Supporting Information

Electric field distribution regulation of zinc anode toward long cycle life zinc metal battery

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Experimental section

Material preparation: The bare Zn was first washed with ethanol and deionized water to remove the surface oil, then immersed with a 5% mass of hydrochloric acid solution and stirred for 30 minutes at 800 rpm, then washed with deionized water to remove the surface acid residue, ultrasonic for 30 min and finally dried in a vacuum oven at 30°C to obtain Zigzag Zn. Finally, the processed samples are kept in gloves under argon atmosphere to avoid surface oxidation.

Preparation of V_2O_5 cathode: Typically, 2 mmol (0.36 g) V_2O_5 was dissolved in 80 mL of deionized water under stirring for 30 min and transfer it into 100 mL PTFE liner. 2 mL of H_2O_2 was added into liner and stir for another 30 min and then hydrothermal react at 120°C for 6 h. The obtained product was directly freeze-dried for 96 h. Then, the obtained product was ground into powder and set aside.

Zn anode characterization: XPS is used to analysis the SEI composition in the Zn anode (Thermo-Fisher Scientific ESCALAB Xi, microfocus monochrome Al Kα X-ray light source: 20 μm ~ 900 μm continuously adjustable). The morphology of the Zn anode surface is observed by SEM (Sigma 500).

Symmetric cell assembling: CR2032-type coin cell was assembled by using Zn plate electrode, electrolyte, and glass microfiber separators (Whatman CAT No. 1825.047). Zn foil with a thickness of ~50 μm was used and pouched into plates with a diameter of 15 mm. 3 M zinc trifluoromethanesulfonate solution was used as electrolyte and the add amount was 100 μL.

In-situ optical microscope: Zn|Zn symmetric cell is fabricated in the custom-designed electrochemical cell to observe the stripping/plating process of Zn metal. The current density applied is 5 mA cm^{-2}.

Electrochemical testing: A Neware electrochemical testing system was used to measure the electrochemical performance of these cells. The CV measurements were carried out on CHI660 electrochemical workstation. EIS was measured under the frequency from 100 mHz to 100 kHz with an amplitude of 10 mV. The mass loading of V_2O_5 cathode material was ~5 mg cm^{-2}.

Density functional theory calculations: Density Functional Theory (DFT) calculations for surface adsorption were conducted using the Vienna ab-initio simulation package (VASP) software, with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional based on the generalized gradient approximation (GGA) approximation. The Gamma method was used to set the Brillouin zone K-point grid sampling size at 2×2×1 to generate the K-point grid. The energy convergence criterion was set at 1.0×10^{-5} eV, the force convergence criterion was set at 0.02 eV/atom, and the cutoff energy was set at 400 eV. The Zn(002) surface model was created from a 4×4 supercell with a thickness of four in the ab direction. The bottom two layers of atoms were fixed during the structural relaxation process. In the c direction, a 15 Å vacuum layer was used to avoid the effect of periodic boundary conditions on the surface model, and a DFT-D3 dispersion correction was used to calculate weak interactions. All structures and charge density differences were visualized and analyzed using VESTA. The adsorption energy (E_{ads}) between the Zn slab and different molecules was calculated using Equation:

$$E_{ads} = E_{total} - (E_{molecule} + E_{slab})$$

where E_{total}, $E_{molecule}$, and E_{slab} are the total energy of the Zn(002) surface after molecule adsorption, the energy of the adsorbate, and the energy of the Zn(002) surface model, respectively. All energies are reported in eV.

The formula for calculating surface energy is:

$$\gamma_{hkl}^{\sigma} = \frac{E_{slab}^{hkl,\sigma} - E_{bulk}^{hkl} \times n_{slab}}{2 \times A_{slab}}$$

where "γ_{slab}^{σ}" represents the specific surface energy, "$E_{slab}^{hkl,\sigma}$" is the energy required to create the surface, E_{bulk}^{hkl} is energy per atom of bulk Zn, n_{slab} is total number atoms in the slab structure, and "A_{slab}" denotes the surface area.

Finite element simulation: In the proposed model, a lithium-ion battery is utilized, with the Deformed Geometry entry from the Model Wizard incorporated. This particular entry allows for the concurrent addition of the lithium-ion battery interface and the deformed geometry into the model. As a result, both the lithium-ion battery

interface and deformed geometry have been integrated.

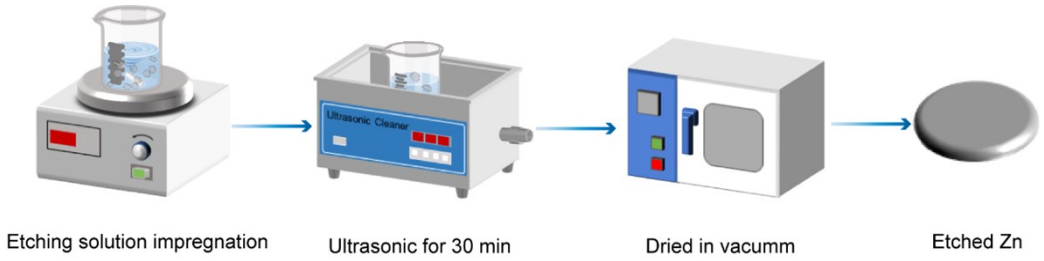

Figure S1. Preparation flow chart of zigzag Zn anode.

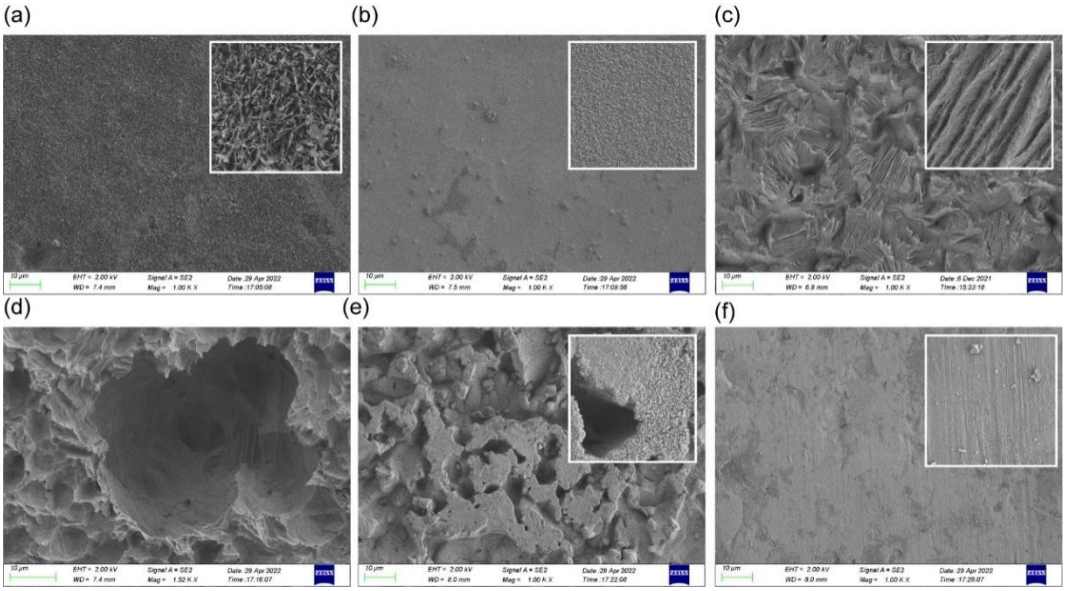

Figure S2. SEM morphology obtained after etching with different etchants (a)-(f) 5% NaOH, 5% HNO_3, 5% HCl, 5% H_2SO_4, 5% $H_2C_2O_4$, Bare Zn. Scale bar is 10 μm and the top right zoom is 1 μm.

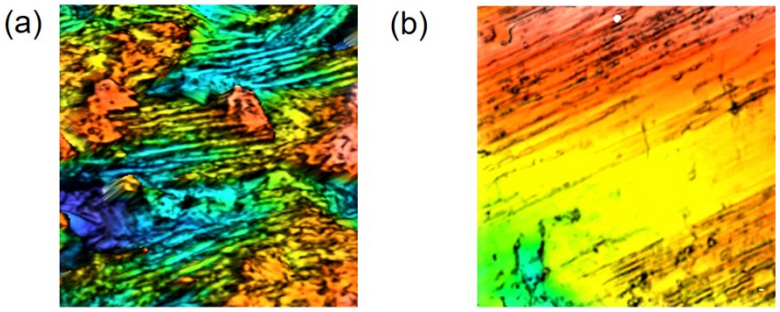

Figure S3. Comparison of profilometer maps of Zigzag Zn(a) and bare Zn(b).

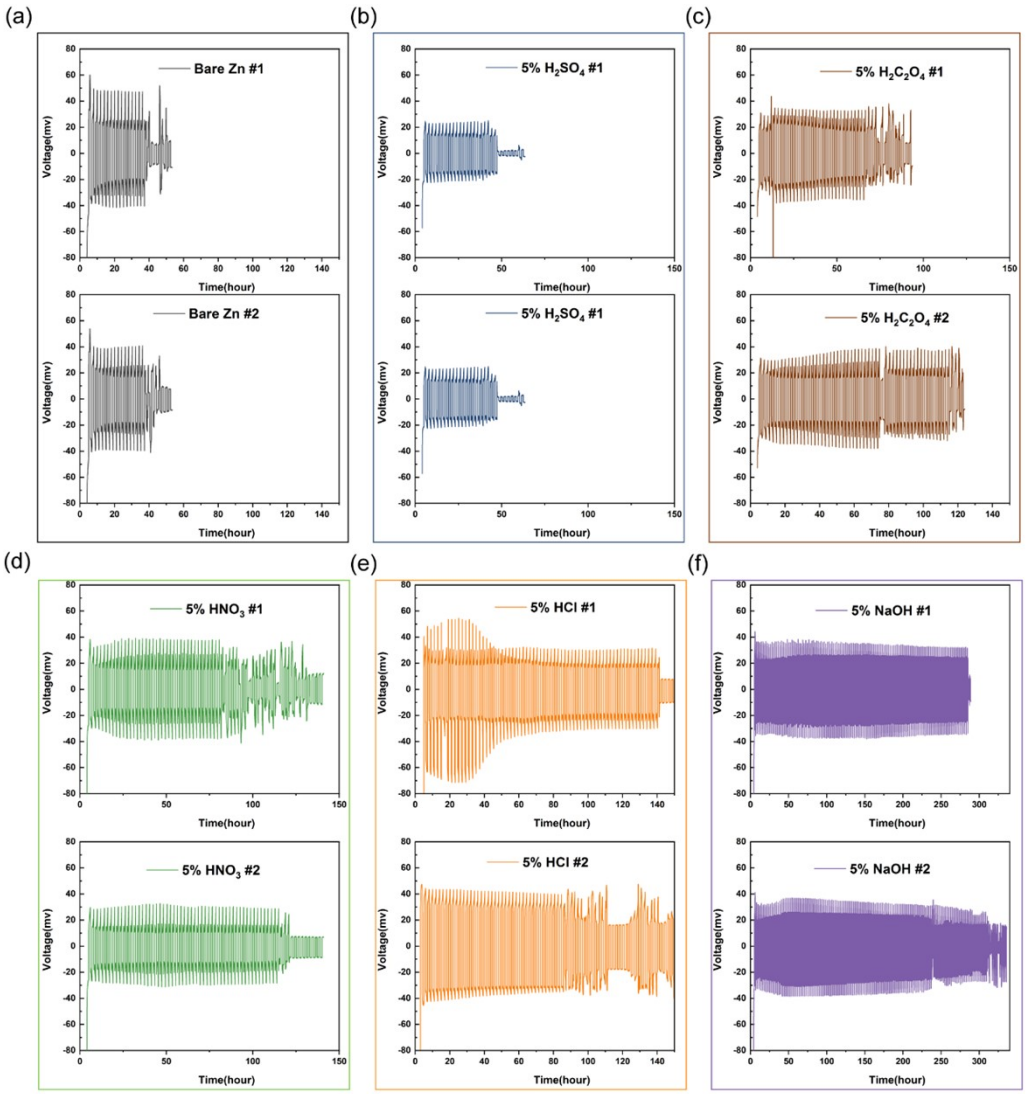

Figure S4. Cycling performance of symmetric cells assembled from Zn foil after etching with different reagents.

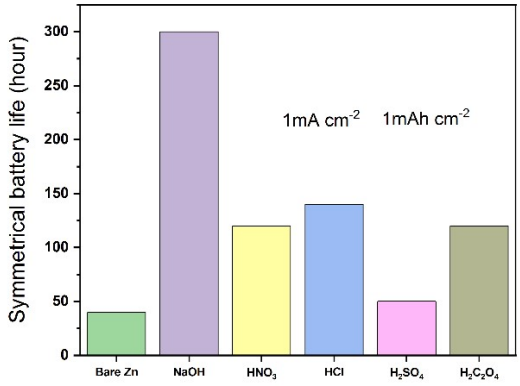

Figure S5. Cycle life of different symmetric cells.

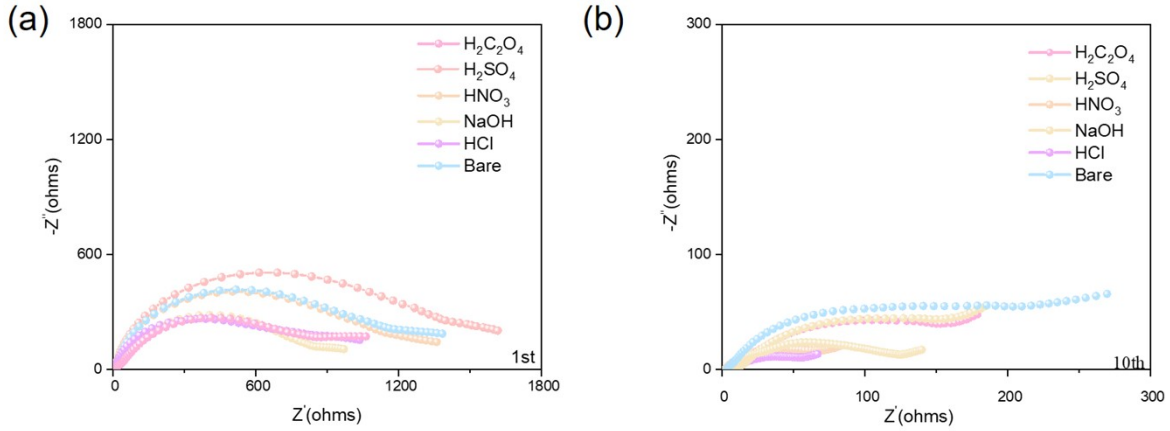

Figure S6. Comparisons of EIS spectra for bare,HCl, NaOH, HNO_3, H_2SO_4, $H_2C_2O_4$ Zn batteries after the 1st (a) and 10th (b) cycles in aqueous $Zn(OTf)_2$ electrolyte.

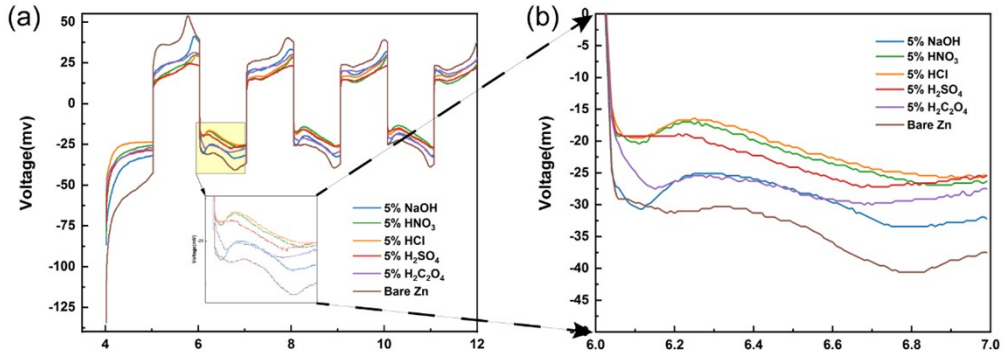

Figure S7. Polarization curves of symmetric cells using different etching reagents at the current density of 1 mA cm^{-2} and areal capacity of 1 mAh cm^{-2} and the (b) zoomed-in partial view.

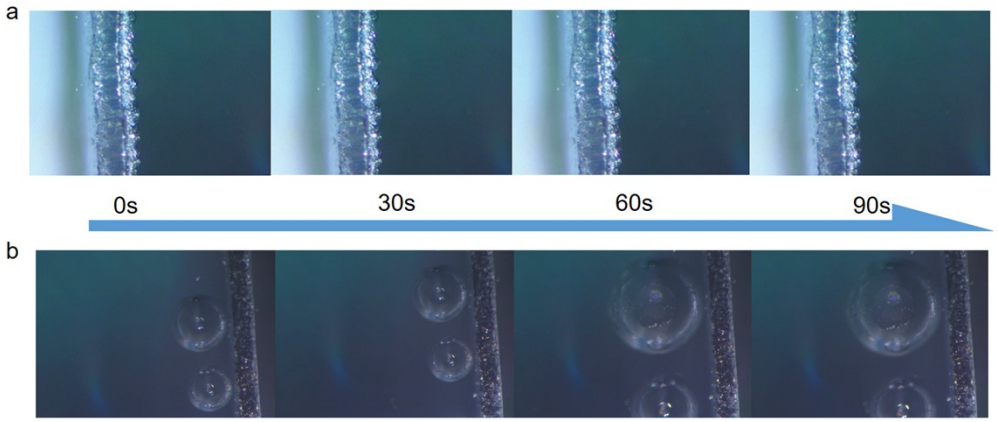

Figure S8. Under an in-situ optical microscope, photographs were taken of the surface morphology

of zinc plates after being deposited for 40 minutes (0s,30s,40s,90s) using a zigzag zinc (a) and for 15 minutes (0s,30s,40s,90s) using a regular zinc plate (b).

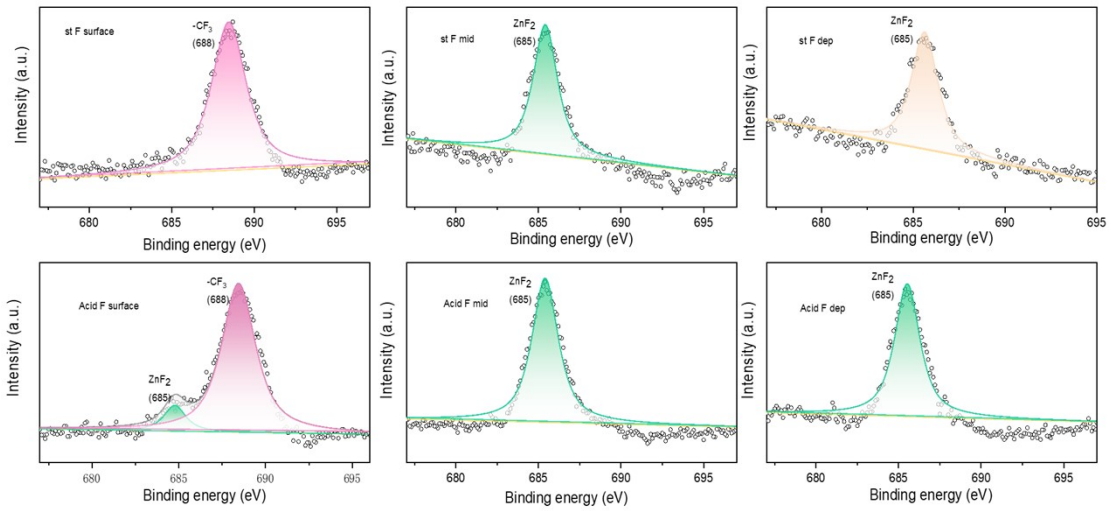

Figure S9. Comparison the XPS of surface, middle, and deep regions between the bare (a, b, c) and Zigzag Zn (d, e, f).

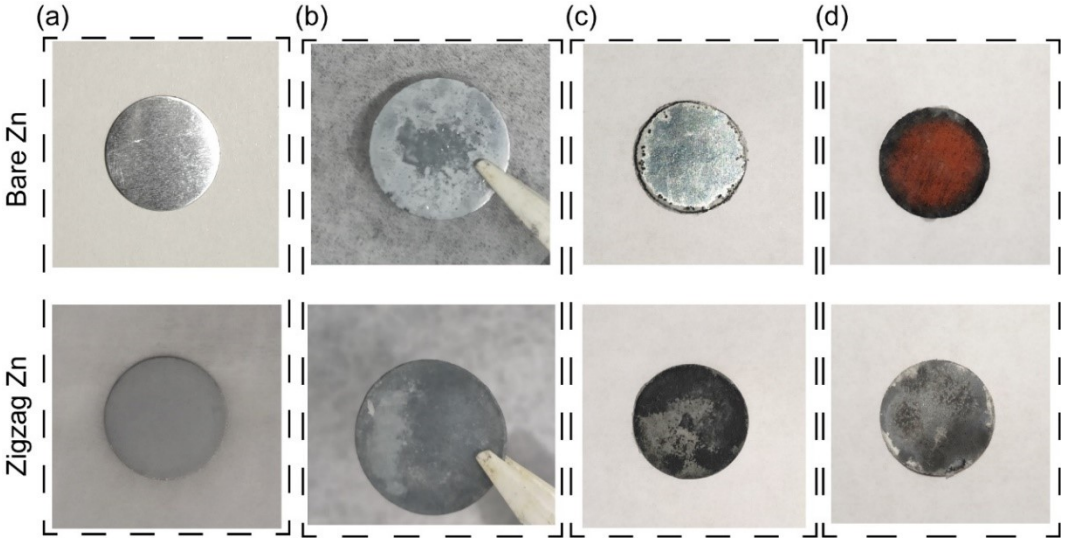

Figure S10. (a) Photograph of bare Zn and zigzag Zn after HCl etching and (b) Zn electrode in symmetric cell after 30 cycles under1 mA cm^{-2}. (c) Photograph of the Zn electrode of Zn-Cu half-cell after 30 cycles of 1 mA cm^{-2} and (d) the corresponding Cu electrodes.

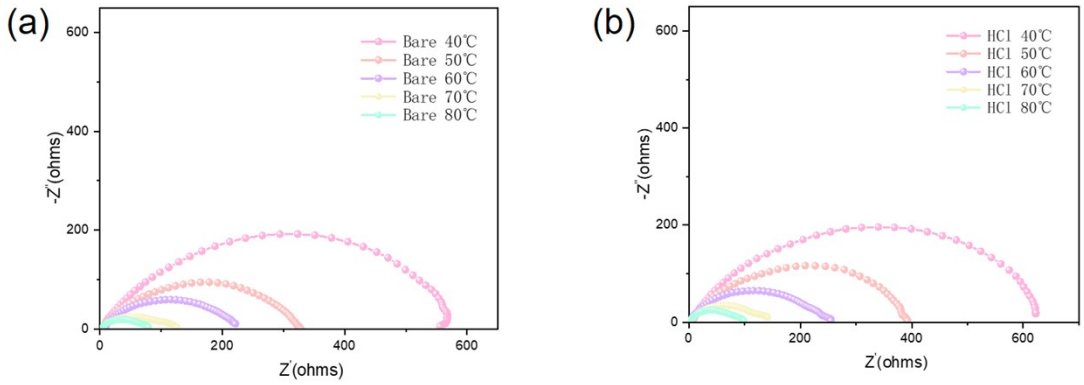

Figure S11. Nyquist plots of Zn//Zn cells at different temperatures in (a) bare Zn and (b) Zigzag Zn.

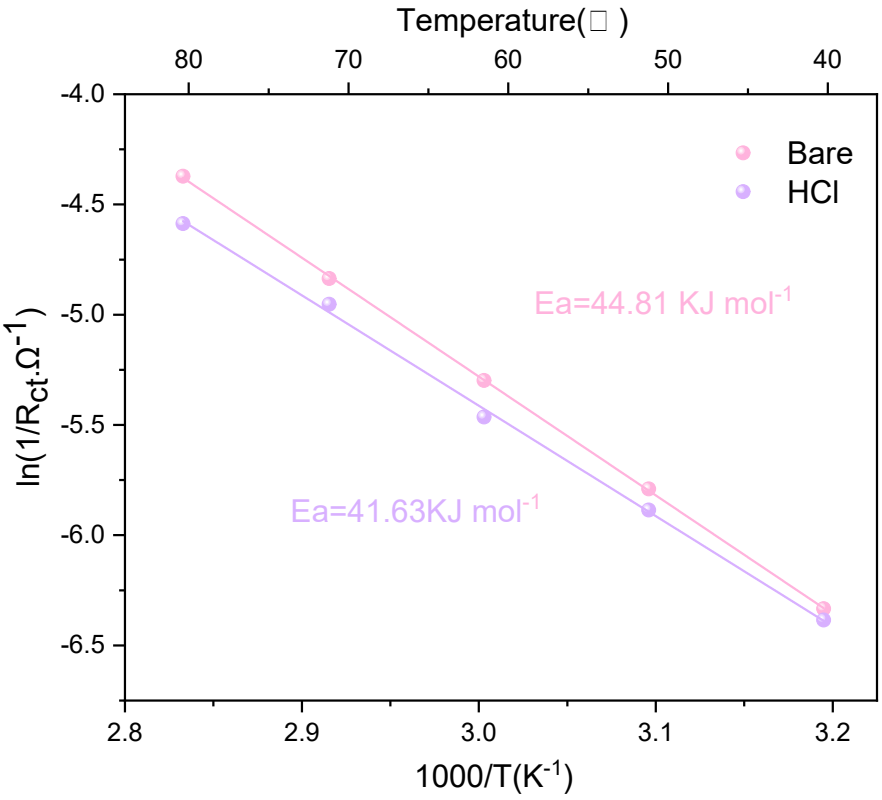

Figure S12. Arrhenius curves and activation energy of zinc ion diffusion.

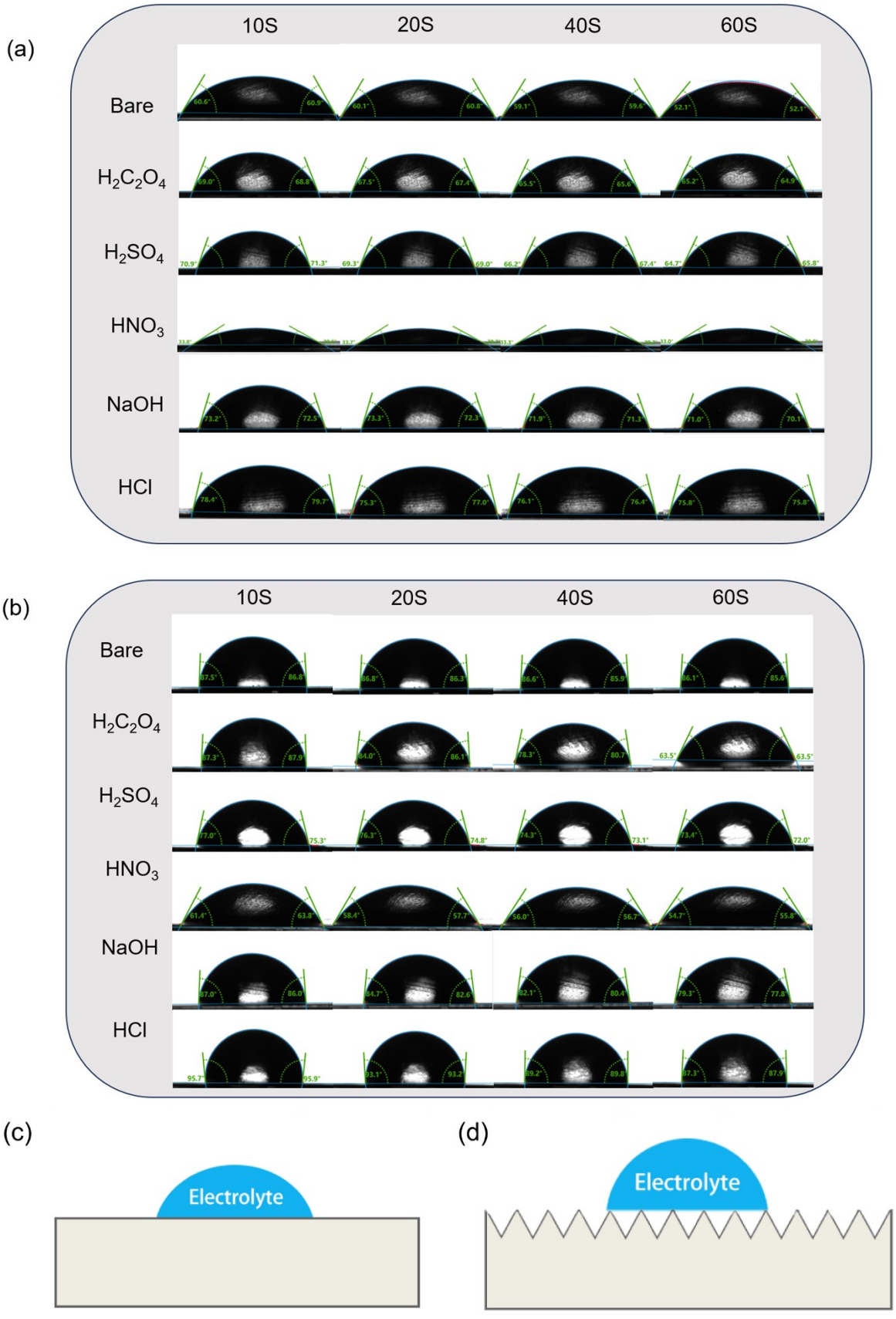

Figure S13. Contact angle measurement. (a) Contact angle of of zinc plates treated in different ways

at different times in 3M $Zn(OTf)_2$. (b) Contact angle of of zinc plates treated in different ways at different times in 2M $ZnSO_4$. Contact angle diagram of (c) bare Zn and (d) zigzag Zn.