Optimizing sulfonic group of polymer to coat zinc anode for dendrite suppression

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Experimental section

1) Material synthesis

The PEEK powder (2 g) was gradually added into 40 mL sulfuric acid under vigorously mechanically stirring in a three-neck flask. After the PEEK powder was dissolved at room temperature, the reaction was carried out at 70 ℃ in a water bath for a prescribed time. Then the sulfonated polymer was recovered by precipitating the solution into a large excess of ice water under stirring. The polymer was washed repeatedly with deionized water until the pH of the water was 6-7. After washing, the SPEEK polymer was then dried at 80 ℃ for 24 h.

V_2O_5 (0.5456 g) and $Zn(CH_3COO)_2$ (0.4280 g) were dissolved into 70 mL deionized water, then 5 mL acetone and 2 mL 10% nitric acid were added into the solution. After ultrasonic treatment for 5 min, the solution was poured into a 100 mL Teflon-lined stainless-steel autoclave. The autoclave was then sealed and heated in an oven at 180°C for 24 h. The obtained green powder was filtrated and washed by deionized water and ethanol, followed by drying at 80°C for 12 h.

2) Material Characterization

The PEEK and SPEEK was investigated by Fourier Transform Infrared Spectrometer (FTIR, PerkinElmer Frontier). The Nuclear magnetic resonance (NMR) spectrum was recorded on a Bruker Avance-III 400 MHz spectrometer. The degree of sulfonation (DS) in SPEEK is calculated by the following equation:

$$\frac{DS}{12-DS}=\frac{A_n}{A}$$

where A_n is the peak area of the shifted hydrogen nucleus at 7.5 ppm, and A is the sum of the peak area of all hydrogen nuclei. The Contact angle was measured on a commercial contact angle meter (PT-705B, Dong Guan Precis Test Equipment Co., Ltd., China). The morphology of the SPEEK coating Zn electrodes was characterized by field emission scanning electron microscope (SEM, ZEISS SUPRA® 55), combined with energy dispersive X-ray spectroscopy (EDX, Oxford X-Max 20) for the determination of the elemental composition. X-ray diffraction (XRD) patterns of Zn anode was recorded using a Bruker-AXS diffractometer (Bruker D8 Advance) with Cu K_α radiation (λ = 1.541 Å).

3) Electrochemical measurements

The Zn/Zn symmetric cells were assembled in coin cells (CR2032-type), with commercial Zn foil electrodes (50 μm in thickness) and a double-layer dust-free paper separator. Cycling performance was carried out at 0.5 mA cm^{-2} or 5 mA cm^{-2}, with the capacity of 0.5 mAh cm^{-2}. Impedance measurements were carried out from 10 kHz to 0.01 Hz with an AC amplitude of 10 mV using an electrochemical workstation (Solartron 1470E). The 3 mol L^{-1} $ZnSO_4$ electrolyte is used as the electrolyte in all the electrochemical measurements.

The full cells were assembled in coin cells (CR2032-type), while the cathode electrodes were made by casting the mixture which contains ZnVO powder (70%wt), Super P carbon (20%wt), and polyvinylidene fluoride (10 wt%), onto titanium foil (10 mm in thickness).

The rate and cycling performance of cells were tested by the Neware battery test system (BTS-5V5mA)

4) Ab initio calculations

All calculations were performed using the plane-wave projector-augmented wave method with an energy cut-off of 520 eV, as implemented in the Vienna ab initio simulation package (VASP). The Perdew-Burke-Ernzerhof (PBE) form of generalized gradient approximation (GGA) was chosen as the exchange-correlation potential. The structures were relaxed until the forces were less than 0.03 eV/Å, and the energy convergent standard was 10^{-5} eV. The Monkhorst-Pack mesh of unit cells was set to 1 × 1 × 1.

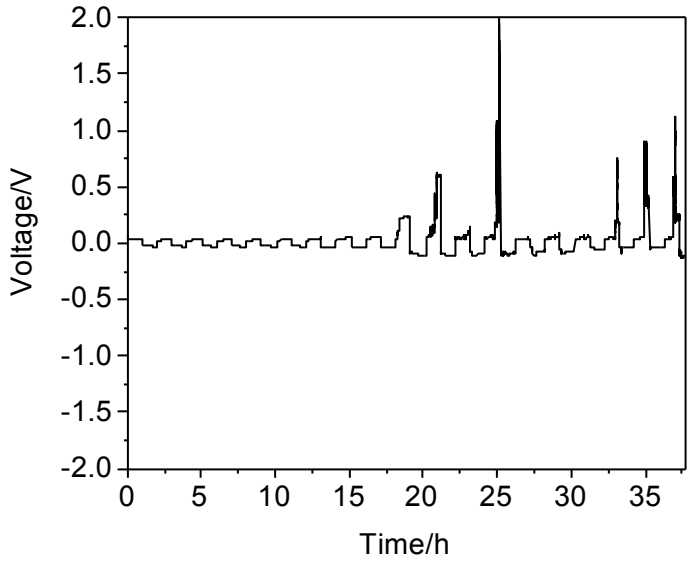

Figure S1 Cycling performance of Zn@PEEK electrode

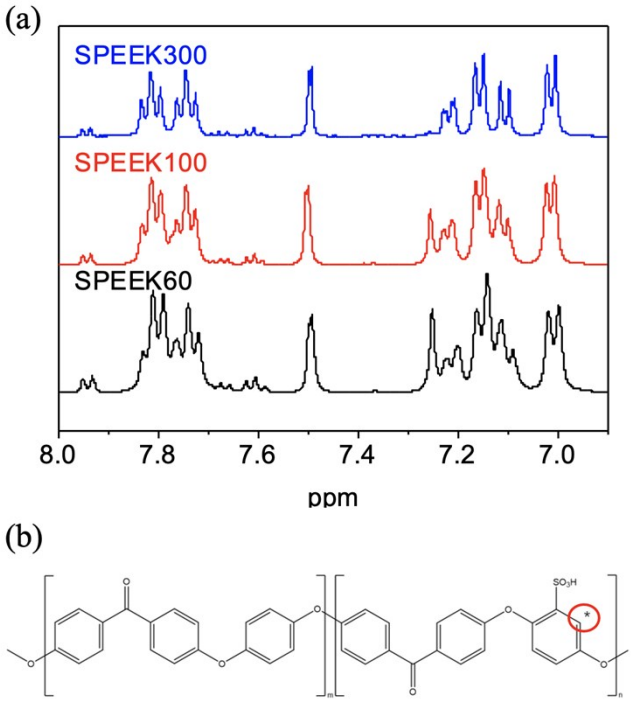

Figure S2 NMR profile of SPEEK material

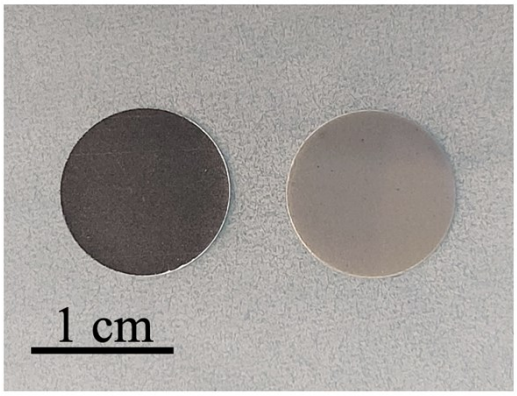

Figure S3 Optical image of bare zinc and Zn@SPEEK100

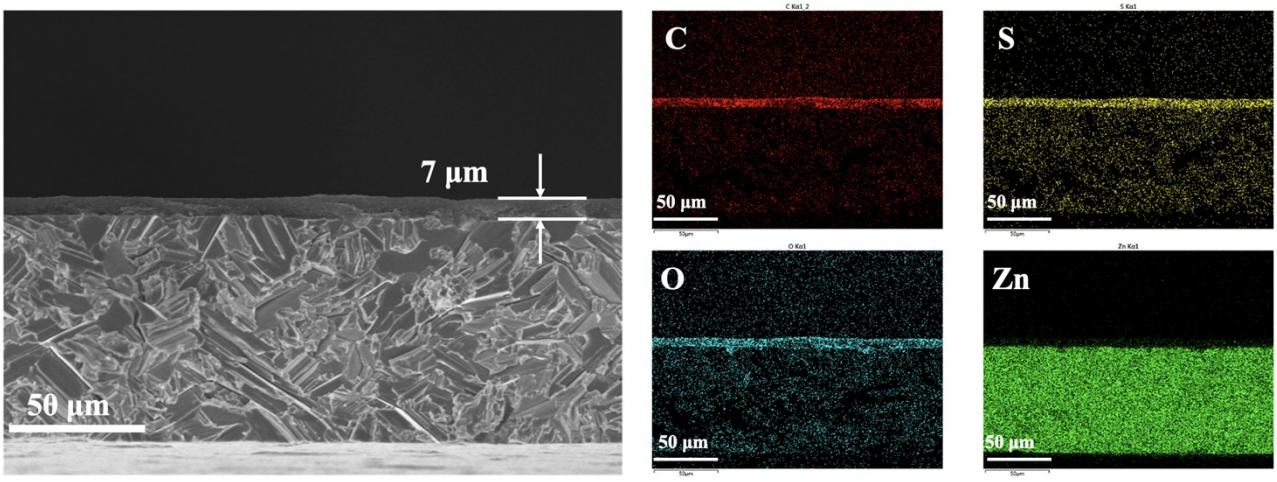

Figure S4 Cross-section of Zn@SPEEK100

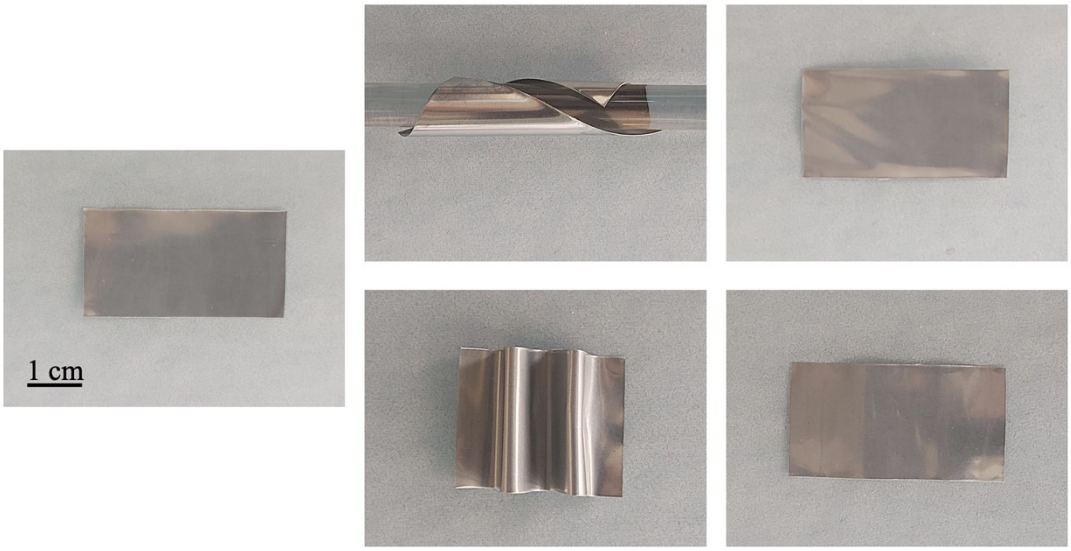

Figure S5 Bending and twisting of Zn@SPEEK100

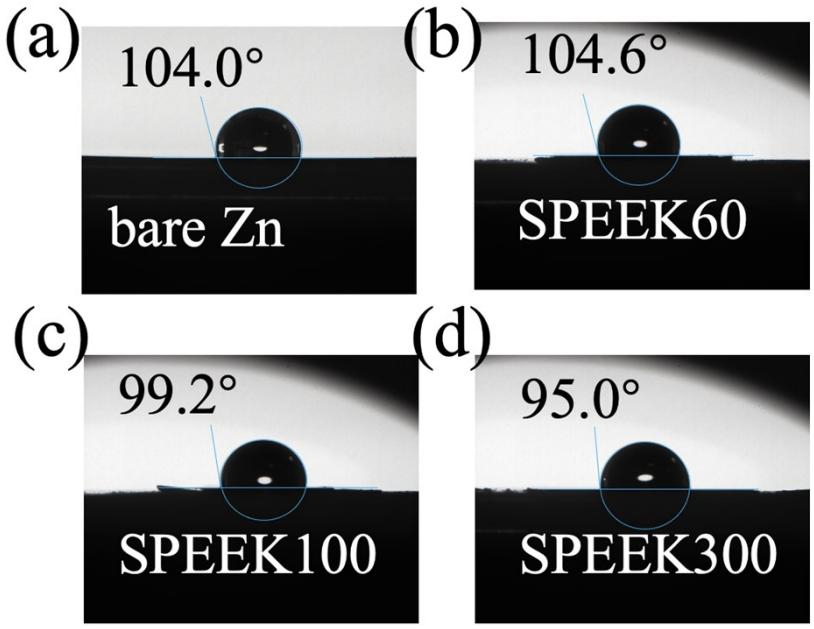

Figure S6 Contact angle of (a) bare zinc, (b) Zn@SPEEK60, (c) Zn@SPEEK100, and (d) Zn@SPEEK300

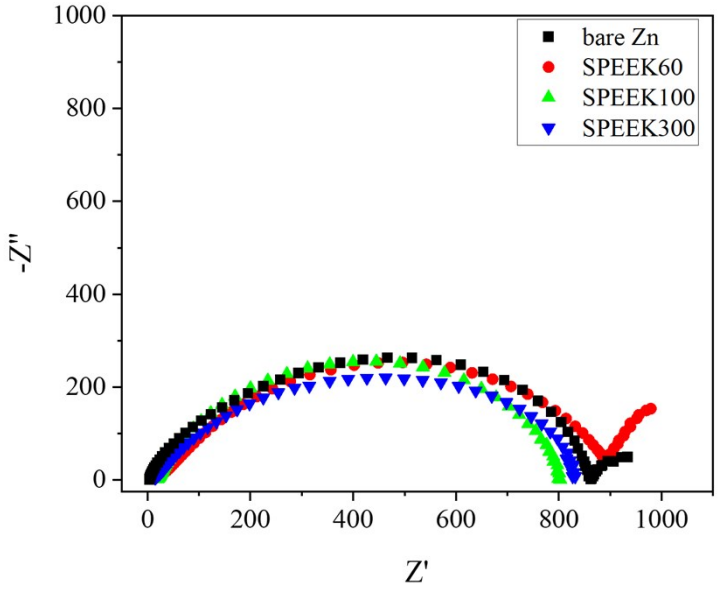

Figure S7 EIS results of bare zinc and SPEEK coated zinc

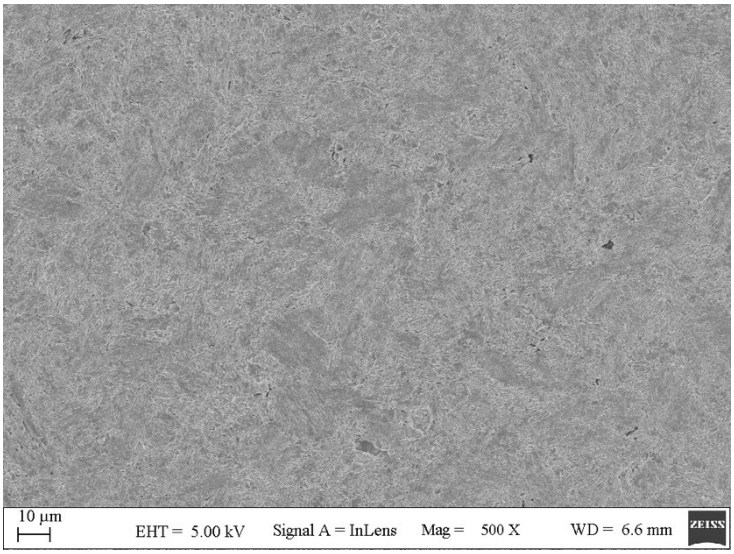

Figure S8 SEM images of Zn@SPEEK60 after 10 cycles

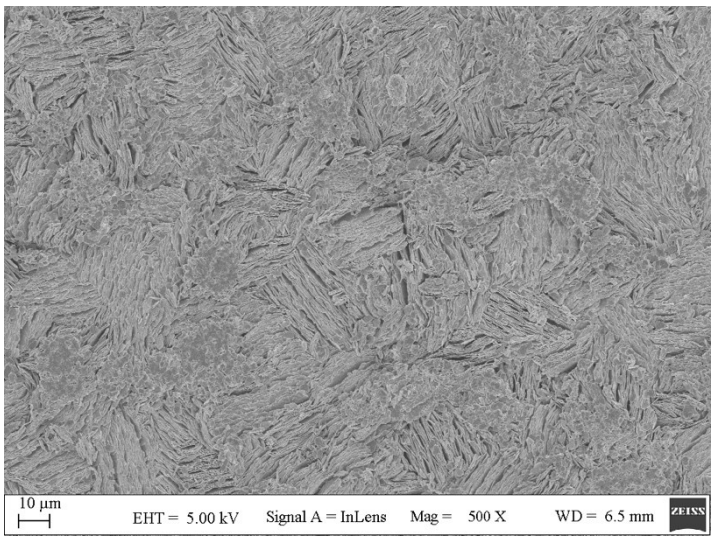

Figure S9 SEM images of Zn@SPEEK100 after 100 cycles

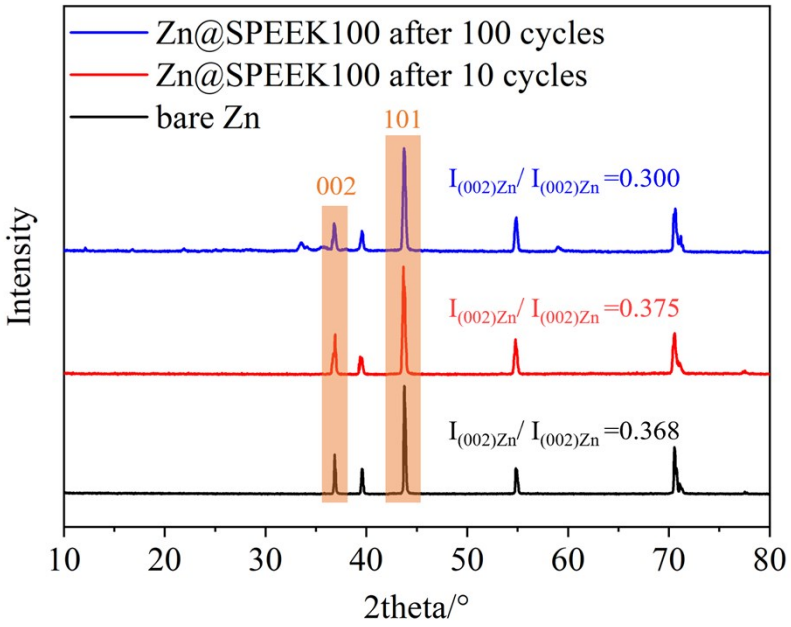

Figure S10 XRD profiles of pristine zinc and Zn@SPEEK100 after cycles

Figure S11 Swelling and peeling off of SPEEK300 membrane

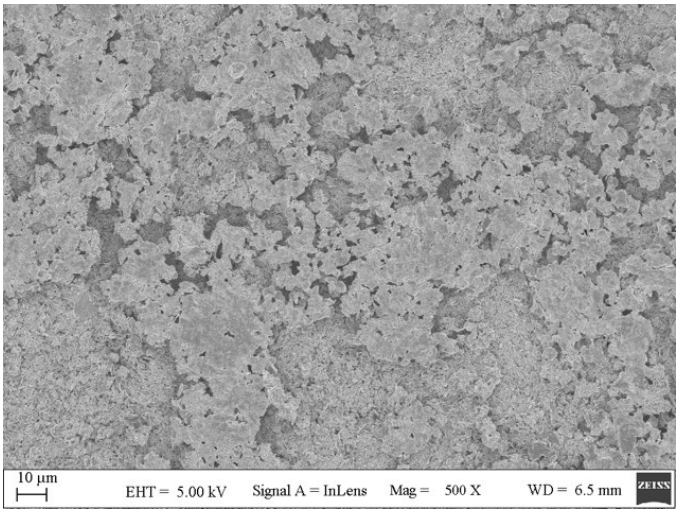

Figure S12 SEM images of Zn@SPEEK300 after 10 cycles

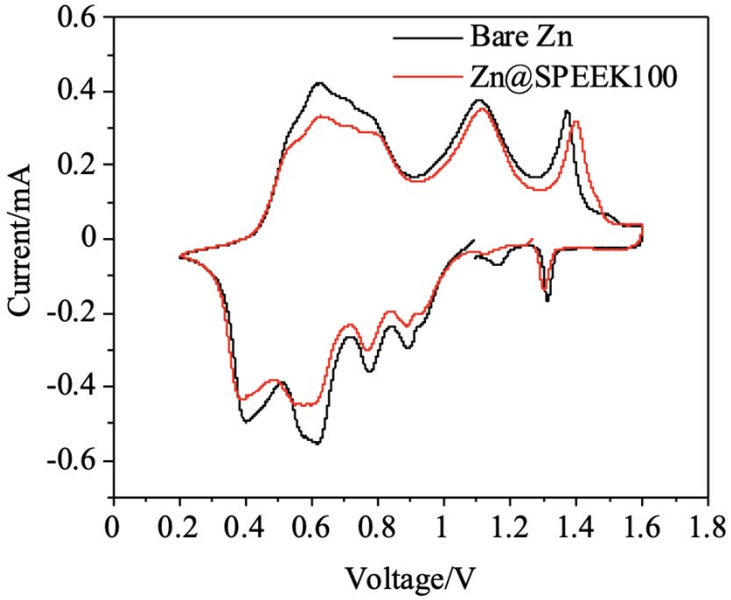

Figure S13 CV profiles of bare zinc and Zn@SPEEK100 in full cell

Table S1 Comparison of the Zn/Zn cycling performance with organic coatings

Number	Cycling lifetime /h	Current density /mA cm^{-2}	Capacity /mAh cm^{-2}	Coating material	Reference
1	1600	0.5	25	SPEEK	this work
2	2200	0.5	0.5	PVB	[1]
3	8000	0.5	0.25	PA	[2]
4	1145	1	1	PAN	[3]
5	2000	0.25	0.05	β-PVDF	[4]
6	800	0.5	0.25	Cyanoacrylate	[5]
7	900	0.2	0.2	KGM	[6]
8	2220	0.2	0.1	PAM/PVP	[7]
9	1000	1	0.5	Nafion	[8]