In-situ Generated Tin Protective Layers from Stannous Oxalate for Dendrite-Free Zinc Anodes

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Calculation method

The density functional theory computations were carried out by using the CASTEP, employing the ultrasoft pseudopotential.^{1–3} The exchange correlation potential was represented by the Perdew–Burke–Ernzerhof (PBE) functional within the generalized gradient approximation (GGA).⁴ Then, a 5×5 supercell Zn (002) surface (100 Zn atoms) with four atomic layers were built. Then a layer of Sn atom is constructed on the surface of Zn (002) to simulate the hydrophobic layer (abbreviated as Zn(002)/Sn). In the process of optimizing the structure, the bottom two layers of atoms are fixed, and the other layers of atoms are relaxed. The cutoff energy is set to be 500 eV. The convergence tolerances of energy, force and maximum displacement are set to 1.0×10^{-5} eV/atom, 3.0×10^{-2} eV/Å and 1.0×10^{-3} Å, respectively. The *k*-points grid sampling is set as $2 \times 2 \times 1$. The vacuum layer is set to 15 Å. Meanwhile, the DFT-D correction method is used to describe the van der Waals interaction.⁵ The adsorption energy (*E*_{ad}) of H₂O molecule on Zn (002)/Sn surface can be calculated by:

$$E_{ad} = E (slab + H_2O) - E(slab) - E (H_2O)$$

where E (slab + H₂O) is the energy after H₂O molecule adsorption on the Zn (002)/Sn surface, E(slab) is the energy of the Zn (002)/Sn surface, and E(H₂O) is the energy of the H₂O molecule.

Supporting Information Figures



Figure S1. The full FT-IR spectrum of bare Zn and Zn@SCO anodes.



Figure S2. Sn XPS spectrum of Zn@SCO anodes.



Figure S3. C XPS spectrum of Bare Zn and Zn@SCO anodes.



Figure S4. O XPS spectrum of Bare Zn and Zn@SCO anodes.

Electron Image 1



Figure S5. SEM image of coated Zn@SCO anode.



Figure S6. SEM image of cross section of coated Zn@SCO anode.



Figure S7. Corresponding EDS mapping of cross section of coated Zn@SCO anode.



Figure S8. Contact angle of different zinc anode surfaces. The left is bare Zn, the middle is Zn@CMC and the right is Zn@SCO.



Figure S9. Schematic illustration of different Zn crystal planes.



Figure S10. Adsorption energy of H₂O molecules on the Zn@SCO (002) crystal plane.



Figure S11. Adsorption energy of H₂O molecules on the Zn (002) crystal plane.



Figure S12. The corresponding voltage polarization at different current densities from

1 to 20 mA cm^{-2}



Figure S13. Charge/discharge curves of the Zn plating/stripping process for Zn@SCO with a current density of $1.0 \text{ mA} \cdot \text{cm}^{-2}$ at different cycles.



Figure S14. Charge/discharge curves of the Zn plating/stripping process for bare Zn with a current density of $1.0 \text{ mA} \cdot \text{cm}^{-2}$ at different cycles.



Figure S15. Charge/discharge curves of the Zn plating/stripping process for Zn@CMC with a current density of $1.0 \text{ mA} \cdot \text{cm}^{-2}$ at different cycles.



Figure S16. Schematic diagrams for Zn deposition processes on Zn metal surface of a) bare Zn and b)Zn@SCO.



Figure S17. Images of bare Zn, Zn@CMC and Zn@SCO after cycling.



Figure S18. SEM image bare Zn after cycling at 10.0 µm.



Figure S19. SEM image Zn@CMC after cycling at 10.0 μ m.



Figure S20. SEM image Zn@SCO after cycling at 10.0 μ m.



Figure S21. Surface topography of the Zn@SCO corresponding to surface roughness

curves.



Figure S22. Surface topography of the bare Zn corresponding to surface roughness

curves.



Figure S23. XRD pattern of MnO₂ powder and standard card (PDF#72-1984).



Figure S24. The cycling performance and CE of Zn@SCO //MnO2 coin full cell at 3

 $A\!\cdot\!g^{-1}$



Figure S25. Schematic diagram of MnO₂//Zn pouch cell structure.



Figure S26. Localized magnification of XRD about Sn (200) and Sn (101) peaks for Zn@SCO electrodes.



Figure S27. The cycling performance and CE of Zn@SCO $//NH_4V_4O_{10}$ coin full cell

at 1 $A \cdot g^{-1}$



Figure S28. Changes in the Sn characteristic peaks of Zn@SCO symmetrical cells at

0, 50, and 100 cycles

	Electrolyt e	Additives/T reatment method	Mechanism	Performances (Zn//Zn cells)	Ref
Interfa ce enginee ring	ZnSO ₄	graphene	regulate nucleation, growth, and reversibility of metal anodes.		6
	ZnSO ₄	Zn-Cu alloys	suppress the chemical corrosion of Zn metal anode	150 h at 1 mA cm ⁻² and 0.5 mAh cm ⁻²	7
	ZnSO ₄	Zn-Al alloys	tackle irreversibility issues of Zn metal anode	2000 h at 0.5 mAh cm ⁻²	8
	ZnSO ₄	Au	heterogeneous seed strategy with quasi- isolated	2000 h at 0.25 mA cm ⁻² and 0.05 mAh cm ⁻²	9
	ZnSO ₄	BaTiO ₃	mitigate the inhomogeneous cation diffusion and sluggish cation replenishment	4000 h at 1 mA cm ⁻² and 1 mAh cm ⁻²	10
	ZnSO ₄	Ta ₂ O ₅	suppress by-productions	3000 h at 0.25 mA cm ⁻² and 0.05 mAh cm ⁻²	11
	ZnSO ₄	polyamide	isolate O ₂ and active water	8000 h at 0.5 mA cm ⁻² and 0.25 mAh cm ⁻²	12
	ZnSO ₄	β-PVDF	stabilize the stripping/plating process	2000 h at 0.25 mA cm ⁻² and 0.05 mAh cm ⁻²	13
	ZnSO ₄	hydrogenate d graphyne	mediate the redistribution of the Zn^{2+} concentration	2400 h at 1 mA cm ⁻²	14
	ZnSO ₄	soak pieces of Zn foil in a PPA solution	The ion conductive Zn phosphate layer serves as an SEI	$\begin{array}{c} 6500 \text{ h at 2} \\ \text{mA cm}^{-2} \text{ and 1} \\ \text{mAh cm}^{-2} \end{array}$	15

Table S1. The table of different strategies to optimize zinc anodes and electrochemical performance.

	Additives/T reatment method	Method	Mechanism	Performances (Zn//Zn cells)	Ref
Interf ace engin eerin g	Zn@SCO (This work)	<i>In-situ</i> constructi on of an artificial interphase protection layer	The metal hydrophobic protective layer regulates the zinc nucleation site, isolates the active water from the zinc anode, and inhibits corrosion and hydrogen evolution	More than 2300 h at 1 mA cm ⁻² and 1 mAh cm ⁻²	
	Zn@ILDO	Utilizing In ³⁺ isomorphi c substitutio n of Al ³⁺ in Zn-Al LDO (LDO), Zn-Al-In LDO (ILDO) is obtained	Reorganisation of interfacial layers and formation of uniform electric fields	1800 h at 0.5 mA cm ⁻² and 0.5 mAh cm ⁻²	16
	Zn@ZFA	<i>In-situ</i> constructi on of an artificial interphase protection layer	Shielding of active water molecules on the anode, rich in C@O and CAF groups to promote the uniform deposition of Zn ²⁺ , high ionic conductivity	2200 h at 1 mA cm ⁻² and 1 mAh cm ⁻²	17
	Zn(OTf) ₂	Growth of an artificial interfacial layer on a zinc anode with continuous ly applied	Artificial SEI promotes the interfacial kinetics, depresses the side reaction, and meantime maintains its integrity during cycling	250 h at 10 mA cm ⁻² and 10 mAh cm ⁻² 800 h at 50 mA cm ⁻² and 50 mAh cm ⁻²	18

current

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Table S2. The table of relatively complex strategies for protecting zinc anodes.

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