Supporting Information

Perfluoro-1-butanesulfonic Acid Etching Strategy for Dendrite Suppression in Aqueous Zinc Metal Batteries

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EXPERIMENTAL SECTION

Materials. Commercial Zn foil (0.1 mm) and Cu foil (0.1 mm) were purchased from Ailian of Tianjin, Ltd. $ZnSO_4 \cdot 7H_2O$ (>99.0%), and Perfluoro-1-butanesulfonic acid (PFBS) (>99.0%) of analytic grade were purchased from the Aladdin and used as received without further purification. Commercial separator GF-A (1.6 μm) was purchased from Whatman of England.

Preparation of the Zn@PFBS. The 10 mm × 30 mm × 2 mm zinc foil were ultrasonically cleaned with acetone, anhydrous ethanol, and deionized water using 2000# sandpaper, followed by immersion in an aqueous solution of 10% perfluoro-1-butanesulfonic acid by mass fraction for 0.5 h, 3 h, and 18 h. The surfaces were cleaned with deionized water. After the treatment, the $C_4F_9O_3S$-Zn (Zn@PFBS) surfaces with hydrophobic properties were prepared by standing at room temperature for one day.

Preparation of the $Na_5V_{12}O_{32}$ (NVO) anode. In the experimental section, we describe the synthesis of the NVO precursor. Firstly, 1.819 g V_2O_5, 40 mL H_2O and 2 mL NaOH (pH≈10) were added in a beaker and then magnetically stirred for 15 min until a wine-red solution was formed. After that, the above solution was transfer to a 50 mL autoclave and kept at 180 ℃ for 48 hours. The precursors were collected by centrifugation and washed with deionized water and ethanol for 3 times, respectively, and dried at 80 ℃ in vacuum for 12 h. The NVO powders were obtained by heating the precursors at 300 ℃ in the air for 2 hours.

Electrochemical Measurements. Linear scanning voltammetry (LSV), Tafel plot, CV and Electrochemical Impedance Spectroscopy (EIS) tests are performed on a CHI760E electrochemical workstation. The LSV was tested using a Zn@ PFBS batteries with a scan rate of 1 mV s^{-1}. The Tafel plot test used a three-electrode system (Working electrode: Zn, Counter electrode: Pt, Reference electrode: Ag/AgCl, Salt bridge: Saturated KCl solution) with a scan rate of 1 mV s^{-1}. The electrochemical performances of Zn//Zn half-batteries, and Zn//NVO full batteries were tested in the form of encapsulated coin batteries (CR2032) in air and at room temperature. Testing of

batteries for galvanostatic charge/discharge cycles is performed on the Neware battery testing system. The Zn//Zn symmetric batteries were cycled with different current densities and capacities. For full Zn//NVO batteries, NVO cathode loading is 1-2 mg cm^{-2}. The scan rate for CV testing of Zn//NVO full batteries is 1 mV s^{-1}. Zn//NVO full batteries were cycled in the voltage range of 0.4-1.4 V.

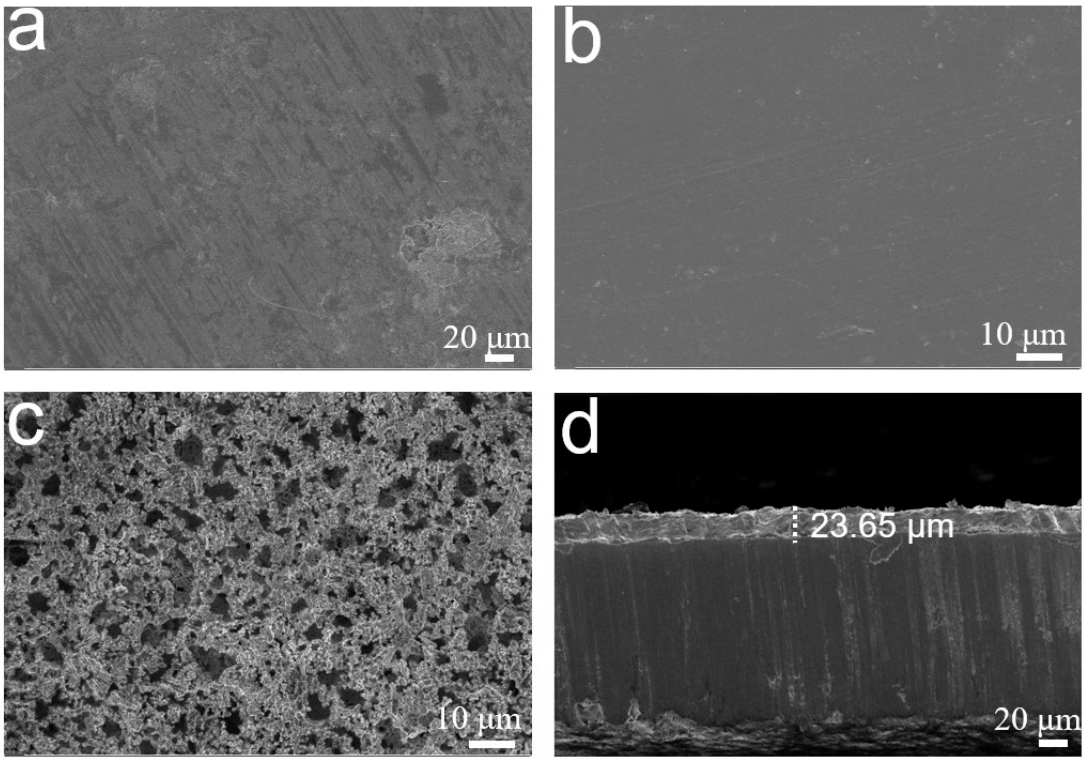

Fig. S1 SEM images (a, b) Images of the bare zinc sheet (c) Surface of the zinc sheet after PFBS etching (d) Interface layer thickness.

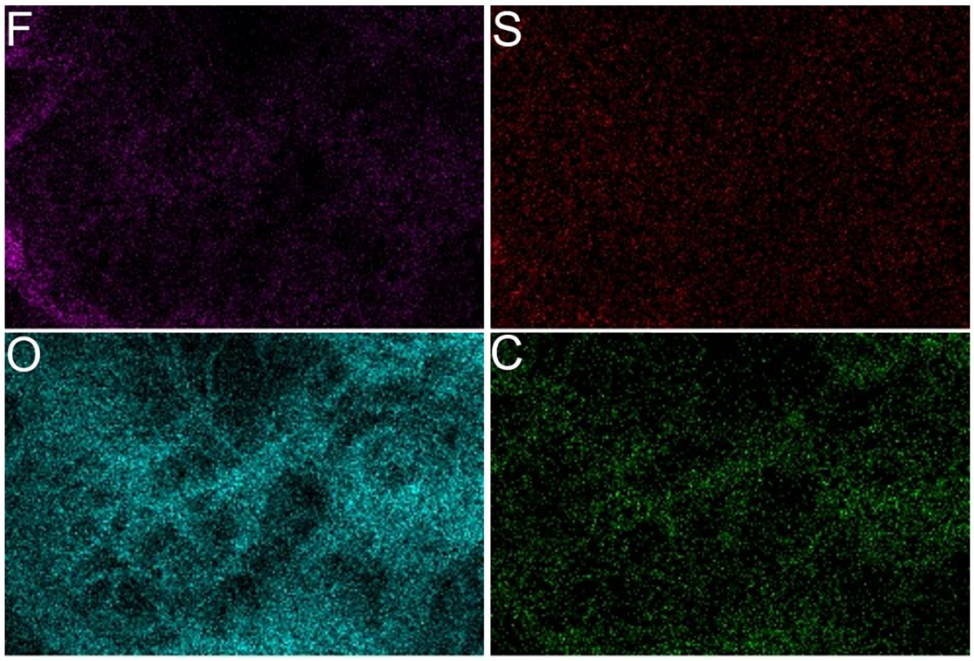

Fig. S2 EDS spectrum of the Zn@PFBS interface layer.

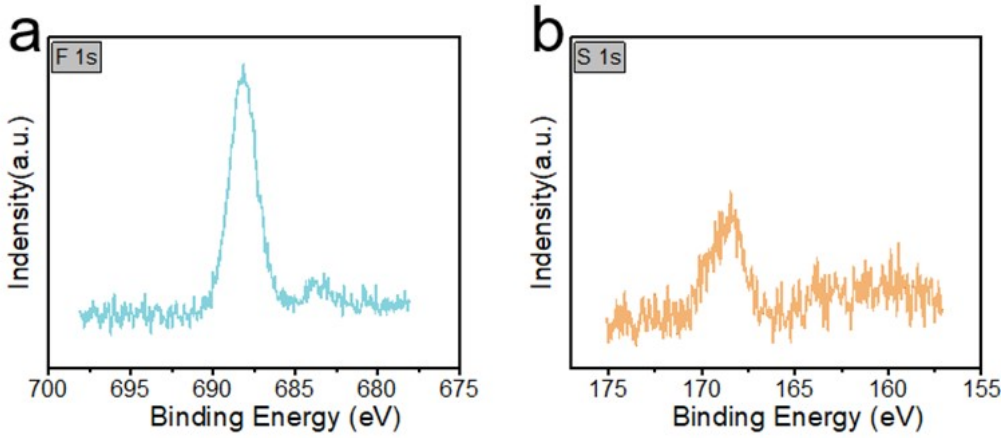

Fig. S3 XPS spectra of the Zn@PFBS interface layer (a) F 1s; (b) S 1s.

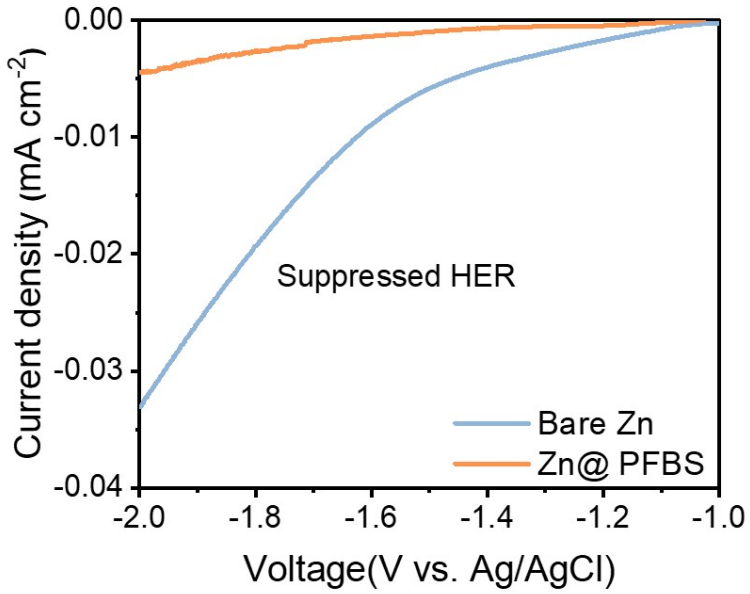

Fig. S4 Linear polarization curve of a 2 M Zn_2SO4 solution.

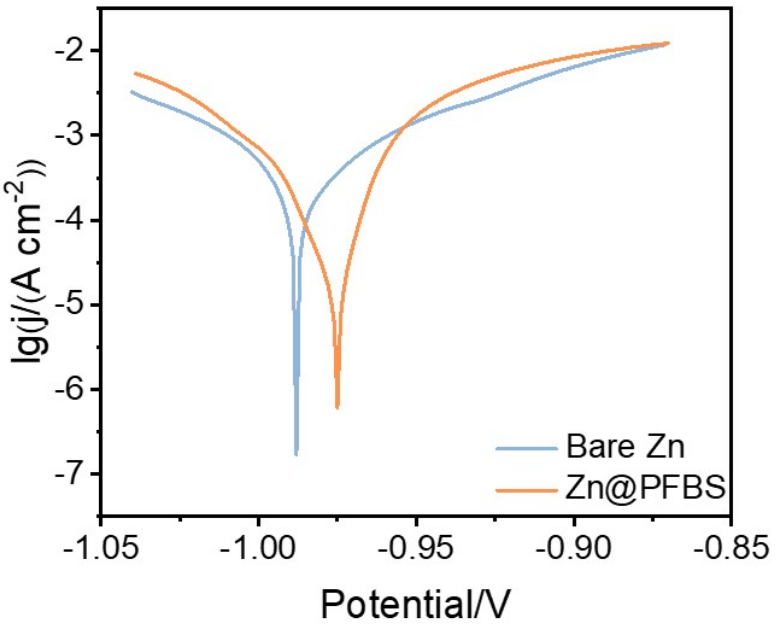

Fig. S5 Tafel of the 2 M $ZnSO_4$ electrolyte with different anode surfaces.

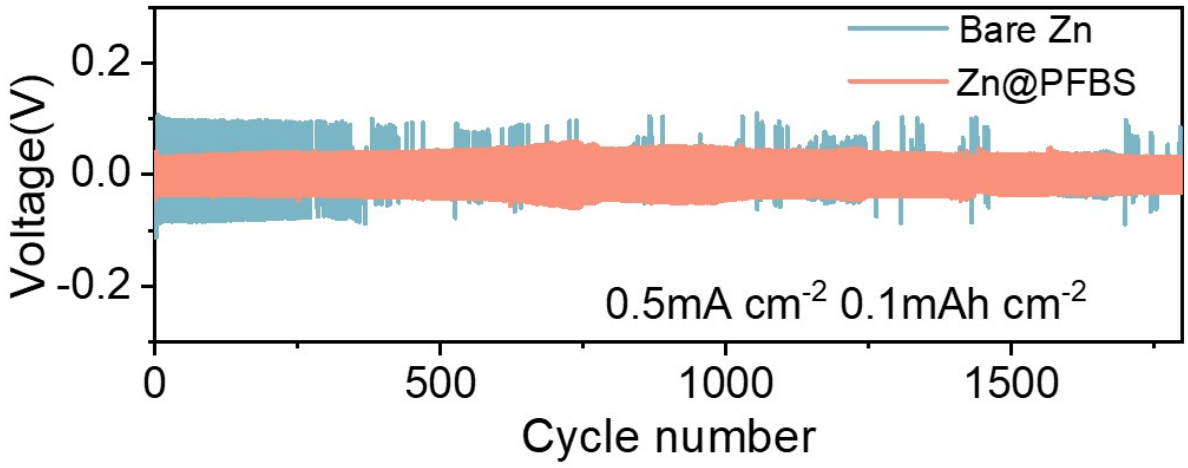

Fig. S6 Long-term cycling performance of symmetric Zn//Zn and Zn@PFBS half-cells at 0.5 mA cm^{-2}-0.1 mA h cm^{-2}.

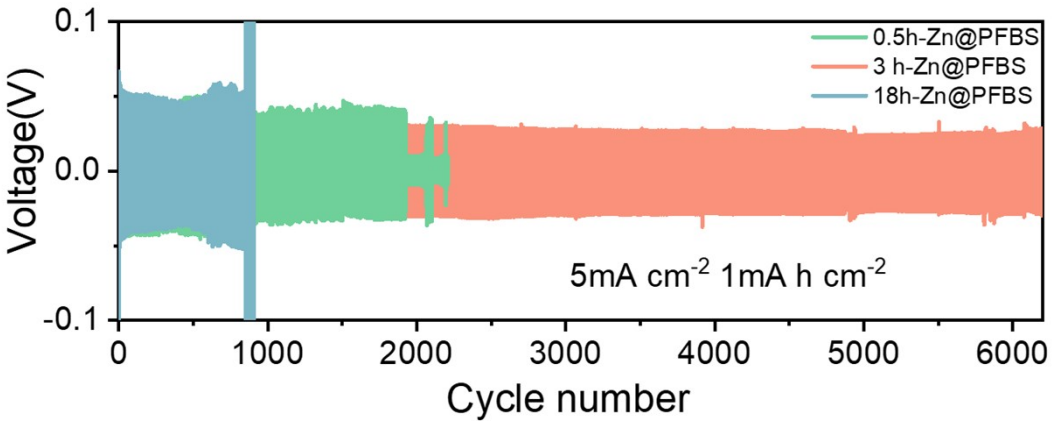

Fig. S7 Long-term cycling performance of Zn@PFBS half-cells at 5 mA cm^{-2}-1 mA h cm^{-2} with different etching durations.

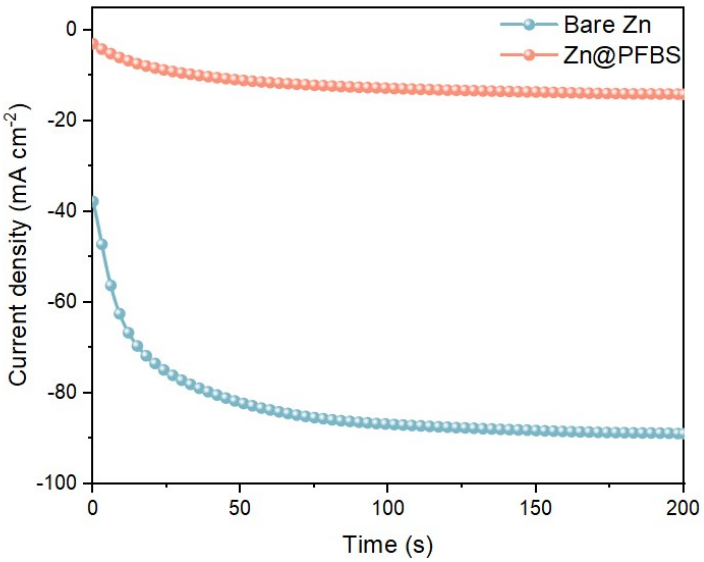

Fig. S8 *CA profiles of Zn//Cu and Zn@PFBS //Cu foil half cells under a voltage of −150 mV.*

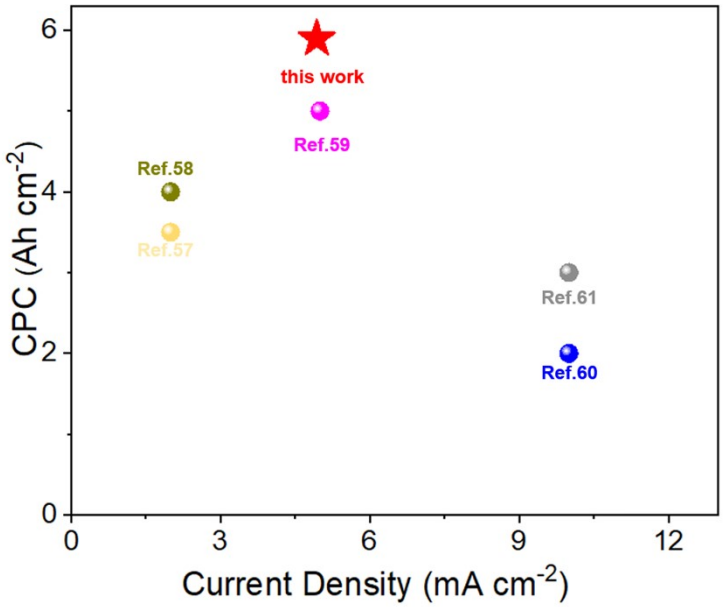

Fig. S9 *CPC comparison of the Zn symmetric cell using Zn@PFBS electrode with other reported literature studies.*

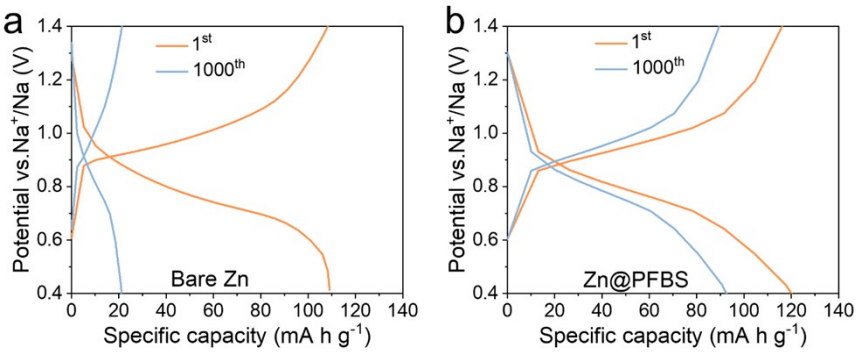

Fig. S10 Charge-discharge curves for different numbers of cycles (a) Bare zinc anode; (b) Zn@PFBS anode after etching.