

Electronic Supplementary Information

A highly conductive gel electrolyte with favourable ion transfer channels for long-lived zinc-iodine batteries

Yadong Tian, Song Chen, Siyu Ding, Qianwu Chen and Jintao Zhang*

Key Laboratory for Colloid and Interface Chemistry, Ministry of Education, School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, China.

Email: jtzhang@sdu.edu.cn

Experimental section

1. Preparation of IC-Zn gel electrolyte

1 g of I-carrageenan was added to 10 ml of ultrapure water under stirring in a water bath at 80°C. Subsequently, pouring into a mold, the solid-state IC gel was obtained and immersed into 2 M ZnSO₄ aqueous solution for 36 h. The final sample was denoted as IC-Zn-36 gel electrolyte. The other samples were also prepared by changing the immersing time (T), and named as IC-Zn-T. IC-Zn is generally equal to IC-Zn-36, unless otherwise emphasized.

2. Preparation of I₂ cathodes

The I₂ cathodes were synthesized according to our previous reported method with some modifications.^{1, 2} Typically, 8 ml of phytic acid (50 wt.%) and 12 ml of ultrapure water were stirred in an ice-water bath at about 4 °C to form a homogeneous solution, denoted as solution A. 0.96 g of ammonium persulfate (APS) initiator was dissolved in 5 ml of ultrapure water and recorded as solution 2. 5 ml of aniline monomer was slowly added dropwise to the above solution A under stirring. Solution B was added into solution A and kept at about 4°C overnight. Then, the excess phytic acid was removed with ultrapure water and freeze-dried. Finally, the black product was obtained and recorded as PCM-NP after annealing at 1000 °C for 2 h in N₂. Iodine was successfully loaded onto the PCM-NP cathode via a simple steam method. The PCM-NP (60 mg) and iodine (20 mg) were thoroughly mixed and added to a 20 ml borosilicate glass bottle. Then, the bottle was transferred to an oven at 120°C for 6 h. The areal mass loading for each PCM-NP electrode is about 6 mg cm⁻².

3. Materials characterization

The morphologies of the samples were characterized by field emission scanning electron microscope (FESEM, ZEISS GeminiSEM 300) at 3.0 kV. The crystal structures

of the samples were collected by X-ray diffraction (XRD, Rigaku Dmax X-ray diffractometer) under Ni filtered Cu K α radiation. FT-IR spectra were measured by the Bruker Fourier Transform Infrared Spectrometer. Thermogravimetric analysis (TGA, Mettler Toledo TGA/DSC3+) was used to investigate the composition of material with a heating rate of 10 °C min⁻¹ in the air.

4. Electrochemical Measurements

Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were measured by a CHI 760E electrochemical workstation. Electrochemical impedance spectroscopy (EIS) was carried out from 10 mHz to 100 KHz by an Autolab electrochemical workstation.

Symmetrical cells were consisted of two pieces of Zn foil as both anode and cathode in CR2032 coin cells with 2 M ZnSO₄ aqueous electrolyte and GF separators and IC-Zn gel electrolyte, respectively. Chronoamperometry (CA) was evaluated at a overpotential of -200 mV in symmetric cells. The Zn²⁺ transference number was tested in the Zn symmetric cells. Ionic conductivity was calculated from the bulk resistance of the Ti symmetric cells. Rate performance and galvanostatic charge-discharge were examined via the Neware battery test system under different current densities. Zn||CP cells were used to evaluate the coulombic efficiency (CE).

To prepare I₂ cathodes, the active material, acetylene black and polytetrafluoroethylene (PTFE) were mixed in a mass ratio of 7:2:1. Zn anode and I₂ cathode with 2 M ZnSO₄ aqueous electrolyte and GF separators and IC-Zn gel electrolyte were assembled, respectively into Zn-I₂ full batteries for further measurement.



Figure S1. Thickness test of the IC-Zn gel electrolyte.

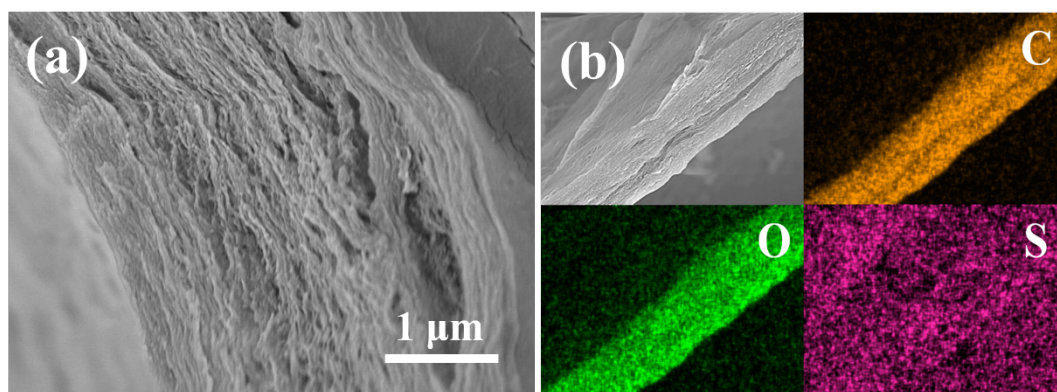


Figure S2. (a) SEM images and (b) elemental mapping images of IC.

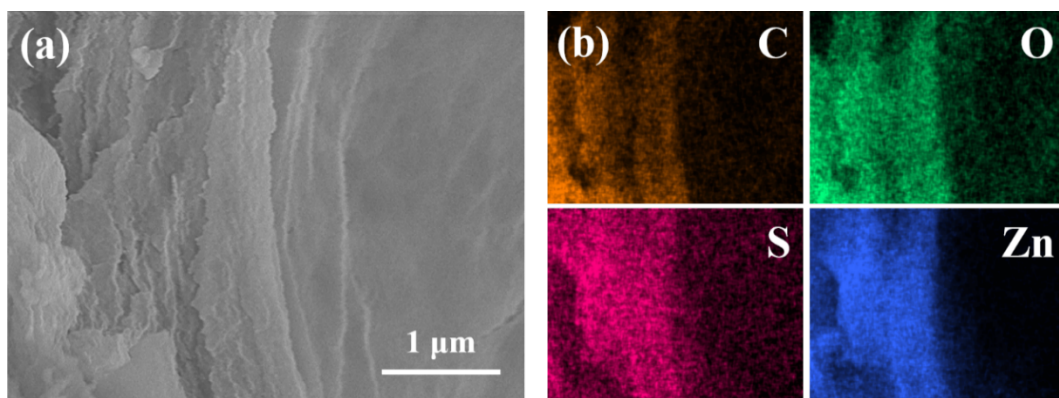


Figure S3. (a) SEM images and (b) corresponding elemental mapping images of IC-Zn.



Figure S4. Optical photographs of IC-Zn-36 gel electrolyte before and after tensile test.

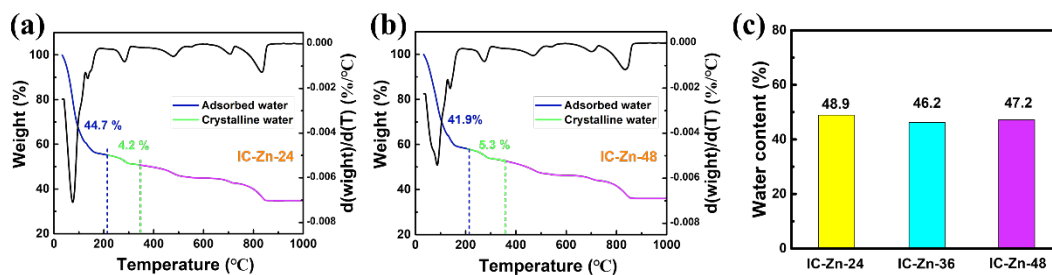


Figure S5. TGA curves of (a) IC-Zn-24 gel and (b) IC-Zn-48 gel. (c) Water content of IC-Zn-T gel electrolytes.

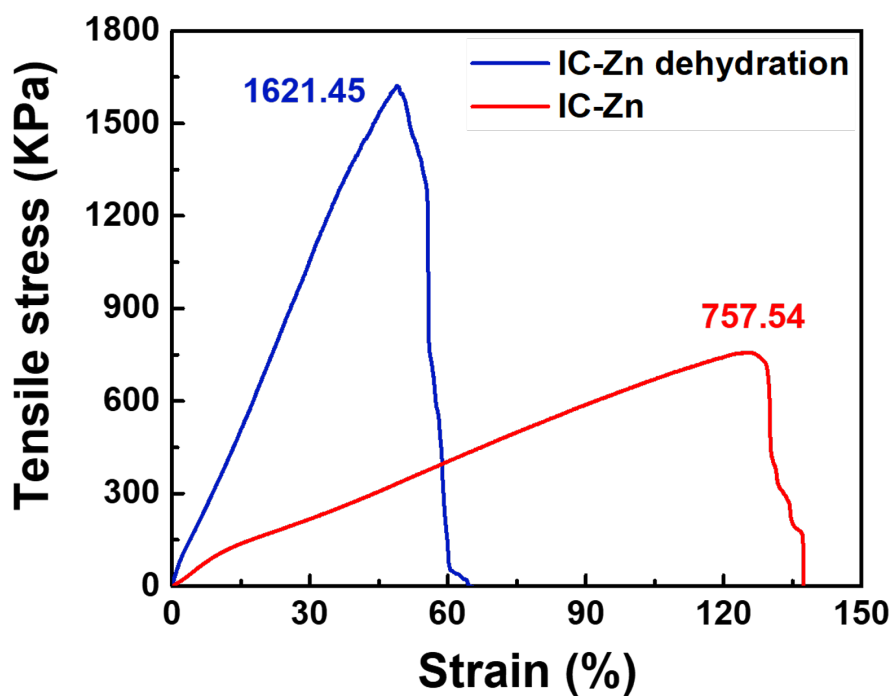


Figure S6. Tensile curves of IC-Zn gel electrolyte before and after dehydration.

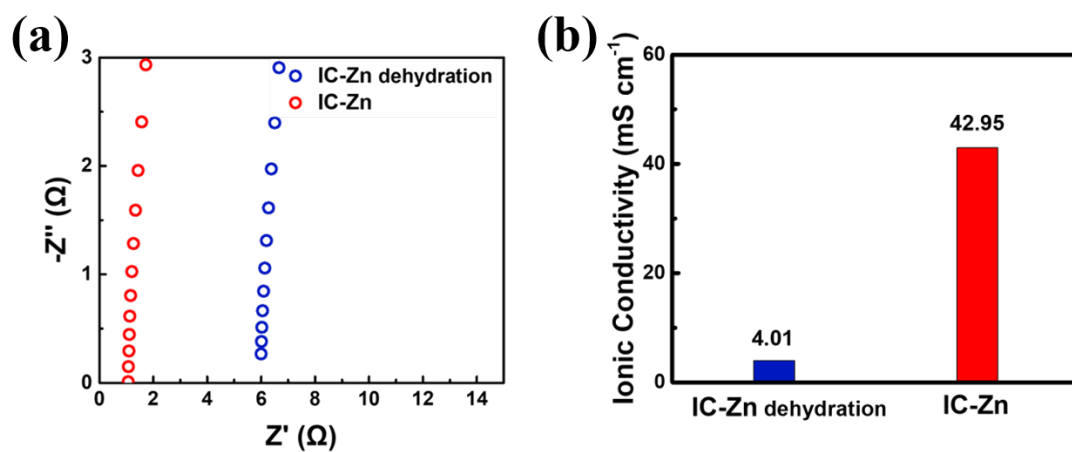


Figure S7. (a) Electrochemical impedance spectra and (b) the corresponding ionic conductivity of IC-Zn gel electrolyte before and after dehydration.

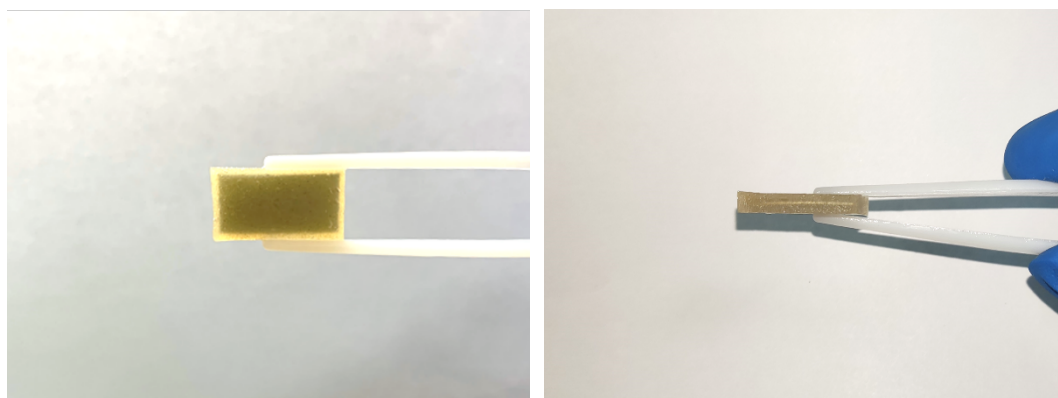


Figure S8. Optical photographs of Zn foils encapsulated in IC-Zn gel electrolyte.

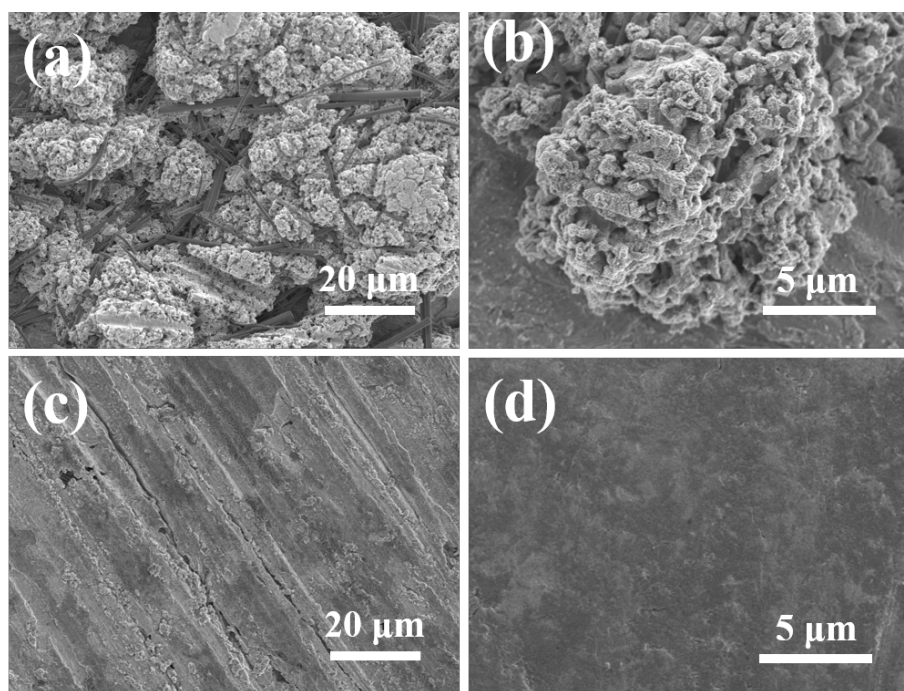


Figure S9. SEM images of Zn anodes after 1 cycle in (a-b) 2 M ZnSO₄ aqueous electrolyte and (c-d) IC-Zn gel electrolyte.

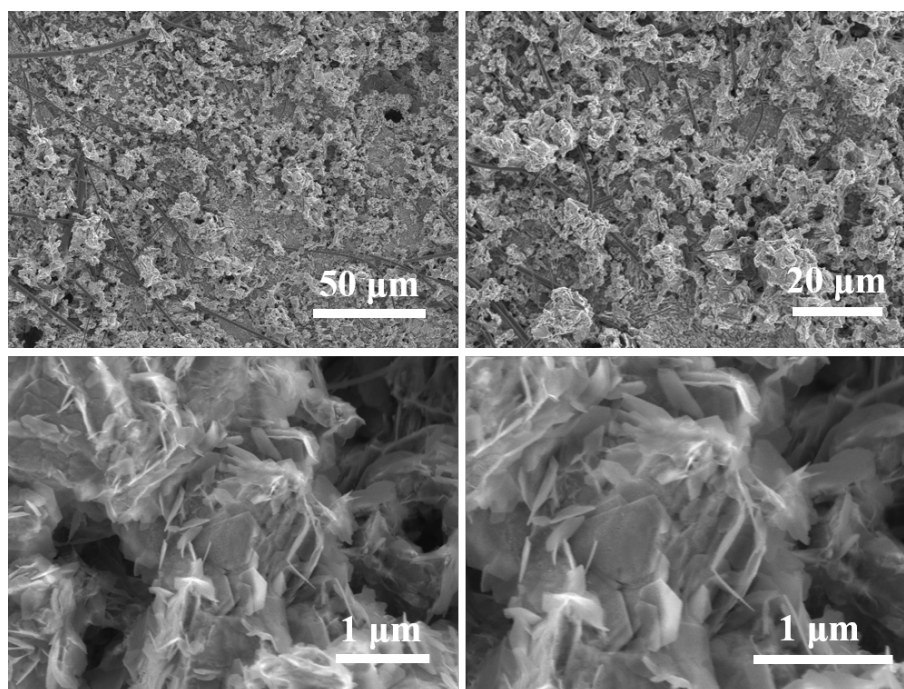


Figure S10. SEM images of Zn anodes after cycling for 50 h in 2 M ZnSO₄ aqueous electrolyte.

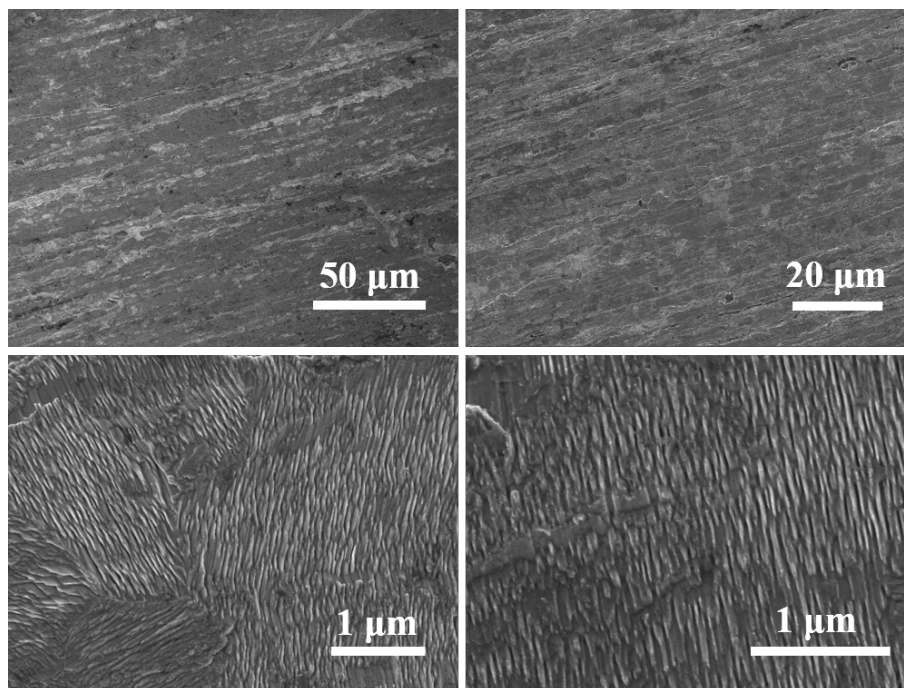


Figure S11. SEM images of Zn anodes after cycling for 50 h in IC-Zn gel electrolyte.



Figure S12. Thickness of IC-Zn gel electrolyte used to measure ionic conductivity.

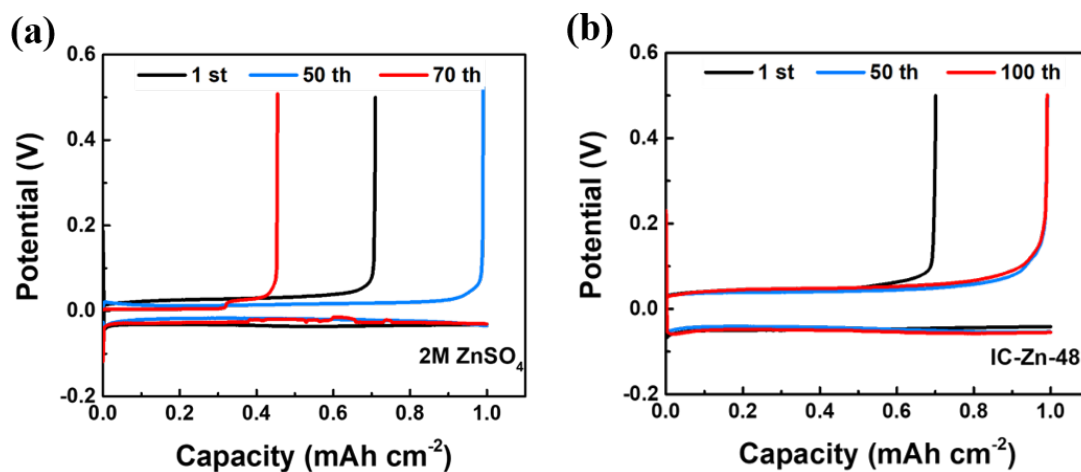


Figure S13. Voltage–capacity curves of Zn||CP cells with (a) 2 M ZnSO₄ and (b) IC-Zn-48 at 1 mA cm⁻² for the capacity of 1 mAh cm⁻²

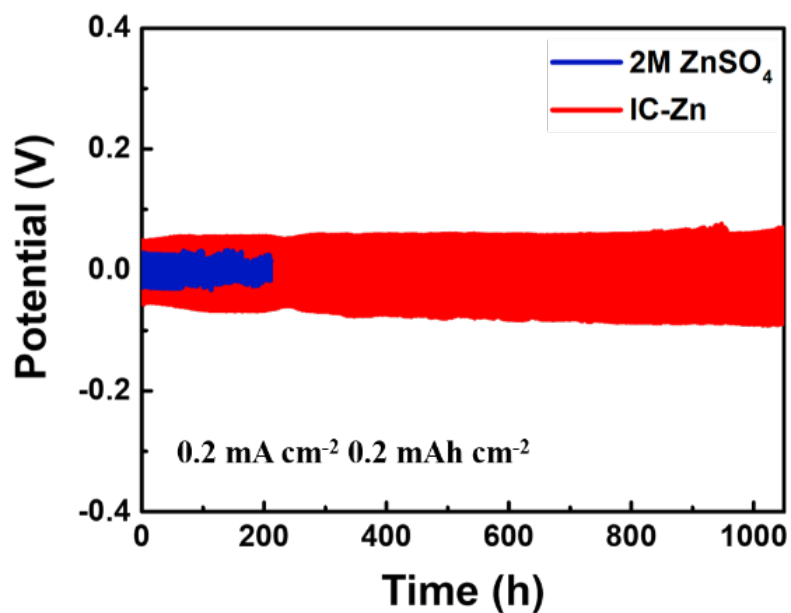


Figure S14. Cycling performance of Zn symmetric cells in 2 M ZnSO₄ aqueous electrolyte and IC-Zn gel electrolyte at 0.2 mA cm⁻².

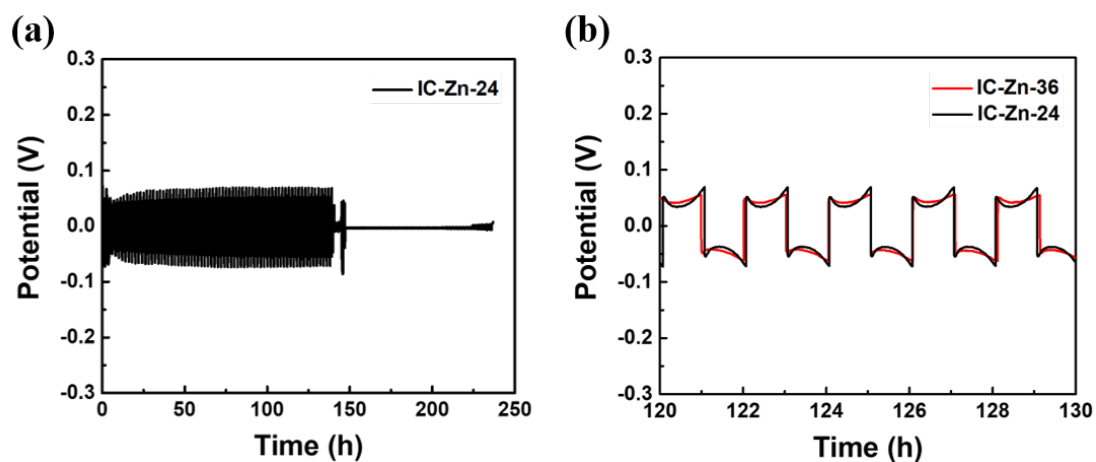


Figure S15. (a) Cycling performance of Zn symmetric cells with IC-Zn-24 gel electrolyte. (b) Corresponding detailed voltage profiles.

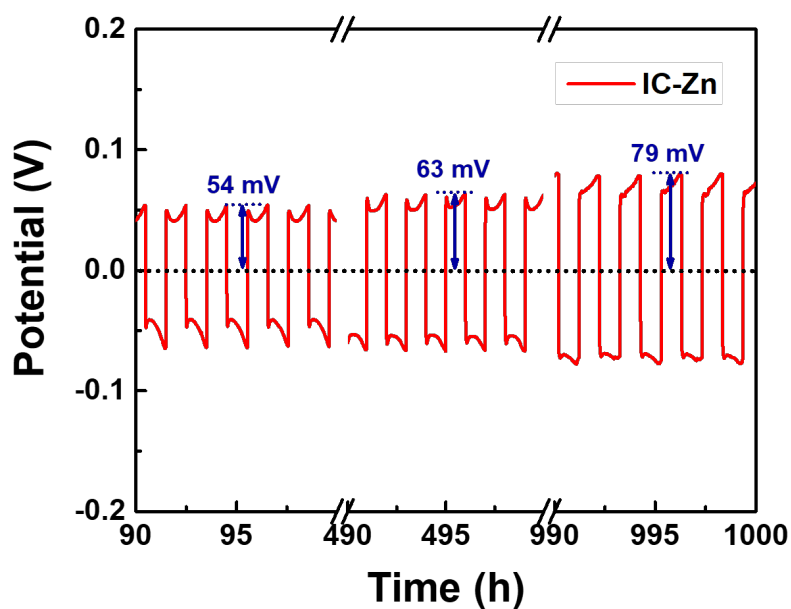


Figure S16. Detailed voltage profiles of Zn symmetric cell assembled with IC-Zn gel electrolyte at 1 mA cm^{-2} for 1 mAh cm^{-2} .

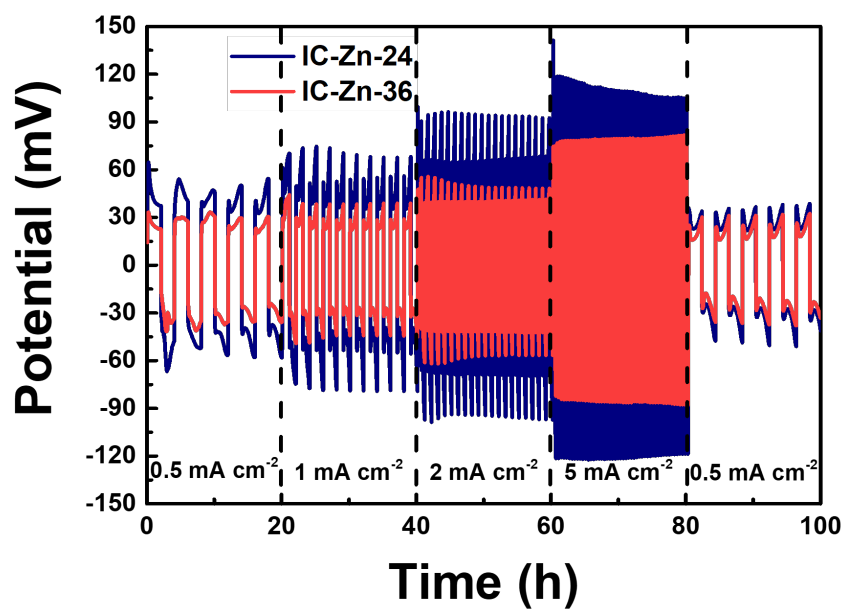


Figure S17. Rate performance of IC-Zn-T (T=24, 36, 48 h) gel electrolyte in Zn symmetric cells at current densities from 0.5 to 5 mA cm⁻².

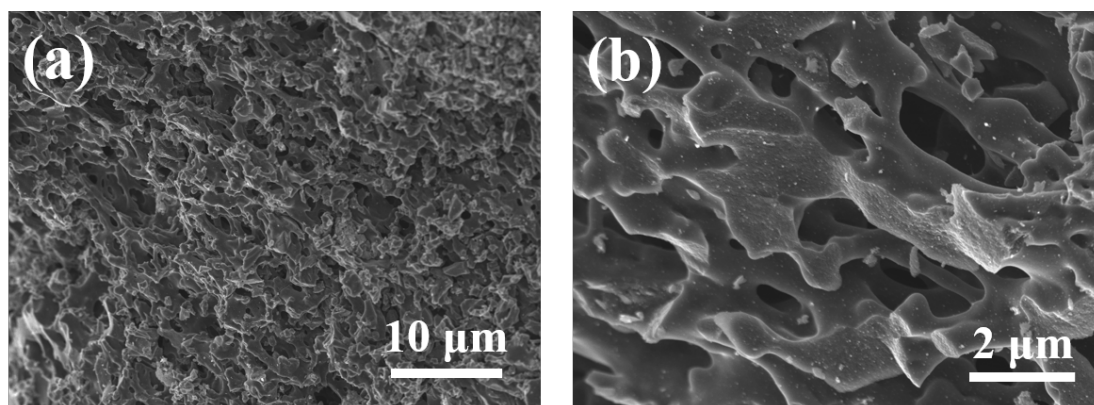


Figure S18. SEM images of PCM-NP at different magnifications.

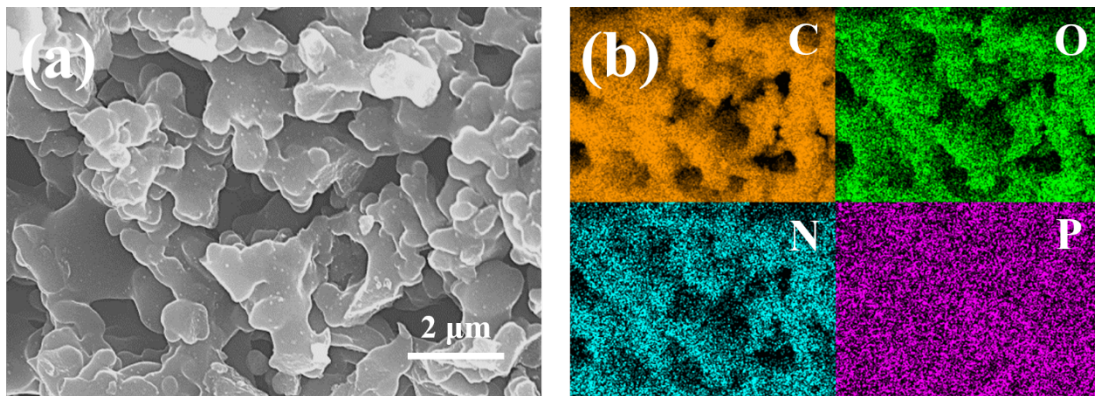


Figure S19. (a) SEM images and (b) corresponding elemental mapping images of PCM-NP.

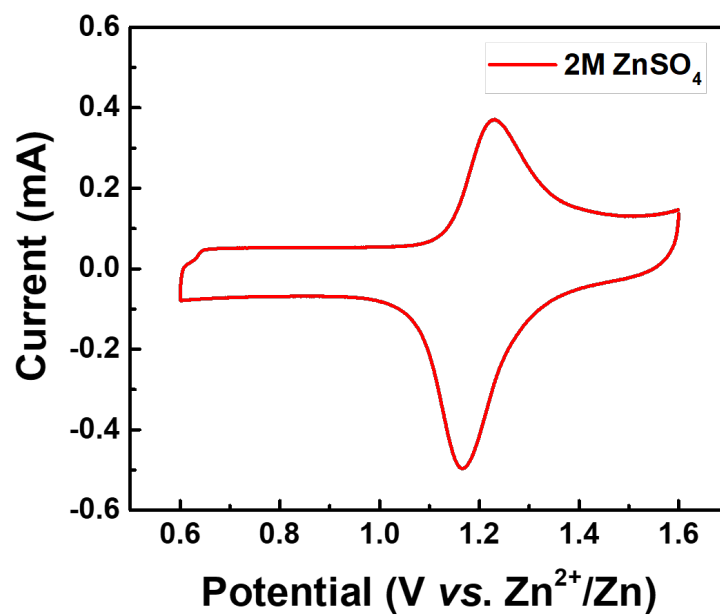


Figure S20. CV curve of Zn-I₂ battery with aqueous electrolyte at 0.1 mV s⁻¹.

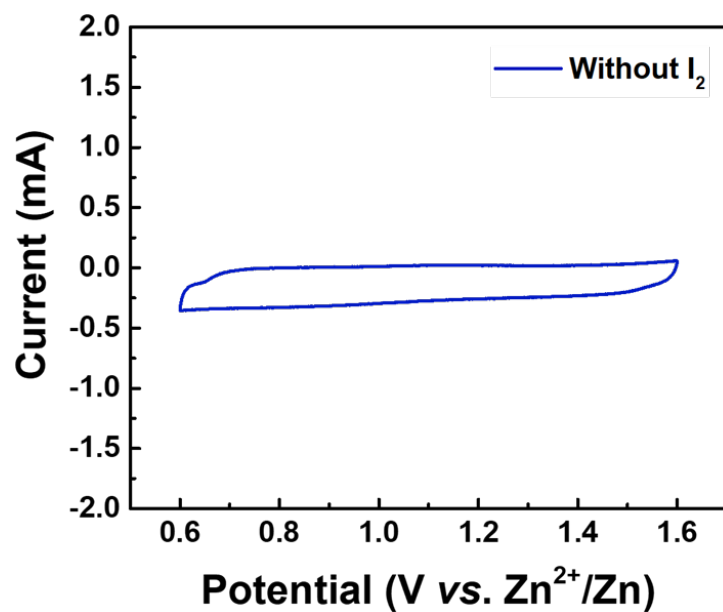


Figure S21. CV curve of the battery assembled with IC-Zn hydrogel electrolyte without I_2 .

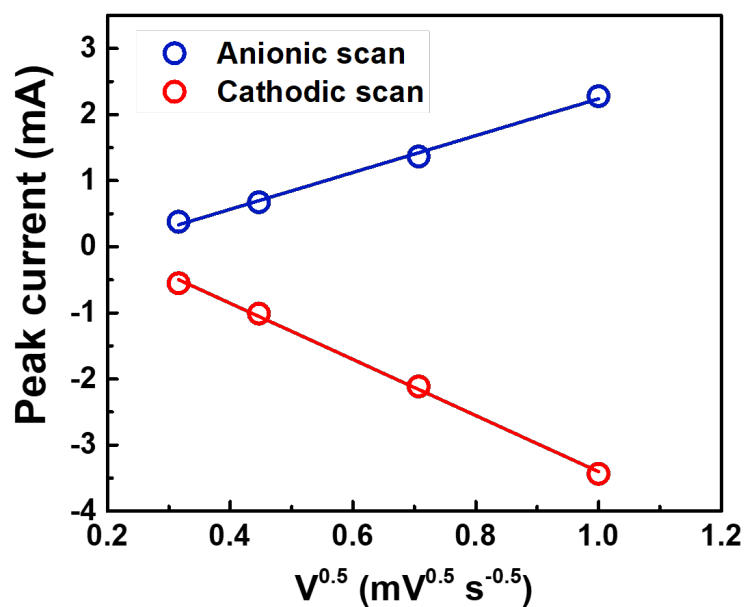


Figure S22. Relationship between redox peak current and the square root of scan rate in CV curves.

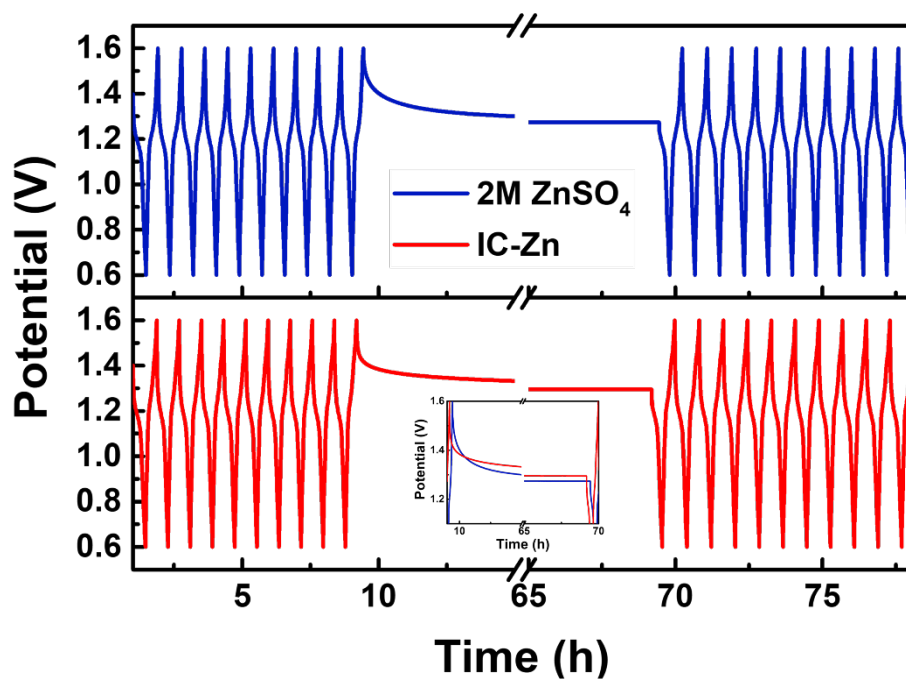


Figure S23. Self-discharge tests of Zn-I₂ batteries assembled with different electrolytes.

References

1. K. Lu, Z. Hu, J. Ma, H. Ma, L. Dai and J. Zhang, *Nat. Commun.*, 2017, **8**, 1-10.
2. Y. Tian, S. Chen, Y. He, Q. Chen, L. Zhang and J. Zhang, *Nano Research Energy*, 2022, **1**, e9120025.