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Facet-governed Zn homoepitaxy via lattice potential regulation

Xianzhong Yang^{1,2†}, Yan Lu^{3†}, Zhetong Liu^{4†}, Haoqing Ji¹, Ziyan Chen¹, Jun Peng⁵, Yiwen Su¹, Yuhan Zou¹, Chao Wu², Shixue Dou², Peng Gao^{4*}, Zaiping Guo^{6*}, and Jingyu Sun^{1*}

- 1. College of Energy, Soochow Institute for Energy and Materials Innovations, Key Laboratory of Advanced Carbon Materials and Wearable Energy Technologies of Jiangsu Province, Soochow University, Suzhou 215006, P. R. China.
- 2. Institute of Energy Materials Science, University of Shanghai for Science and Technology, Shanghai 200093, P. R. China.
- 3. Department of Physics, Nanchang University, Nanchang 330031, P. R. China.
- 4. Electron Microscopy Laboratory, International Center for Quantum Materials, School of Physics, Peking University, Beijing 100871, P. R. China.
- 5. Center for Hybrid Nanostructures, Universität Hamburg, Hamburg 22761, Germany.
- 6. School of Chemical Engineering, The University of Adelaide, Adelaide, SA 5005, Australia.

*Corresponding authors. E-mail: sunjy86@suda.edu.cn. (J.S.); zaiping.guo@adelaide.edu.au (Z.G.); pgao@pku.edu.cn (P.G.).

[†]*These authors contributed equally to this work.*

Experimental Section

Synthesis of ZnF₂@Zn

 $ZnF_2@Zn$ was synthesized by atmospheric pressure CVD. Upon a thorough cleaning, the commercial Zn foil (thickness: 100 or 10 µm) was placed at the center of the tube furnace. 50 mg of NH_4F was placed upstream of the tube furnace as the precursor. 50 standard cubic centimeters per minute (sccm) Ar was used as the carrier gas. Upon reaching 280 °C within 25 min, the furnace was kept at this temperature for 10 min and then cooled down to room temperature under the Ar flow.

Preparation of the modified electrolyte

ZnSO₄ powder was uniformly dissolved into deionized water to obtain the ZS electrolyte. MMImI was subsequently added to ZS electrolyte to prepare the modified electrolyte, which is abbreviated as ZS-IL. The concentration of MMImI was adjusted to achieve the optimized electrochemical performance.

Preparation of ZVO cathode

The $Zn_xV_2O_5 \cdot H_2O$ (ZVO) material was synthesized according to a reported recipe.^[1] The well-mixed slurry containing active material (ZVO), conductive carbon (Super P) and polyvinylidene fluoride binder with a mass ratio of 7:2:1 was cast onto titanium mesh to fabricate ZVO cathode. The prepared electrodes were dried in a vacuum oven under 80 °C for 12 h to remove the residual solvent.

Characterizations

To prepare the metallographic specimen for EBSD characterizations, the bare Zn and ZnF₂@Zn electrodes were electropolished using a three-electrode system controlled by an electrochemical workstation. According to the reported procedure,^[2] a polishing solution was developed with the composition of ethanol (40 mL), ethylene glycol (10 mL), and sodium thiocyanate (5 g). Titanium foil, Zn foil and Ag/AgCl electrode was used as the working electrode, counter electrode and reference electrode, respectively. The current density was set at ~160 mA cm⁻². The polishing time was about 30 min. EBSD was carried out by Nordlys Max 3 detection system (Matching Tescan Mira4 LMH). The cross-sectional TEM samples were fabricated by the ThermoFisher Helios G4 UX focused ion beam system and the related SEM images were also collected on this system. HRTEM images were taken using FEI Tecnai F20 TEM operating at 200 kV. To reveal the surface chemistry of the ZnF₂@Zn, XPS measurements were performed using the Escalab 250Xi (Thermo Fisher) spectrophotometer. XRD patterns were collected at Bruker D8 Advance Diffractometer. Raman spectra of electrolyte were acquired by Raman spectrometer (LabRAM HR Evolution). NMR spectra were collected at the Bruker ADVANCE III at 600 MHz. The surface morphologies of electrodes were examined by SEM (Hitachi, SU-8010).

Electrochemical tests

First, bare Zn, Ti and ZVO electrode foils were cut into discs. Zn||Zn symmetric cell, Zn||Ti asymmetric cell and Zn||ZVO full cells were fabricated. All the cells were assembled with the commercially available glass fiber separator (WhatmanTM) and as-modified electrolytes. The Neware battery-testing instrument was applied to conduct galvanostatic charge/discharge measurements of cells. The LSV and Tafel curves were respectively recorded at a scan rate of 5.0 and 0.2 mV s⁻¹ on an electrochemical workstation (CHI660E). EIS was recorded utilizing CHI660E with the frequency ranging from 10^5 to 10^{-2} Hz.

DFT calculations

DFT calculations were conducted employing the Perdew-Burke-Emzemhof (PBE) functions^[3] within the Vienna *Ab initio* Simulation Package (VASP).^[4, 5] A plane-wave basis set with a kinetic energy cutoff of 400 eV was utilized for both geometry optimizations and self-consistent calculations. Zn (002), Zn (101), and Zn (100) model facet was respectively constructed with four, four, and eight layers of Zn atoms, separated by a 20 Å vacuum region. Van der Waals interactions were accounted for using the DFT-D3 method,^[6] with Brillouin zones sampled exclusively at the Γ point. During geometry optimizations, all atoms, excluding those in the bottom two Zn layers, were allowed to relax until the residual force per atom reached a threshold below 0.02 eV/Å. The adsorption energy (E_{ad}) of molecules onto Zn surfaces was computed according to the formula $E_{ad}=E_{Mol/Zn} - E_{Mol} - E_{Zn}$, where E_{Zn} , E_{Mol} , and $E_{Mol/Zn}$ denote the total energies of the Zn surfaces, the isolated molecules, and the combined system of molecules adsorbed on Zn surfaces, respectively. The visualization of surface potential figures was performed using VESTA software.^[7]

Molecular dynamics simulation

Molecular dynamics simulations were conducted with Gromacs 2019.6 software,^[8] exploring two distinct simulation systems outlined below. In the first system, 400 SO₄^{2–}, 400 Zn²⁺, 400 I[–], and 400 [MMIm]⁺ were uniformly mixed with 7150 water molecules. The second system comprised 400 SO₄^{2–} and 400 Zn²⁺ mixed with 9828 water molecules. The SPC/E model^[9] was adopted to describe water molecules. For Zn²⁺ and I[–], parameters proposed by Merz *et al.*^[10, 11] were used, while parameters proposed by Christopher *et al.*^[12] were adopted for SO₄^{2–}. The GAFF force field^[13] was applied for MMIm⁺. Electrostatic interactions were treated using the PME method. Van der Waals interactions were described by Lorentz-Berthelot combination rules. Energy minimization procedures were conducted for initial configurations, followed by 20-ns production runs at 298.15 K and 1 bar. Motion equations were integrated by the leapfrog algorithm with a time step of 1 fs. Three-dimensional periodic boundary conditions were consistently considered.

Electric field simulation

Finite element analysis was carried out using the COMSOL Multiphysics software to assess the electric field distribution at different stages of crystal growth within the electrolyte. To model the system representatively, two cuboids were initially constructed to simulate the general environment. The first cuboid (8 μ m length × 8 μ m width × 7 μ m height) represented the 2 M ZnSO₄ electrolyte with a conductivity of 5 S m⁻¹. The second cuboid (8 μ m length × 8 μ m width × 1 μ m height) beneath the electrolyte represented the Zn electrode. Subsequently, Regular hexagonal plates were developed to represent the discrete Zn nanoplates and neatly arranged Zn nanoplates based on SEM observations. These representations allowed for a detailed investigation of the electric field distribution in response to crystal growth. In the beginning stage of electrodeposition, an additional cuboid (8 μ m length × 8 μ m width × 0.4 μ m height) was constructed to represent ZnF₂ deposited through CVD. The electrical conductivity values assigned for the Zn electrode and Zn plates were set at 1.67×10⁷ S m⁻¹, while that of ZnF₂ was specified as 6.17×10⁻⁶ S m⁻¹. A voltage hysteresis of 48 mV was utilized as the cathodic potential, while the anodic potential was held at a constant of zero.

Supplemental Figures



Fig. S1: Homoepitaxy diagram for three typical crystal facets (top view).



Fig. S2: Schematic diagram of the CVD setup for synthesizing ZnF₂ on Zn foil.



Fig. S3: (a) Digital photograph of bare Zn. (b) Digital photograph of $ZnF_2@Zn$ grown in a 1-inch-sized quartz tube. (c) Digital photograph of $ZnF_2@Zn$ produced in a 4-inch-sized quartz tube.



Fig. S4: Digital photograph of $ZnF_2@Zn$ grown under different temperatures while all other growth parameters remain identical (gas flow, precursor content, growth time). The surface of the sample maintains its metallic luster at temperatures below 250 °C, suggesting limited ZnF_2 formation. As the temperature exceeds 280 °C, the metallic luster of the Zn foil diminishes. At 400°C, noticeable cracks and folds emerge, indicating the breakage of the grown sample.



Fig. S5: (a) XPS survey spectrum, (b) Zn 2p spectrum, and (c) F 1s spectrum of ZnF₂@Zn.



Fig. S6: XRD pattern of ZnF₂@Zn.



Fig. S7: Contact angles of 2 M $ZnSO_4$ (ZS) electrolyte on (a) bare Zn foil, (b) $ZnF_2@Zn$ foil, and (c) annealed Zn foil.



Fig. S8: (a) SEM image of bare Zn foil. (b) Enlarged view of (a). (c) SEM image of $ZnF_2@Zn$ grown within 10 min. (d) Enlarged view of (c).



Fig. S9: SEM images of $ZnF_2@Zn$ grown under different temperatures: (a) 200 °C; (b) 250 °C; (c) 350 °C; (d) 400 °C.



Fig. S10: (a) SEM image of $ZnF_2@Zn$ grown within 60 min. (b) Enlarged view of (a). At a fixed growth temperature of 280 °C, extending the growth time to 60 min results in a surface morphology similar to that of samples grown for 10 min (Fig. S8c). The primary difference observed is an increase in the grain size.



Fig. S11: Galvanostatic cycling profile of $ZnF_2@Zn-IL$ symmetric cells with different growth temperatures of ZnF_2 under 30.0 mA cm⁻²/10.0 mAh cm⁻².



Fig. S12: Top-view optical microscopy images of (a) bare Zn and (b) $ZnF_2@Zn$ electrodes after electropolishing. Side-view optical microscopy images of (c) bare Zn and (d) $ZnF_2@Zn$ electrodes before and after electropolishing. Upon comparing the interface thicknesses of the Zn foil before and after electropolishing, our analysis revealed the removal of approximately 50 µm of Zn under the applied polishing conditions (See Experimental Section).



Fig. S13: SEM image of Zn electrodes after electropolishing: (a) bare Zn; (b) ZnF₂@Zn.



Fig. S14: (a) SEM image showing the cutting status via focused ion beam. (b) Enlarged view of (a).



Fig. S15: (a) HAADF-STEM image of ZnF₂@Zn. (b,c) Corresponding EDS maps.



Fig. S16: (a) Filtered HRTEM image of commercial Zn foil. (b) Enlarged view of the area marked by the dotted box in (a). (c) FFT pattern of (b).



Fig. S17: (a) HRTEM image of ZnF₂@Zn foil. (b),(c) Enlarged views of the area marked by the dotted box in (a).



Fig. S18: Digital photograph of electrolytes with different concentrations of MMImI dosage.



Fig. S19: Galvanostatic cycling profile of $ZnF_2@Zn-IL$ symmetric cells with different concentrations of IL under 30.0 mA cm⁻²/10.0 mAh cm⁻².



Fig. S20: Coordination configuration of Zn^{2+} in ZS electrolyte: (a) Six H₂O molecule coordination, (b) five H₂O molecules and one SO₄²⁻ coordination. (c) Coordination configuration of Zn^{2+} in ZS-IL electrolyte.



Fig. S21: Raman spectrum of O–H stretching vibration for ZS-IL (0.05 M) electrolyte.



Fig. S22: In situ optical microscopy visualization of Zn plating process under 10.0 mA cm⁻²: (a) Bare Zn-ZS, (b) $ZnF_2@Zn-ZS$, and (c) $ZnF_2@Zn-IL$ system.



Fig. S23: Digital photograph of electrodeposited Zn electrodes: (a) bare Zn-ZS, (b) ZnF₂@Zn-ZS, and (c) ZnF₂@Zn-IL.



Fig. S24: Representative SEM images of $ZnF_2@Zn$ electrodes ($ZnF_2@Zn-IL$) after plating for 0.2 mAh cm⁻² under 10 mA cm⁻². Yellow arrow markers are employed for convenient observation of the growth direction of Zn islands, while the grain boundary is delineated by yellow dashed line. As depicted in Fig. S24a-c, it is evident that within a specific domain, all Zn islands exhibit a uniform and well-aligned growth direction. Although a small quantity of Zn is plated (0.2 mAh cm⁻²), the ZnF₂ layer experiences breakage and detachment, with only fragmented remnants observable. This implies that the function of ZnF₂ is confined to the initial stages of Zn nucleation.



Fig. S25: (a) SEM image of $ZnF_2@Zn$ after electropolishing. SEM images of $ZnF_2@Zn$ electrodes after plating $(ZnF_2@Zn-IL)$ for 1.0 mAh cm⁻² under 10.0 mA cm⁻²: (b) Low magnification; (c,d) High magnification. The grain boundary is marked with yellow dashed lines. As illustrated in Fig. S25a, after heat treatment via chemical vapor deposition (CVD), the transverse scale of the crystal domain within the $ZnF_2@Zn$ is approximately 55 µm. Remarkably, the electrode electroplated with a capacity of 1 mAh cm⁻² manifests analogous domain dimensions (Fig. S25b), accompanied by a uniform orientation of Zn within each domain. Noteworthy is the seamless integration observed among distinct domains (Fig. S25c,d), indicative of a structurally cohesive interface.



Fig. S26: Representative SEM images of $ZnF_2@Zn$ electrodes ($ZnF_2@Zn$ -IL) after plating for 1.0 mAh cm⁻² under 10.0 mA cm⁻².



Fig. S27: (a) Top-view FIB-SEM image of plated $ZnF_2@Zn$ electrode across two grains in Fig. 3g. (b) Top-view and (c) side-view FIB-SEM images of platted $ZnF_2@Zn$ electrode within a single grain.



Fig. S28: SEM images of $ZnF_2@Zn$ electrodes ($ZnF_2@Zn-IL$) after stripping for 10.0 mAh cm⁻² under 10.0 mA cm⁻². The yellow dotted lines indicate the location of grain boundaries.



Fig. S29: Optical microscopy images of $ZnF_2@Zn$ electrodes ($ZnF_2@Zn$ -IL) after stripping for (a) 5.0 mAh cm⁻² and (b) 10.0 mAh cm⁻² under 10.0 mA cm⁻².



Fig. S30: Nyquist plots of bare Zn-ZS, ZnF₂@Zn-ZS, and ZnF₂@Zn-IL symmetric cells.



Fig. S31: (a) Schematic illustration of two-electrode testing system. (b) Nyquist plots for Ti-Ti cell in ZS and ZS-IL electrolytes. (c) Enlarged view of (b). The conductivity of electrolyte (σ) could be obtained using the following equation: $\sigma = L/(R \times S)$, where *L* is the distance between two electrodes (15 mm), *R* is the resistance, and *S* is the area of electrode (1 cm²). The acquired conductivity for ZS and ZS-IL is 115 and 130 mS cm⁻¹, respectively.



Fig. S32: (a) Nyquist plots for bare Zn-ZS symmetric cell at different temperatures. (b) Nyquist plots for $ZnF_2@Zn-IL$ symmetric cell at different temperatures.



Fig. S33: Linear sweep voltammetry profiles.



Fig. S34: Charge-discharge voltage profiles of (a) bare Zn-ZS||Ti cell and (b) $ZnF_2@Zn-IL||Ti$ cell at the 1st, 100th, 500th and 1000th cycles under 10.0 mA cm⁻²/1.0 mAh cm⁻². (c) CE for bare Zn-ZS||Ti cell and ZnF₂@Zn-IL||Ti cell under 20.0 mA cm⁻²/5.0 mAh cm⁻².



Fig. S35: Galvanostatic cycling of bare Zn-ZS and ZnF₂@Zn-IL symmetric cells at 40.0 mA cm⁻²/4.0 mAh cm⁻², Insets: Detailed voltage profiles at specific cycling duration.



Fig. S36: (a)-(d) Detailed voltage profiles for the rate test (Fig. 4h) at specific cycling duration. (e) Long-term galvanostatic cycling of $ZnF_2@Zn-IL$ symmetric cell after rate test (Fig. 4h). Insets: Detailed voltage profiles at specific cycling duration.



Fig. S37: Galvanostatic cycling of bare Zn-ZS and ZnF₂@Zn-IL symmetric cells at (a) 100 mA cm⁻²/1.0 mAh cm⁻² and (b) 200 mA cm⁻²/2.0 mAh cm⁻². Insets: Detailed voltage profiles at specific cycling duration.



Fig. S38: (a) SEM image of $ZnF_2@Zn$ electrode ($ZnF_2@Zn$ -IL) after plating for 1.0 mAh cm⁻² under 100 mA cm⁻². (b) Enlarged view of (a).



Fig. S39: Nucleation overpotential for bare Zn-ZS and $ZnF_2@Zn-IL$ symmetric cells at different current densities and areal capacities: (a) 1.0 mA cm⁻²/1.0 mAh cm⁻²; (b) 5.0 mA cm⁻²/5.0 mAh cm⁻²; (c) 10.0 mA cm⁻²/10.0 mAh cm⁻² and (d) 20.0 mA cm⁻²/20.0 mAh cm⁻².



Fig. S40: SEM images of bare Zn electrodes (Bare Zn-ZS) after 100 cycles under 10.0 mA cm⁻²/1.0 mAh cm⁻²: Top view of (a) plating side and (b) stripping side; (c) Side view of the plating side. SEM images of $ZnF_2@Zn$ electrodes ($ZnF_2@Zn-IL$) after 100 cycles under 10.0 mA cm⁻²/1.0 mAh cm⁻²: Top view of (d) plating side and (e) stripping side; (f) Side view of the plating side.



Fig. S41: Optical surface profilometry images of Zn electrodes after 100 cycles under 10.0 mA cm⁻²/1.0 mAh cm⁻²: (a) $ZnF_2(@Zn-IL and (b) bare Zn-ZS.$



Fig. S42: Nyquist plots of (a) bare Zn-ZS and (b) $ZnF_2@Zn-IL$ symmetric cells before and after polarization. Inset: Current evolution of symmetric cell under polarization of 10 mV. The Zn^{2+} transfer number can be deduced

from the equation $T_{Zn^2} + \frac{I_s(\Delta V - I_0R_0)}{I_0(\Delta V - I_sR_s)}$, where I_0/I_s and R_0/R_s are the initial/steady current and interfacial resistance, respectively. ΔV was set as 10 mV. The calculated transfer number for bare Zn-ZS and ZnF₂@Zn-IL symmetric cell is 0.19 and 0.45, respectively.



Fig. S43: (a) XRD patterns of bare Zn and $ZnF_2@Zn$ electrodes after 100 cycles under 10.0 mA cm⁻²/1.0 mAh cm⁻². (b) Enlarged view of (a).



Fig. S44: Surface potential fluctuation maps on the standard lattice: (a) Zn (101); (b) Zn (100).



Fig. S45: (a) SEM image of annealed Zn electrode after plating in ZS-IL electrolyte for 1.0 mAh cm⁻² under 10.0 mA cm⁻². (b) Enlarged view of (a).



Fig. S46: Galvanostatic cycling of annealed Zn in ZS-IL electrolyte under 30.0 mA cm⁻²/10.0 mAh cm⁻².



Fig. S47: (a) COMSOL simulation model for Zn electrode before the detachment of ZnF_2 overlayer. Schematic showing (b) horizontal (Fig. 5c) and (c) longitudinal location for electric field simulation. (d) The simulated electric field for longitudinal location. (e) COMSOL simulation model for Zn electrode after the detachment of ZnF₂ overlayer. Schematic showing (f) horizontal (Fig. 5d) and (g) longitudinal location for electric field simulation for electric field simulation. (h) The simulated electric field for longitudinal location.



Fig. S48: CV curves and plots of capacitive currents for symmetric cells with different Zn electrodes/electrolytes: (a),(b) bare Zn-ZS; (c),(d) ZnF₂@Zn-IL (0.05 M); (e),(f) ZnF₂@Zn-IL (0.1 M).



Fig. S49: Adsorption energy of [MMIm]⁺ on different crystal planes of Zn metal: (a) Side view of Zn (100) surface, (b) Side view of Zn (002) surface, (c) Top view of Zn (101) surface, and (d) Side view of Zn (101) surface. The gray, blue, cyan, and white balls denote the zinc, nitrogen, carbon and hydrogen atoms, respectively.



Fig. S50: Structural configurations of four types of ILs and their adsorption energies on different Zn facets. The substituent group attached to cations plays a key role in determining its adsorption energy on Zn surface. Ensuring the uniform epitaxy requires the minimization of discrepancies in the adsorption energy of cations across different facets. Any significant variance in this regard could disrupt the deposition rate of Zn on different facets, consequently undermining the integrity of the homogeneous epitaxy. Upon meticulous comparison, it becomes apparent that MMIm⁺ exhibits a relatively balanced adsorption energy across the different crystal facets. Therefore, the MMIm⁺ has been selected as the optimal candidate.



Fig. S51: (a,b) Representative (a) low-magnification and (b) high-magnification SEM images of electroplated $ZnF_2@Zn$ electrodes within ZS-MMImBF₄ (1,3-dimethylimidazolium tetrafluoroborate) electrolyte under 10.0 mA cm⁻²/1.0 mAh cm⁻². (c) Galvanostatic cycling of $ZnF_2@Zn-IL$ (MMImBF₄) symmetric cell at 30.0 mA cm⁻²/10.0 mAh cm⁻². Here, 0.1 M MMImBF₄ was introduced into a 2 M ZS solution to prepare the ZS-MMImBF₄ electrolyte. Homoepitaxial deposition can be obtained on the $ZnF_2@Zn$ electrode within the ZS-MMImBF₄ electrolyte, similar to the ZS-IL (MMImI) case. Note that during high-rate charge-discharge cycles, there is a notable HER behavior in (c).



Fig. S52: (a) Nyquist plots of full cells before cycling. (b) Nyquist plots of full cells after rate test.



Fig. S53: Galvanostatic charge/discharge profiles for bare Zn-ZS||ZVO full cell.



Fig. S54: SEM images of Zn anode in full cells: (a) ZnF₂@Zn anode cycled in ZS-IL electrolyte for 10000 cycles; (b) bare Zn anode in ZS electrolyte after 1000 cycles.



Fig. S55: Galvanostatic charge/discharge curves of $ZnF_2@Zn-IL||ZVO$ full cell: (a) the first cycle; (b) the 7000th cycle.

Supplementary Tables

Ionic Liquid	Protection mechanism	Current density (mA cm ⁻²)	Areal capacity (mAh cm ⁻²)	Voltage hysteresis (mV)	Lifespan (h)	Ref.
ZnF ₂ +MMImI	Facet-governed Zn homoepitaxy	1 30	1 10	24 155	6500 500	This work
$BMIm^+$	Solvation structure design and electrostatic shielding	5	5	25	1400	[14]
BMIMTFSI	Water-in-ionic liquid	1	0.5	200	1000	[15]
PCAVImBr	Artificial SEI	1	1	88	2700	[16]
[EMIM]BF ₄	Solvation structure design	2	0.5	207	1500	[17]
[EMIM]FSI	Solvation structure design and artificial SEI	1	1	128	680	[18]
BMPTFSI	Artificial SEI	0.1	0.1	100	1000	[19]
SiO ₂ @MIM ⁺	Solvation structure design, in-situ AIL	0.2 20	0.2 10	70 268	1800 75	[20]
PZIL	Artificial SEI	1	1	100	2600	[21]
C12VImPF ₆	Artificial SEI	1	1	80	1600	[22]
ChCl	Leveling effect	1	1	73	2040	[23]
EMImCl	Solvation structure design	1	1	68	500	[24]

Table S1. Performance comparisons of reported Zn anode protective strategies based on ionic liquid.

Material	Protection mechanism	Current density (mA cm ⁻²)	Areal capacity (mAh cm ⁻²)	Voltage hysteresis (mV)	Lifespan (h)	Ref.
ZnF2+ MMImI	Facet-governed Zn homoepitaxy	1 30	1 10	24 155	6500 500	This work
$Zn_yO_{1-x}F_x$	In-situ SEI	1	1	20.4	100	[25]
$3D ZnF_2$	Artificial SEI	1	1	71.5	800	[26]
ZnF_2	Artificial SEI	1	1	80	2500	[27]
ZnF_2	Artificial SEI	0.5	0.5	120	720	[28]
Zn(OTF) ₂	Artificial SEI	0.5	0.25	80	6000	[29]
ZnF_2	In-situ SEI	5 1	1 0.5	100 60	1200 1000	[30]
ZnF ₂ - Zn ₅ (CO ₃) ₂ (OH) ₆ –organic bilayer SEI	In-situ SEI	0.5	0.5	30	1200	[31]
Zn ₃ (PO ₄) ₂ -ZnF ₂ (ZCS)	In-situ SEI	2 5	4 10	55 50	1200 800	[32]
Zn ₃ (PO ₄) ₂ -ZnF ₂ ZnS-Organic	In-situ SEI	1 2	0.5 1	120 140	2500 1900	[33]
$\begin{array}{c} Poly-ZnP_2O_6\\ and\ ZnF_2 \end{array}$	In-situ SEI	1	1	150	1500	[34]
$ZnF_2/Zn_3(PO_4)_2/CFX$	Artificial SEI	1 14.2	2 7.1	45 80	500 185	[35]
ZnF ₂	Artificial SEI	2	1	227	1600	[36]

Table S2. Performance comparisons of reported Zn anode protective strategies based on ZnF_2 .

Mechanism	Materials	Crystal facet	Lifespan (h)	Cycle condition	Ref.
Homoepitaxy	ZnF2@Zn-IL	Multiple crystal facets	6500	1 mA cm ⁻² , 1 mAh cm ⁻²	This work
Homoepitaxy	Annealed Zn	Multiple crystal facets	1000	0.5 mA cm ⁻² , 0.5 mAh cm ⁻²	[37]
Homoepitaxy	(101)-Zn	(101)	5350	4 mA cm ⁻² , 2 mAh cm ⁻²	[38]
Homoepitaxy	(002)-Zn	(002)	3000	1 mA cm ⁻² , 1 mAh cm ⁻²	[39]
Homoepitaxy	Gel-MA	Multiple crystal facets	4000	1 mA cm ⁻² , 1 mAh cm ⁻²	[40]
Homoepitaxy	Zn(002)/Zn ₃ (PO ₄) ₂	(002)	3500	1 mA cm ⁻² , 1 mAh cm ⁻²	[41]
Heteroepitaxy	CuNWs	(002)	1000	1 mA cm ⁻² , 1 mAh cm ⁻²	[42]
Heteroepitaxy	NGO	(002)	1200	1 mA cm ⁻² , 1 mAh cm ⁻²	[43]
Heteroepitaxy	1T-VSe ₂	(002)	2500	1 mA cm ⁻² , 1 mAh cm ⁻²	[44]
Interfacial cultivation	ZnSe	(002)	1530	1 mA cm ⁻² , 1 mAh cm ⁻²	[45]
Interfacial cultivation	FCOF	(002)	1700	5 mA cm ⁻² , 1 mAh cm ⁻²	[46]
Interfacial cultivation	FAG	(002)	4000	1 mA cm ⁻² , 0.5 mAh cm ⁻²	[47]
Interfacial cultivation	SFPAM-Zr	(002)	2500	0.5 mA cm ⁻² , 0.5 mAh cm ⁻²	[48]
Crystal facet anchoring	Bet	(002)	4200	0.5 mA cm ⁻² , 0.5 mAh cm ⁻²	[49]
Crystal facet anchoring	$BMIm^+$	(002)	3162	2 mA cm ⁻² , 1 mAh cm ⁻²	[14]
Crystal facet anchoring	Disodium lauryl phosphate	(100)	1650	1 mA cm ⁻² , 1 mAh cm ⁻²	[50]
Crystal facet anchoring	Theophylline	(101)	2340	2 mA cm ⁻² , 2 mAh cm ⁻²	[51]
Crystal facet anchoring	Serine cation	(100)	1200	1 mA cm ⁻² , 1 mAh cm ⁻²	[52]
Current density regulation	(002)-Zn	(002)	3000	1 mA cm ⁻² , 0.5 mAh cm ⁻²	[53]
Current density regulation	(002)-Zn	(002)	520	2 mA cm ⁻² , 2 mAh cm ⁻²	[54]

Table S3. Performance comparisons of reported strategies for orientational Zn deposition.

Material	Cathode material	Protection mechanism	Current density (A g ⁻¹)	Areal capacity (mAh g ⁻¹)	Capacity retention ratio	Cycle number	Ref.
ZnF ₂ @Zn-IL	Zn _x V ₂ O ₅ ·H ₂ O	Homoepitaxy	10	146.9	85%	11000	This work
ZnS/Zn/Cu	$Na_2V_6O_{16} \cdot 1.63H_2O$	Double-sided engineering	2	263.7	34%	1400	[55]
ZnO-rich ASEI@Zn	MnO ₂	Artificial SEI	0.5	262.84	62.6%	1000	[56]
3D-Zn(002)	$\mathrm{NH_4V_4O_{10}}$	Homoepitaxy	5	127.7	75.7%	4000	[57]
Zn	V ₂ O ₃	Heteroepitaxial	2	361.8	85.5%	2000	[58]
Zn@Ag	V_2O_5	Heteroepitaxial deposition	2	281.8	74.8%	1500	[59]
Theophylline/ ZnSO ₄	CC@MnO	Cystal facet anchoring,	1	/	76.7%	1000	[51]
(101)-Zn	MnO ₂	Heteroepitaxial	1	95.4	/	1000	[38]
Zn(002)	MnO ₂	homoepitaxy	1	/	74%	1500	[39]
Zn(002)	$K_{0.51}V_2O_5$	Current density regulation	5	161	/	2000	[54]
Zn@Cu	$Zn_xV_2O_5$ · nH_2O	Current density regulation	0.2	338.5	92.4%	200	[53]
VSe ₂ /Zn	MnO ₂	Artificial SEI	1	195	94.7%	500	[44]
ZnSe@Zn	V ₂ O ₅	Artificial SEI	5	194.5	84%	1000	[45]
Zn	V ₂ O ₅	Homoepitaxy	5	345.1	74.1%	2000	[52]
FAG@Zn	MnO ₂	Homoepitaxy	1	190	92%	800	[47]
Zn	V ₂ O ₅	Crystal facet anchoring	1	250	92%	1200	[50]

 Table S4. Performance comparisons of AZIB full battery.

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