Supporting Information

Enhanced lifetime of the zinc-iodine batteries using hydrocarbon cation-exchange polymer-protected zinc anodes

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Experimental

Materials: The synthesis of sPPB was reported in one of our previous paper.[1] Zn foil, Ti foil, activated carbon, $ZnSO_4 \cdot 7H_2O$, K_2SO_4, Nafion solution, starch, $Na_2S_2O_3$, were purchased from Sigma Aldrich; glass fiber seperator and KOH were purchased from Fisher Scientific.

Anode electrode preparation: sPPB membrane was firstly soaked in 1M KOH solution for 2 days to exchange the proton to the potassium form. The sPPB-K^+ membrane was washed with DI water and dried in oven overnight, dissolved in DMSO to the concentration of 10 mg mL^{-1} solution. 50 µL of the solution was dropcast onto polished a Zn foil disk (diameter: 12 mm), and transfered to an oven at 80 °C to remove residual solvent. For comparison, Nafion coated Zn electrodes was prepared using the same procedure.

Preparation of cathode electrodes: Sigracet 22BB carbon paper was cut into 12 mm diameter disks and used as the cathode current collector. A mixture of 80 wt% activated

carbon and 20 wt% PTFE was dispersed in the solvent of MeOH:H_2O (3:1), and drop-cast onto 22BB to achieve a loading of ~3 mg cm^{-2}.

Electrolyte: 1M $ZnSO_4$ electrolyte was prepared for Zn symmetric cells. The catholyte mixture was 0.5M $ZnSO_4$ + 1M KI + 0.1M I_2. The anolyte is 0.5M $ZnSO_4$ + 0.5M K_2SO_4.

Iodometric titration: 100 mg/L starch solution was prepared as an indicator. 1.39 (and 7.53) mmol $Na_2S_2O_3$ solution was prepared to titrate the unknown I_3^--containing solution ($2S_2O_3^{2-} + I_3^- = S_4O_6^{2-} + 3I^-$). Aliquots of solutions were taken from the H-cell at different times. Dilute triiodide solutions are yellow; higher concentrations are brown; in the presence of starch, the color is blue. The end point corresponds to a sudden loss of blue color during titration.

Electrochemical measurements: Battery charge/discharge measurements were carried out on 2032-type coin-cells. For Zn symmetric cells, the Zn plating/stripping behaviors were conducted under 1 mA cm^{-2} or 2 mA cm^{-2} with a capacity of 1 mAh cm^{-2} or 2 mAh cm^{-2} (the charge or discharge time is 1 h for each cycle). For the Zn//I_2 full cell, the bare Zn foil (or Zn-sPPB), glass fiber, and cathode with 30 μL catholyte were assembled in 2032-type coin-cells. The galvanostatic discharge/charge measurements were conducted under different current densities in the range of 0.6~1.6 V using a Neware battery testing system. Cyclic voltammetry (CV) was performed in the range from 0.6 to 1.6 V at scan rates of 0.2/0.3/0.5/1.0/2.0/3.0 mV s^{-1}. Based on the mass of iodide in the catholyte, 1 C equals to 211 mA g^{-1}; specifically, the theoretical capacity can be calculated by Faraday's law [$Q_{theoretical} = (nF) / (3600 \cdot M_w)$ mAh g^{-1}] to be 211 mAh g^{-1}.

Zn deposition was studied in a three-electrode configuration: Ti foil as working

electrode; Zn foil as counter electrode; and SCE as reference electrode. Cyclic voltammograms (CV) were carried out at a scan rate of 5 mV s^{-1} towards the positive direction in the range from -1.3 V to - 0.6 V. Chronoamperometry (CA) was conducted at -1.19 V (vs. SCE) for 300 s. All measurements were conducted at room temperature.

Physical characterizations: X-ray diffraction measurements were conducted on a Bruker D8 Advanced diffractometer fitted with Cu-Kα X-rays (λ =1.5406 Å) radiation at a scan rate of 0.02 ° s^{-1}. SEM measurements were carried out on the FEI Nova NanoSEM 430 system, and SEM images obtained using an electron current of 50 pA with an accelerating voltage of 5 kV. For the cross-view of SEM, the Zn-sPPB sample was first sputtered with a thin layer of Ir. A 4 nm Ga ion beam was used to cut the sample in the FIB-SEM characterization experiment. The Zn electrodes were taken out under ambient environment and rinsed by water and ethanol several times to wash electrolyte salt and attached glass fiber. The electrodes were transferred to oven to remove solvent. The dried cathodes were carefully transferred into the SEM sample chamber. The electrodes were not sensitive to air environment and the short-time of exposure to air did not damage their morphology. ATR spectra were collected using a PerkinElmer Spectrum Two Universal FTIR spectrophotometer. Spectra were collected in the range 4000–550 cm^{-1} at a resolution of 4 cm^{-1} at room temperature. Each sample was compressed against a diamond crystal with a force of at least 80 N. X-ray photoelectron spectroscopy (XPS) were conducted in an Axis Ultra DLD instrument; the sample pretreatment was the same as for SEM. The C 1s peak (BE = 284.6 eV) was used as the reference to accurately determine the positions of other spectral lines. Casa XPS software was used for analyzing the spectra. Surface topographies were analyzed by a Contour GT-K profilometer.

DFT calculations: Density functional theory calculations were performed at the

B3LYP-6-311G(2d,2p) level of theory using Gaussian 16. Initial geometries were assembled using the GaussView 5 program, and intermediate optimizations were calculated at the B3LYP/6-31G(d) level of theory. Optimizations were performed using the provided tight convergence criteria, and convergence was confirmed by calculating vibration modes analytically using the provided *freq* keyword. Desolvation energies were computed by taking the difference of the energies of the optimized coordinated polymer-ion-water geometries and the optimized polymer-ion geometries and water molecules; i.e., $E = E_{wet} - E_{dry} - n \, E_{water}$, where E_{wet} is the solvated complex, E_{dry} is the desolvated complex, E_{water} is the energy of a single water molecule, and *n* is the number of coordinated water molcules in E_{wet}.
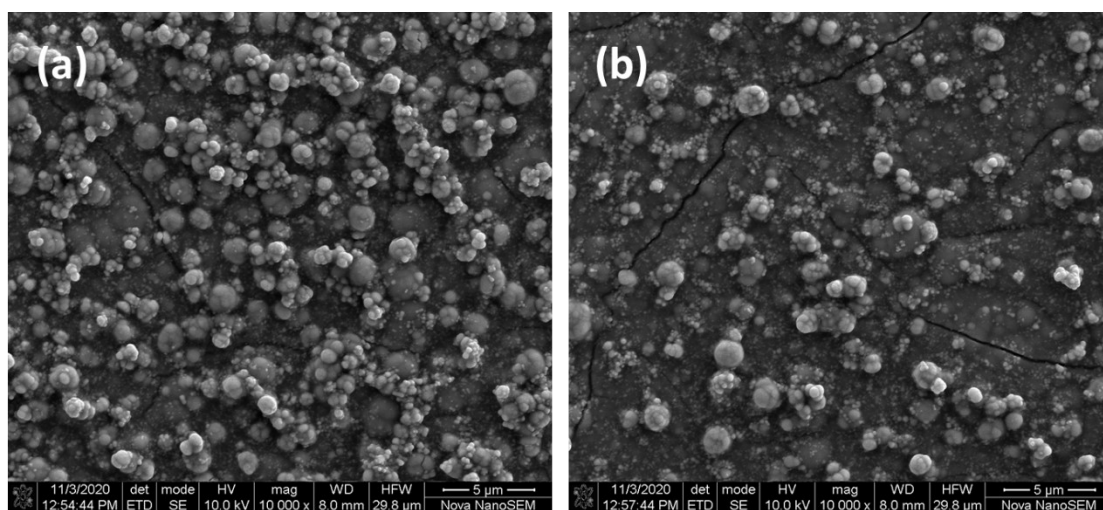
Figure S1. SEM images of sPPB coated Zn foil.
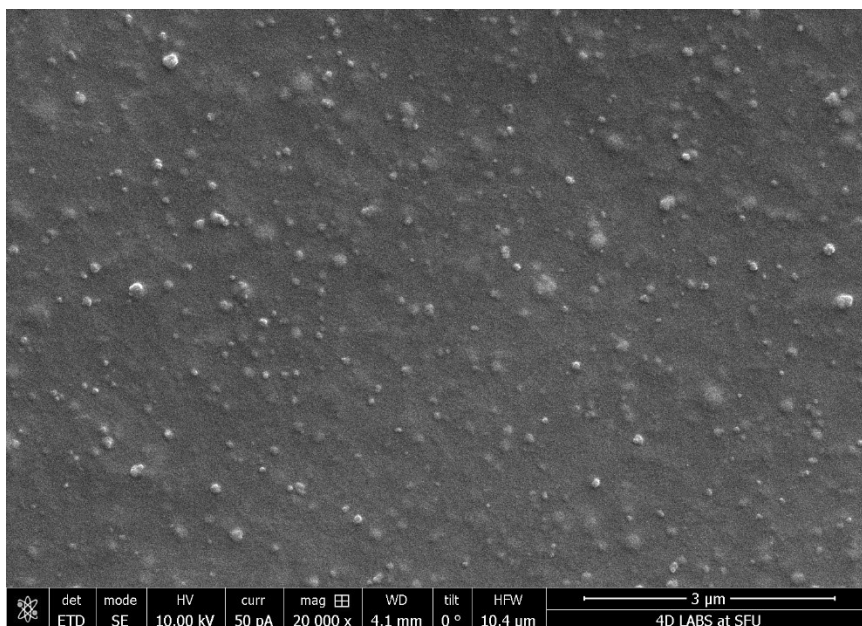
Figure S2. Top-view of Zn-sPPB for EDX.

Table S1. EDX spectrum of Zn-sPPB.

| Mag: 50097 | Takeoff: 33.1 | Live Time(s): 50 | Amp Time(µs): 7.68 | Resolution:(eV) |

Selected Area 1
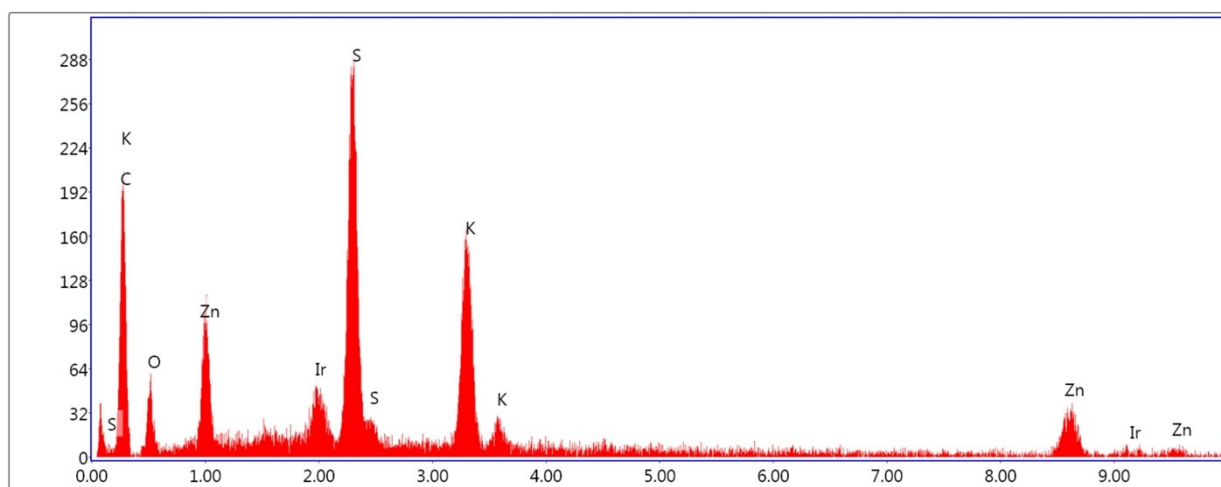
Lsec: 50.0 0 Cnts 0.000 keV Det: Octane Super Det

5

PeBaZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Error %	P/B Ratio	R	F
C K	48.95	62.92	44.62	15.95	0.0000	1.0000	1.0000
O K	30.25	29.19	10.47	23.03	0.0000	1.0000	1.0000
S K	8.56	4.12	103.19	9.16	128.7536	1.0123	1.0151
K K	6.65	2.62	65.60	13.82	113.8746	1.0169	1.0203
ZnK	4.42	1.04	17.16	21.81	66.5661	1.0289	1.1739
IrL	1.18	0.09	1.40	75.44	12.7643	1.0297	1.2807
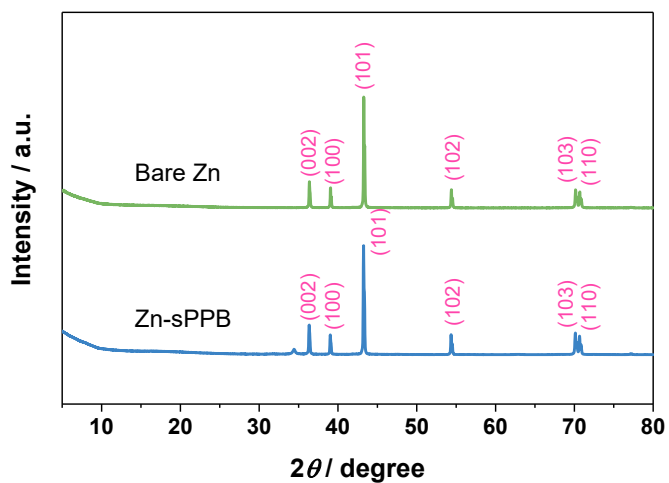
Figure S3. XRD patterns of bare Zn and Zn-sPPB.
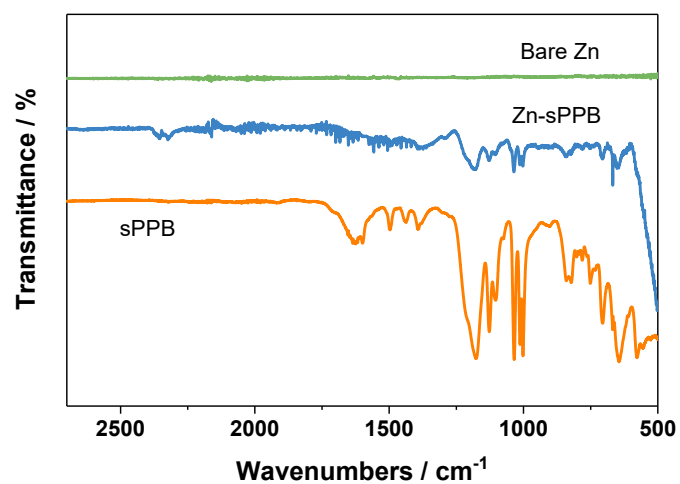
Figure S4. ATR spectra of sPPB, bare Zn, and Zn-sPPB.
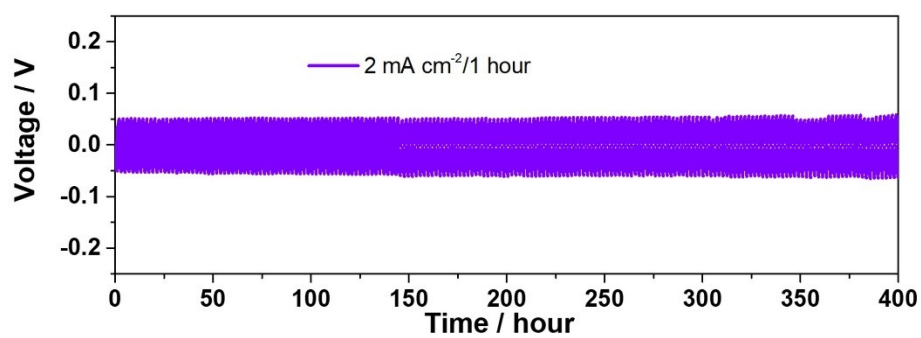
Figure S5. Cycling performance of a Zn-sPPB based symmetric cell at 2 mA cm^{-2} with areal capacity of 2 mAh cm^{-2}.
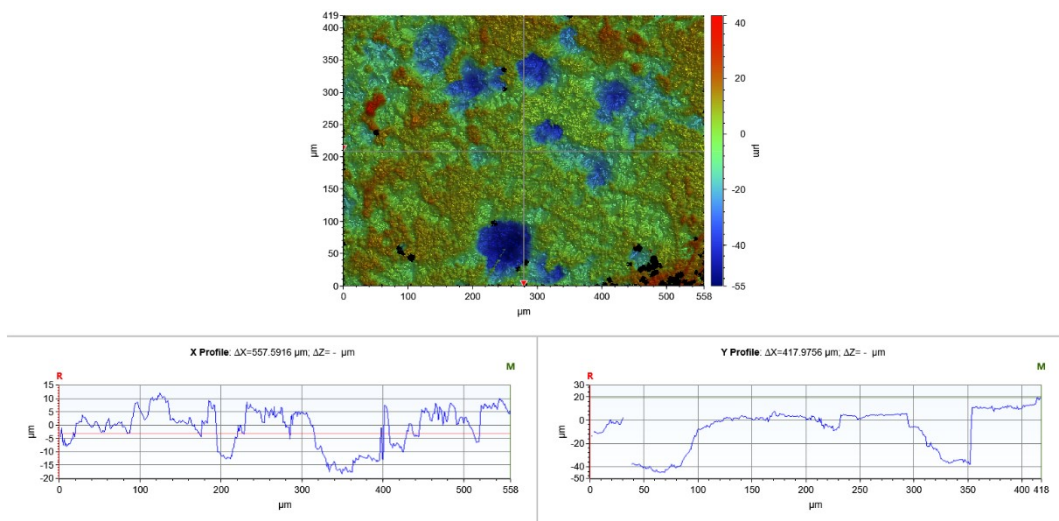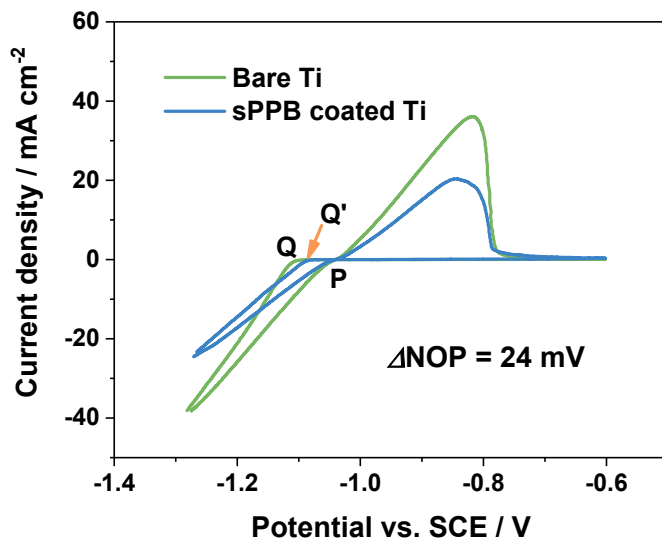
Figure S6. Surface intercept profile and the 2D mapping curve of the bare Zn electrode after 40 h plating/stripping at 1 mA cm^{-2}.
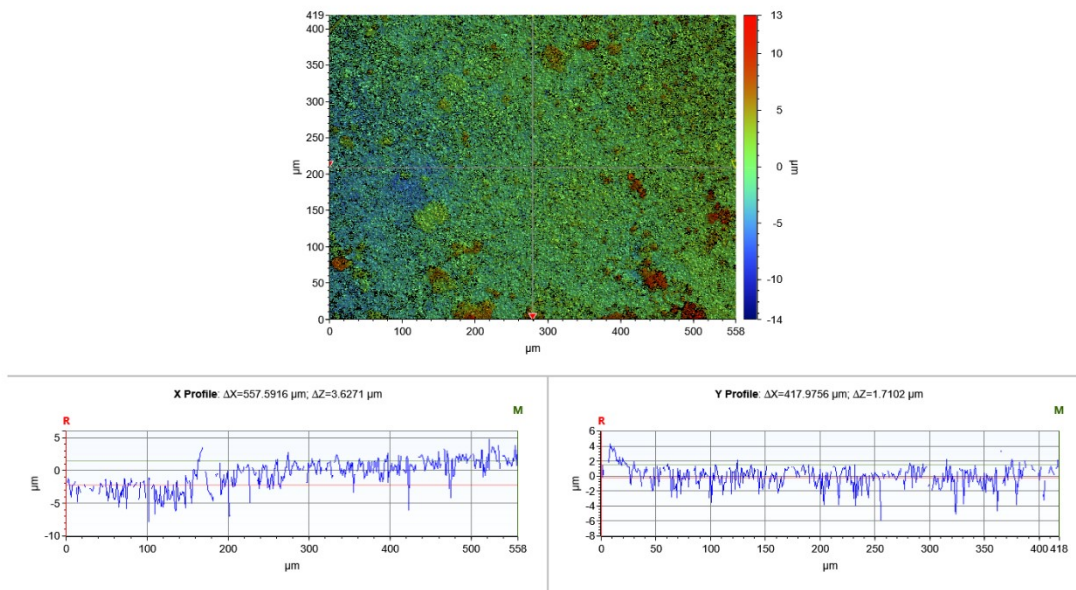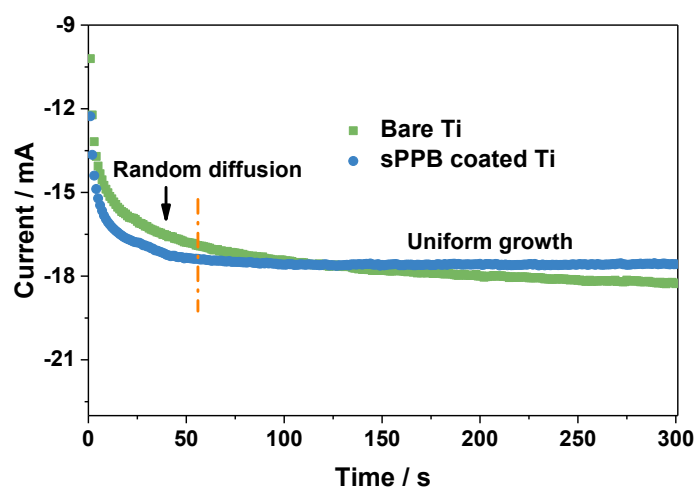
Figure S7. Surface profile and the 2D mapping curve of a Zn-sPPB electrode after 80 h plating/stripping at 1 mA cm^{-2}.
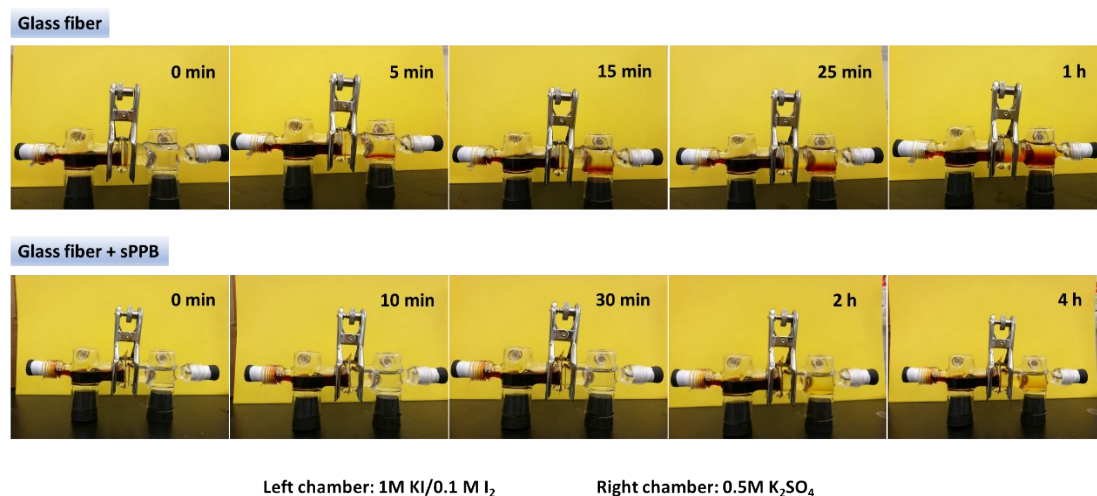

**Figure S8**. CVs for Zn nucleation on bare Ti foil and sPPB coated Ti.

**Figure S9**. Chronoamperometry of bare Zn growth on bare Ti foil and sPPB coated Ti. (n) Zn growth mechanism with and without sPPB.


Figure S10. Optical images of H-type glass with anolyte (left: 1M KI and 0.1M I_2) and catholyte (right: 0.5M K_2SO_4) with glass fiber separator (top) and glass fiber/sPPB (GF+sPPB) composite separator (bottom).
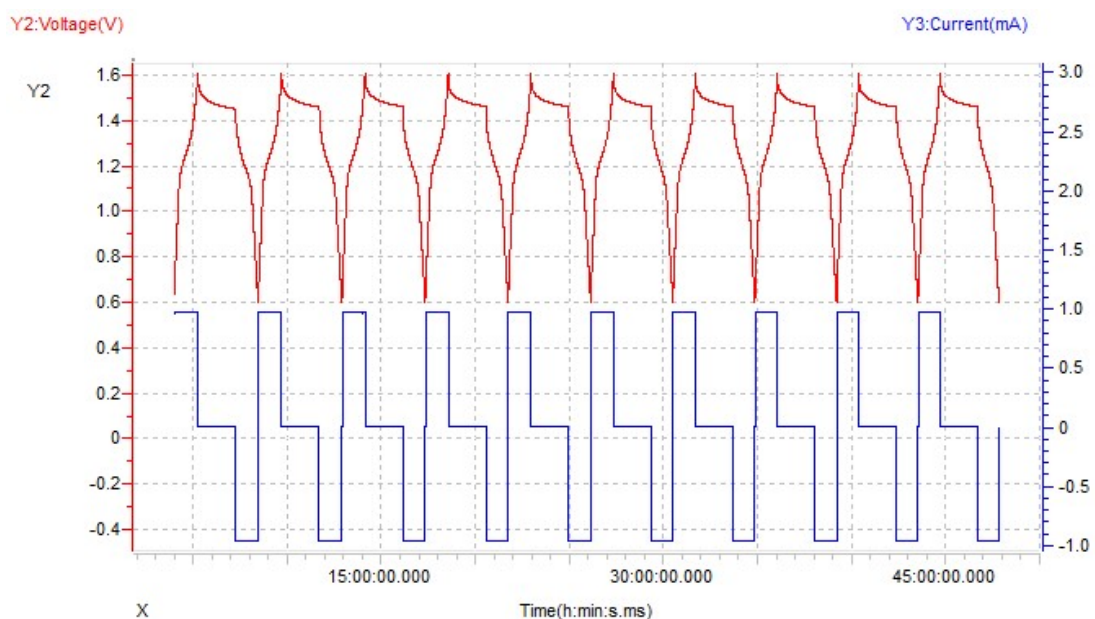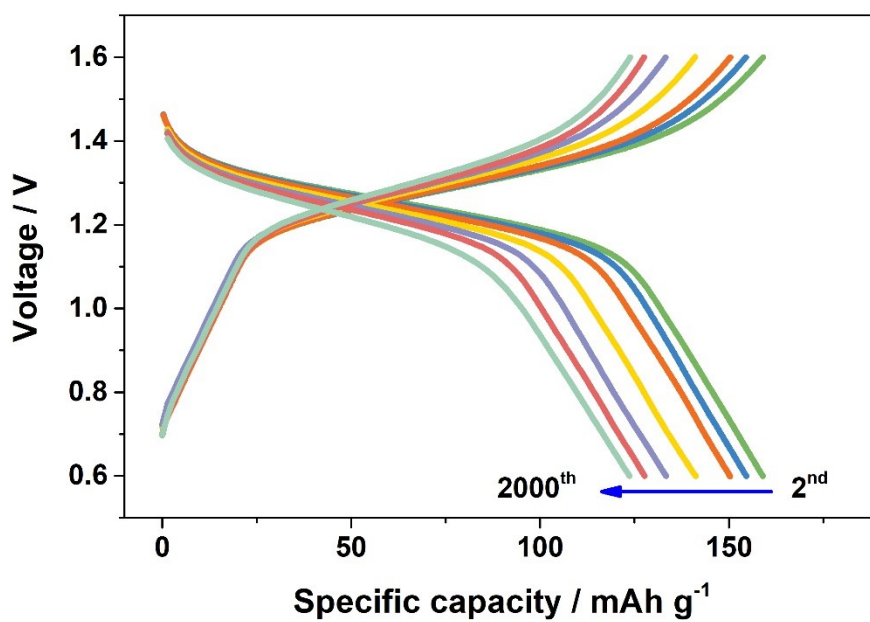
Figure S11. The charge-discharge protocol used to examine the crossover of iodide species in a Zn//I$_2$ battery (holding time after charging: 2 h).
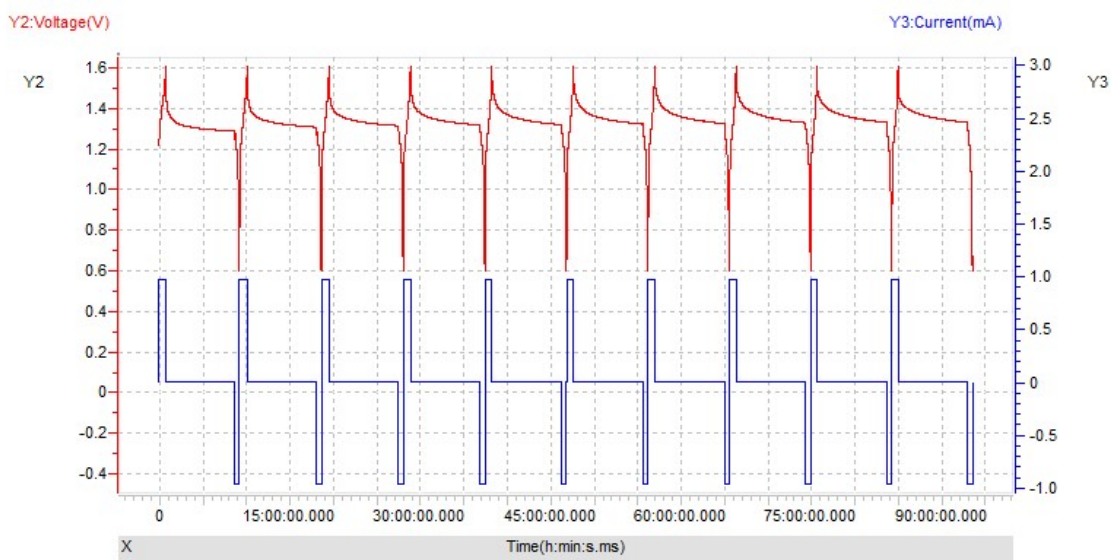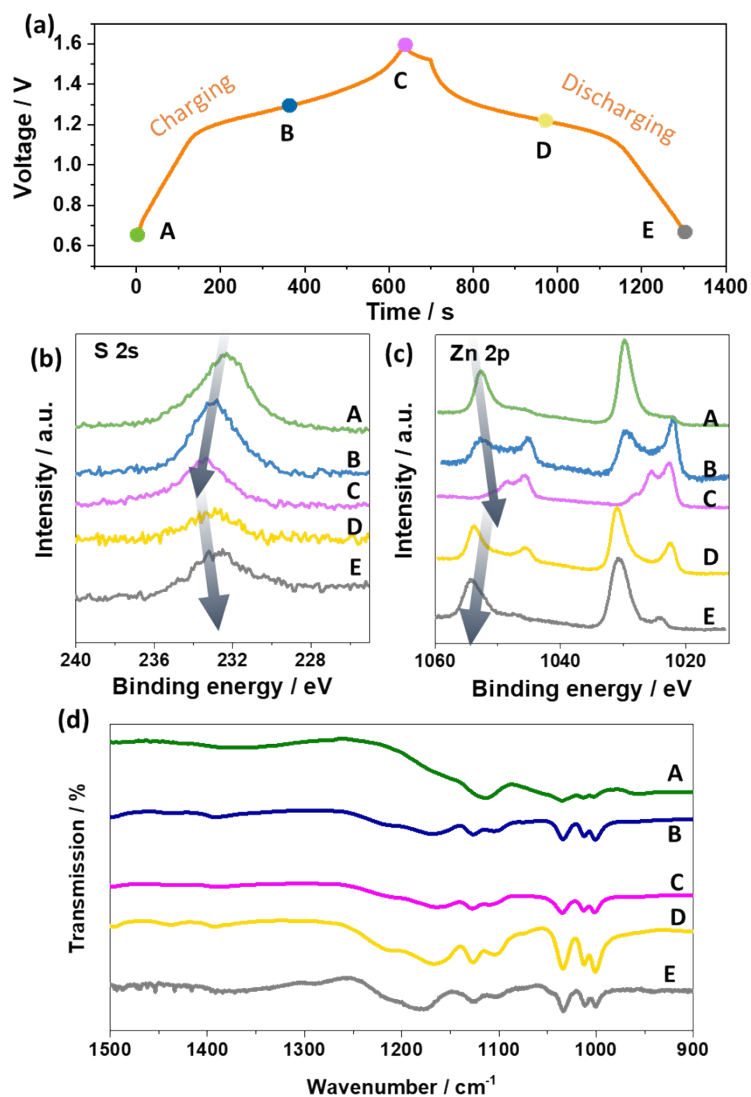

Figure S12. The charge-discharge protocol used to examine the crossover of iodide species in a Zn//I$_2$ battery (holding time after charging: 8 h).
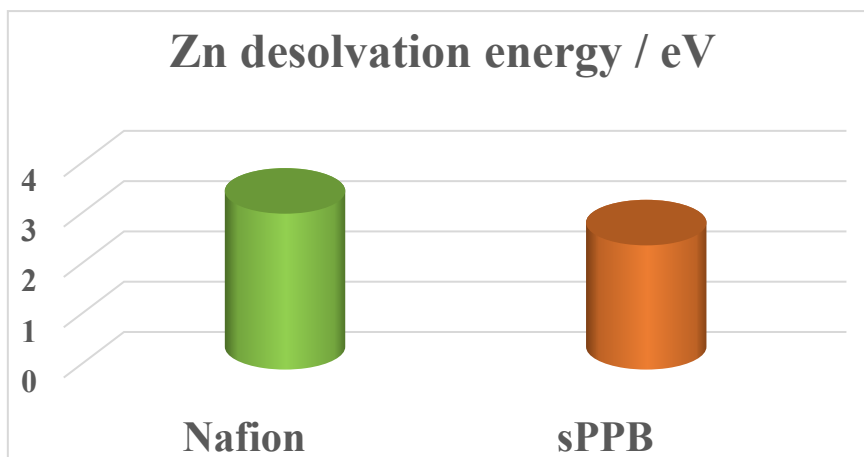
Figure S13. Desolvation energy of Zn^{2+} with Nafion and sPPB.

Figure S14. Galvanostatic discharge–charge profiles of a bare $Zn//I_2$ battery obtained in the first 2000 cycles at 5 C.

Figure S15. (a) Charge–discharge profile of a Zn-sPPB//I$_2$ battery. (b) S 2s and (c) Zn 2p regions of the high resolution XPS spectra in different discharge/charge states as stated in figure a. (d) ATR spectrum in different selected discharge/charge states.

Reference

[1]   M. Adamski, T.J.G. Skalski, B. Britton, T.J. Peckham, L. Metzler, S. Holdcroft, Highly Stable, Low Gas Crossover, Proton-Conducting Phenylated Polyphenylenes, Angewandte Chemie International Edition 56 (2017) 9058-9061.