreased the surface energy of Zn(002) by strong interactions between O and Zn atoms of the (002) plane, facilitating the growth of (002) orientation.

Finite element analysis was carried out to visualize the concentration distribution of Zn²⁺ in cells with pristine Zn,

SnO_{1 92}(a)Zn, and SnO_{1 17}(a)Zn at 0.5 V. As illustrated in Fig. 6(f), pristine Zn exhibited the highest Zn²⁺ concentration gradient, compared to the SnO_{1.92}@Zn and SnO_{1.17}@Zn, which was ascribed to the high electric field region on the tip of Zn metal as shown in Fig. S34 (ESI†). In the case of SnO_{1.92}@Zn and SnO_{1 17}@Zn, Ohmic and Schottky contact was built to reflect the charge carrier transmission and inhibition characteristics at the interface between the Sn-O interphase and Zn metal. The SnO_{1.92}@Zn exhibits a higher Zn²⁺ concentration gradient above the SnO_{1,92} interphase compared to that above the SnO_{1.17} interphase in SnO_{1.17}@Zn, corresponding to the stronger EDL presented in SnO_{1.92}@Zn. The Zn²⁺ concentration of SnO_{1.92}@Zn below the Sn-O interphase is drastically decreased due to the limited migration capability of Zn2+ in SnO1.92. Consequently, Zn2+ ions tend to accumulate and undergo reduction by gaining electrons at the surface of the SnO_{1,92} interphase. In contrast, the Zn2+ concentration beneath the $SnO_{1.17}$ interphase is similar to that above it, as Zn^{2+} ions easily migrate in SnO_{1,17} with a lower energy barrier (as in Fig. 6(a) and (b)) and are subsequently reduced to (101)-oriented Zn underlying the SnO_{1.17} interphase. As a result, SnO_{1.17}@Zn facilitates rapid Zn2+ diffusion with a lower energy barrier (liquid-solid) and the faster growth rate of Zn (101) plane (solid) as illustrated schematically in Fig. 6(g).

Various cathodes have been adopted to assemble Zn-based full batteries to evaluate the reliability of SnO_{1.92}@Zn and SnO_{1.17}@Zn for practical applications. The cycling stability of the Zn-based full batteries was tested at low rates because the most stringent proof of stability is not necessarily manifested by the number of cycles but rather by the time the system spends in the fully charged state. 56,57 The sulfur cathode was selected due to its high specific capacity, leading to a higher ZUR than the other commonly used cathode with the same mass loading. The sulfur cathode was manufactured based on the method reported in our previous research.⁵⁸ The manufactured PEDOT@S cathodes with a mass loading of around 6 mg cm⁻² were coupled with commercialized Zn metal anodes (40 μ m), contributing to an N/P ratio of 4.6 at 0.5 A g⁻¹. The PEDOT@S||SnO_{1 17}@Zn cell demonstrates excellent reversibility and rate capability, retaining over 95.2% of its capacity and exhibiting an R_{ct} of 317 Ω after 600 cycles, as shown in Fig. 7(a) and Fig. S35 (ESI†). This performance surpasses that of the PEDOT@S||SnO_{1.92}@Zn battery, which has a capacity retention of 77.4% and an $R_{\rm ct}$ of 487 Ω . The PEDOT@S||Zn battery stably cycled for 334 cycles with a capacity retention of 66.9% and an $R_{\rm ct}$ of 834 Ω before a short circuit occurred at cycle 335 due to the growth of Zn dendrites. The SEM image of pristine Zn after cycling in Fig. S36 (ESI†) exhibits a rough surface with protrusions and cracks, which contributes to the unevenness of Zn2+ plating and severe parasite reactions. Several potholes can be observed on the surface of SnO_{1.92}@Zn, suggesting the inevitable corrosion reaction due to the direct contact between Zn(101) and water. In contrast, the smooth morphology of SnO_{1.17}@Zn after cycling in Fig. S37 (ESI†) indicates superior cycling reversibility. The PEDOT@S||SnO_{1.17}@Zn battery delivered higher capacities at various current densities than the

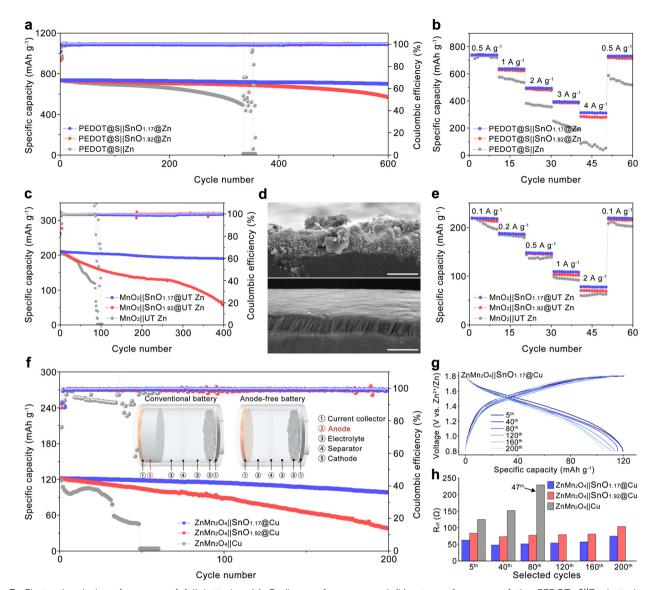


Fig. 7 Electrochemical performance of full batteries. (a) Cycling performance and (b) rate performance of the PEDOT@S||Zn batteries with commercialized Zn foils (40 μm); (c) cycling performance of MnO₂||Zn cells batteries with UT Zn anodes (2.8 μm); (d) cross-sectional SEM images of cycled SnO₁₉₂@UT Zn (top) and SnO₁₁₇@UT Zn (bottom) (scale bar, 5 μm); (e) rate performance of MnO₂||Zn batteries with UT Zn anodes; (f) cycling performance of anode-free $ZnMn_2O_4$ ||Cu with pristine Cu, $SnO_{1.92}$ @Cu, and $SnO_{1.17}$ @Cu. Inset shows the schematic illustration of the conventional Zn-10 cu. Inset shows the schematic illustration of the conventional Zn-10 cu. based and anode-free Zn metal batteries. (g) Voltage-capacity curves and (h) charge transfer resistance of the anode-free battery at selected cycles.

PEDOT@S||SnO_{1 92}@Zn battery and the PEDOT@S||Zn battery, mainly due to faster mass transfer at the (101) Zn orientation in comparison with that at (002) Zn orientation. Moreover, the charge-discharge profiles at different rates in Fig. S37 (ESI†) revealed that the PEDOT@S||SnO_{1.17}@Zn battery show a smaller voltage hysteresis compared with the PEDOT@S||SnO_{1.92}@ Zn battery and the PEDOT@S||Zn battery, originating from the facilitated Zn2+ transfer process at SnO_{1,17}@Zn. To further decrease the N/P ratio during the full cell tests, UT Zn (2.8 µm) was employed to pair with the MnO₂ cathode, which delivered 225 mA h g⁻¹ when paired with a commercialized Zn anode (40 µm) as shown in Fig. S38 (ESI†), leading to an N/P ratio of 1.26 at a current density of 0.1 A g⁻¹. MnSO₄ solution has been added as the electrolyte additive to improve capacity and stability. The MnO₂||UT Zn battery underwent a fast degradation at the initial 84 cycles before experiencing a short circuit, which was caused by the accumulation of by-products and Zn dendrite formation due to the uneven Zn²⁺ plating as identified in Fig. S39 (ESI†). In contrast, the MnO₂||SnO_{1.17}@ UT Zn battery achieved a capacity retention of 90.5% with an average CE of 99.68% after 400 cycles at $0.1 \,\mathrm{Ag}^{-1}$, exceeding the capacity retention of 26.4% and an average CE of 98.92% for the MnO₂||SnO_{1,92}@UT Zn battery. Moreover, the MnO₂||Sn-O_{1.17}@UT Zn battery demonstrates a lower R_{ct} variation of 21 Ω compared to 30 Ω for the MnO₂||SnO_{1.92}@UT Zn battery and 89 Ω for the MnO₂||UT Zn as shown in Fig. S40 (ESI†), respectively. The inferior reversibility of the MnO2||Sn-O_{1,92}@UT Zn battery is mainly attributed to the accumulation

of the by-products on the surface of the anode as indicated in Fig. 7(d). The $SnO_{1.17}@UT$ Zn anode shows a smooth surface and a more compact Zn^{2^+} plating layer, verifying the evenness of Zn^{2^+} plating behavior and restricted parasite reactions at $SnO_{1.17}@UT$ Zn. The $MnO_2||SnO_{1.17}@UT$ Zn battery exhibits higher specific capacities of 109.6 and 78.9 mA h g^{-1} at 1 A g^{-1} and 2 A g^{-1} as shown in Fig. 7(e), compared to 102.3 and 69.7 mA h g^{-1} for the $MnO_2||SnO_{1.92}@UT$ Zn battery and 97.8 and 59.9 mA h g^{-1} for the $MnO_2||UT$ Zn battery, respectively. This should be related to the favorable Zn^{2^+} transfer process at the anode in the $MnO_2||SnO_{1.17}@UT$ Zn battery.

As shown in the inset of Fig. 7(f), conventional Zn-based batteries typically use a thick Zn metal foil (100 to 200 µm), leading to a high N/P ratio (60 to 120) within the battery. This not only results in significant material waste but also substantially compromises the energy density at the battery level. However, the configuration of anode-free Zn aqueous batteries represents a promising technique to improve energy density. To achieve the anode-free configuration in the battery, the ZnMn₂O₄ cathode was chosen to pair with Cu foil as an anode-free Zn aqueous battery, where ZnMn₂O₄ is the sole source of Zn²⁺ during cycling. As shown in Fig. S41 (ESI†), the as-synthesized ZnMn2O4 cathode materials delivered a specific capacity of around 155 mA h g⁻¹ at 0.05 A g⁻¹ when paired with conventional Zn foil (40 µm). Then the as-prepared ZnMn₂O₄ cathode with a mass loading around 2.2 mg cm⁻² was coupled with Cu foil, SnO_{1.92}@Cu, and SnO_{1.17}@Cu, respectively, as anode-free batteries. The ZnMn₂O₄||Cu battery rapidly faded within 47 cycles under these extreme test conditions as shown in Fig. 7(f). However, the ZnMn₂O₄||SnO_{1.17}@Cu battery retained 81.6% of its original capacity after 200 cycles at 0.1 A g^{-1} , which is much higher than 30.9% for the ZnMn₂O₄|| SnO_{1.92}@Cu battery (Fig. 7(f)). Moreover, the ZnMn₂O₄||SnO_{1.17}(a)Cu battery shows a lower voltage decay of 0.03 V, compared to the voltage decay of 0.09 V in the ZnMn₂O₄|| SnO_{1.92}@Cu battery as illustrated in Fig. 7(g) and Fig. S42 (ESI†). The resistance evolution during cycling was evaluated by EIS (Fig. S43, ESI \dagger). The $R_{\rm ct}$ value of the ZnMn₂O₄||Cu battery drastically increased to 231 Ω at the 47th cycle, which should be ascribed to the accumulation of insulated by-products resulting from the corrosion reactions. In contrast, the R_{ct} value of the $ZnMn_2O_4||SnO_{1.17}$ @Cu battery remained lower than 80 Ω during the entire cycling process, suggesting the favorable kinetic conditions for Zn2+ plating in the ZnMn2O4|| SnO_{1.17}@Cu battery. SEM images further confirm the intensive parasitic reactions occurring during the cycling with vast amounts of by-products accumulated on the surface of the Cu foil, leading to the rapid failure of the ZnMn₂O₄||Cu battery (Fig. S44, ESI†). There are a lot of micro-caves that can be observed on the surface of SnO_{1.92}@Cu, implying the presence of severe HERs during battery cycling. In contrast, SnO_{1.17}@Cu shows a flat surface without any accumulation of the byproducts due to the regulated Zn2+ plating behavior and restricted parasitic reactions, which contributes to the superior cycling performance of the ZnMn₂O₄||SnO_{1.17}@Cu battery. The successful demonstration of anode-free Zn aqueous batteries

verifies the advantages of the SnO_{1.17} interphase in promoting the edge of the energy density of the Zn-based energy storage devices

Conclusions

In summary, we successfully induce (101)-oriented Zn²⁺ plating while spontaneously passivating the plated Zn(101) using a thin SnO_{1,17} artificial interphase. Further analyses reveal that the electron transfer from the O 2p orbital of the SnO_{1.17} interphase to the Zn 4s orbital of Zn(101) saturated the Zn dangling bonds at Zn(101), thus lowering the nucleation energy barrier of Zn(101) and leading to the preferential growth of Zn(101). The faster Zn²⁺ transfer at Zn(101) and high ionic conductivity of the SnO_{1.17} interphase brought about favorable Zn²⁺ plating/ stripping kinetics, resulting in the lower Zn nucleation overpotential and the smaller voltage hysteresis. In addition, the Zn^{2+} plating location of the underlying $SnO_{1.17}$ interphase was determined by synergetic effects of low Zn2+ diffusion barriers and electrostatic electron shielding within the SnO_{1.17} interphase, which isolates the plated Zn(101) from water molecules, ensuring high reversibility and rapid Zn2+ migration even at

Consequently, the $SnO_{1.17}$ @Zn symmetric cell operated stably for 600 hours at 20 mA h cm⁻² with a ZUR of 85.7% and a lower overpotential of 72 mV compared to the 140 hours and the overpotential of 124 mV for $SnO_{1.92}$ @Zn. The $SnO_{1.17}$ @UT Zn symmetric cell cycled stably for 800 hours with a ZUR of 91.5% and retained 90.5% of its original capacity when paired with an MnO_2 cathode in a full cell under low N/P ratio (1.26) conditions. Moreover, the Cu||Zn asymmetric cell modified with the $SnO_{1.17}$ interphase achieved an average CE of 99.50% at 5 mA cm⁻² and 5 mA h cm⁻² for 1000 cycles and demonstrated a high-capacity retention of 81.6% after 200 cycles at a low current density of 0.1 A g⁻¹ when applied in an anode-free system. This work outlines the potential of Zn(101) for reversible and kinetically favorable Zn^{2+} plating/stripping to achieve high ZURs at high current densities for practical ZIBs.

Author contributions

Y. Z. and S. L. conceived the idea, designed the experiments, and wrote and revised the manuscript. Y. Z., M. K., F. Q., and D. H. L. performed experiments and formal analysis. C. S. K., J. P. and C. K. conducted related characterization procedures. F. L. helped with the analysis of the electrochemical data. S. L. supervised the project. H.-W. S. and S. L. provided the funding acquisition. All the authors commented on the manuscript.

Data availability

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

Conflicts of interest

There are no conflicts to declare.

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