Supporting Information for

An Ionically Crosslinked Composite Hydrogel Electrolyte Based on Natural Biomacromolecules for Sustainable Zinc-Ion Batteries

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Experimental section

Preparation of ISG hydrogel electrolyte: Typically, 0.5 g of iota-carrageenan (AR grade, Aladin), 0.2 g of sodium alginate (AR grade, Macklin) and 1mg of graphene oxide (GO) were mixed with 20 mL of deionized water and stirred at 60 °C for 4 h until a brown homogenous solution was obtained. The as-prepared solution was held at 60 °C for 20 min and then poured into a glass petri plate for cooling. Finally, the obtained hydrogel was immersed in 2 M $ZnSO_4$ overnight until the hydrogel was cross-linked completely. The obtained hygroscopic composite hydrogel electrolyte was denoted as ISG.

Synthesis of $NH_4V_4O_{10}$: The 1.404 g NH_4VO_3 was added into 60 mL of deionized water under continuous magnetic stirring at 80 °C for 20 min. Then 2.2692 g of $H_2C_2O_4·2H_2O$ solid powders were added to the above-mentioned solution and stirred for 30 min. Subsequently, the above solution was transferred to a Teflon-lined autoclave and kept in an oven maintained at 140 °C for 48 h. Finally, the collected powders were washed repeatedly with deionized water and then dried at 60 °C for 12 h.

Materials characterizations Structural: characterizations of the samples were performed by X-ray diffraction (XRD) in the detected angular range of 5-80° (Rigaku Mini Flex 600 diffractometer, Cu Ka radiation, k = 1.5418 Å). The morphologies were characterized by a field emission scanning electron microscope (FESEM, FEI Nova Nano SEM 230, 10 kV) equipped with an energy-dispersive X-ray spectroscopy (EDS) analyzer. Active species of the composite hydrogel electrolyte were identified by Fourier Transform Infrared Spectrometer (FTIR, Nicolet 6700).

Electrochemical characterization: In preparation of the cathodes, a mixture of $NH_4V_4O_{10}$ (70 wt%), super P (20 wt%), polyvinylidene fluoride (PVDF, 10 wt%) and Nmethyl-2-pyrrolidone (NMP) were pasted onto a stainless-steel mesh and dried in a vacuum oven at 80 °C for 12 h. CR2032 coin cells were assembled with the NH4V4O10 cathode, ISG hydrogel electrolyte or 2 M $ZnSO_4$ liquid electrolyte and Zn anode to evaluate the electrochemical performance by a multichannel battery testing system (LAND CT2001A). Particularly, a glass fiber separator was used when assembling full cells with the 2 M $ZnSO_4$ liquid electrolyte. All the cells were rested for 1 h before testing. The Zn||NVO coin cells cycled at 2 A g^{-1} and the pouch cells cycled at 0.5 A g^{-1} were activated at a current density of 0.2 A g^{-1} for 2 cycles before testing. The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests were conducted by an electrochemical workstation (CHI660E).

Table S1 Detailed test procedures of Zn||Zn symmetric cells.

Test	Current density (mA cm^{-2})	Capacity (mA h cm^{-2})
Plating/Stripping	1	1
Rate Capability	0.2	0.2
	0.5	0.5
	1	0.5
	2	0.5
	2.5	0.525

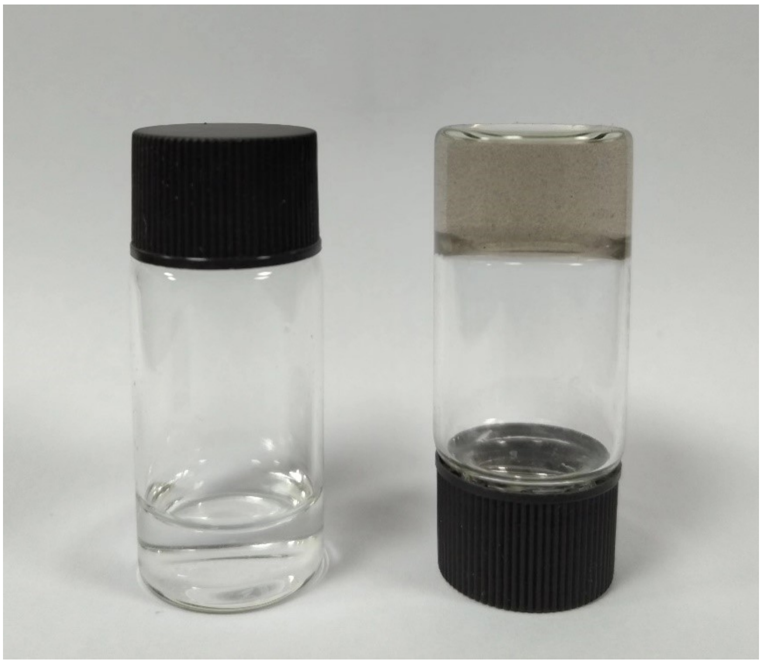

Fig. S1 Optical images of the liquid electrolyte (left) and ISG hydrogel (right).

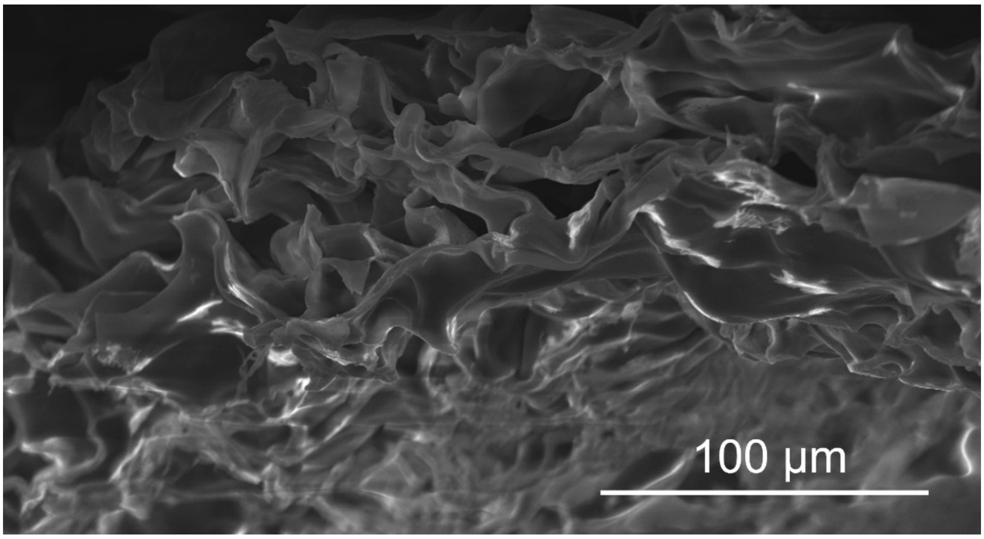

Fig. S2 Cross-sectional SEM image of freeze-dried ISGHE.

Fig. S3 Thickness of (a) ISGHE and (b) glass fiber separator.

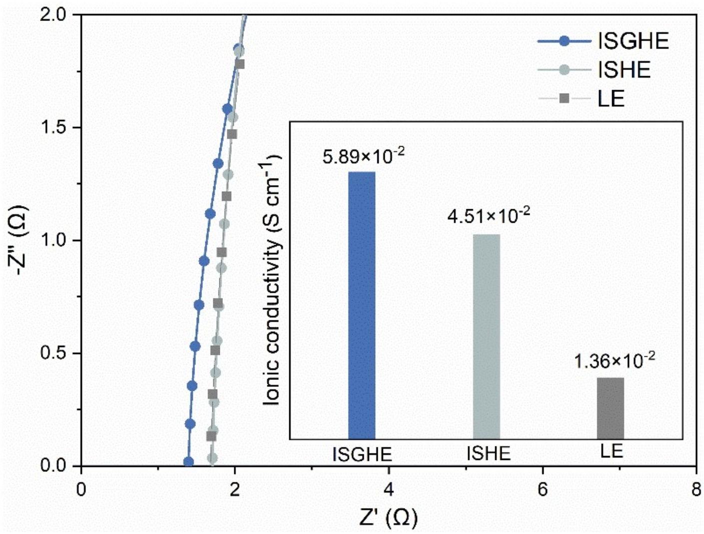

Fig. S4 Ionic conductivity of ISGHE, ISHE and LE.

Calculation of ionic conductivity:

The ionic conductivities of different electrolytes were calculated by the following equations:

ISGHE: $$\sigma = \frac{l}{RA} = \frac{0.1657}{1.4 \times 2.01} = 5.89 \times 10^{-2}\ S\ cm^{-1}$$

ISGE: $$\sigma = \frac{l}{RA} = \frac{0.154}{1.7 \times 2.01} = 4.51 \times 10^{-2}\ S\ cm^{-1}$$

LE: $$\sigma = \frac{l}{RA} = \frac{0.0466}{1.7 \times 2.01} = 1.36 \times 10^{-2}\ S\ cm^{-1}$$

where *l*, *R* and *A* represent the thickness, the bulk resistance and the test area of hydrogel electrolyte, respectively.[1]

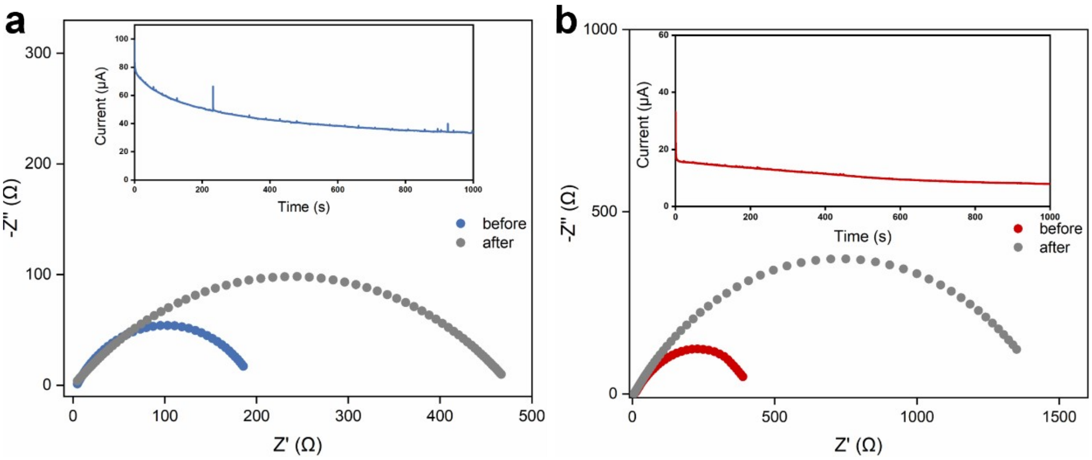

Fig. S5 EIS spectra and I-t curve (inserted) of the (a) ISGHE-based and (b) LE-based Zn||Zn symmetric cell before and after polarization.

Calculation of Zn^{2+} transference number:

To calculate the Zn^{2+} transference number, the resistances of the Zn||Zn symmetric cell before and after the polarization were measured. The transference number was calculated according to below equations:

ISGHE: $$t^+ = \frac{I_s(\Delta V - I_0 R_0)}{I_0(\Delta V - I_s R_s)} = \frac{0.0000336 \times (0.01 - 0.01976)}{0.0000988 \times (0.01 - 0.01567)} = 0.58$$

LE: $$t^+ = \frac{I_s(\Delta V - I_0 R_0)}{I_0(\Delta V - I_s R_s)} = \frac{0.0000079 \times (0.01 - 0.0132)}{0.0000331 \times (0.01 - 0.0119)} = 0.40$$

where I_0 and I_s represent the initial and steady-state currents, respectively. ΔV is the applied potential. R_0 and R_s are the initial and steady-state resistances of the cell determined by impedance spectroscopy, respectively.[2]

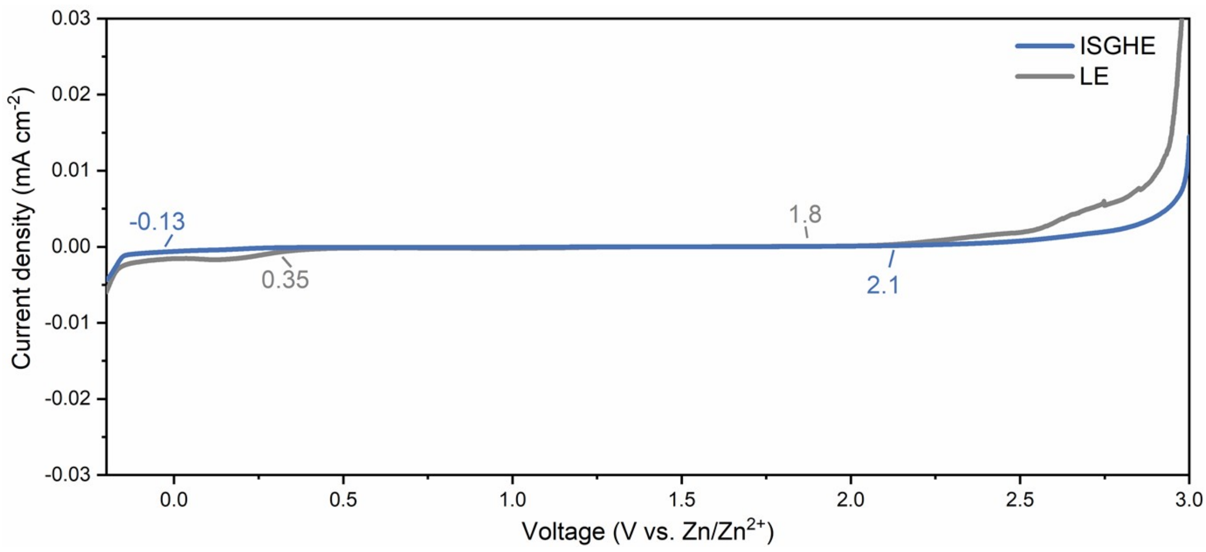

Fig. S6 Electrochemical stability window of ISGHE and LE.

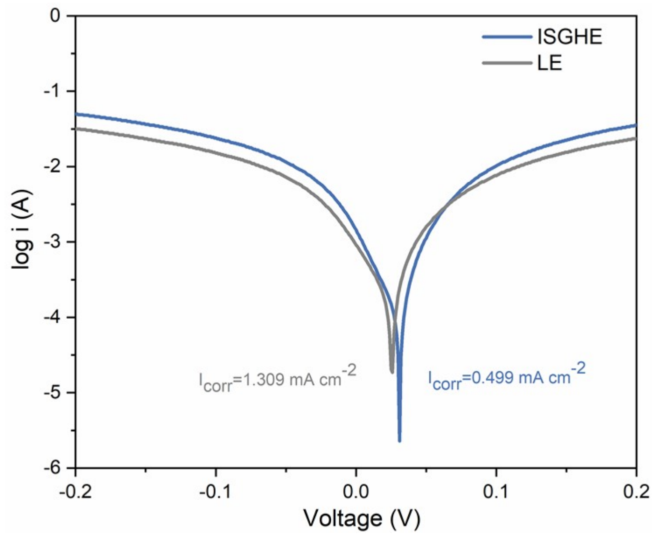

Fig. S7 Tafel tests based on Zn||Zn symmetric cells with ISGHE and LE.

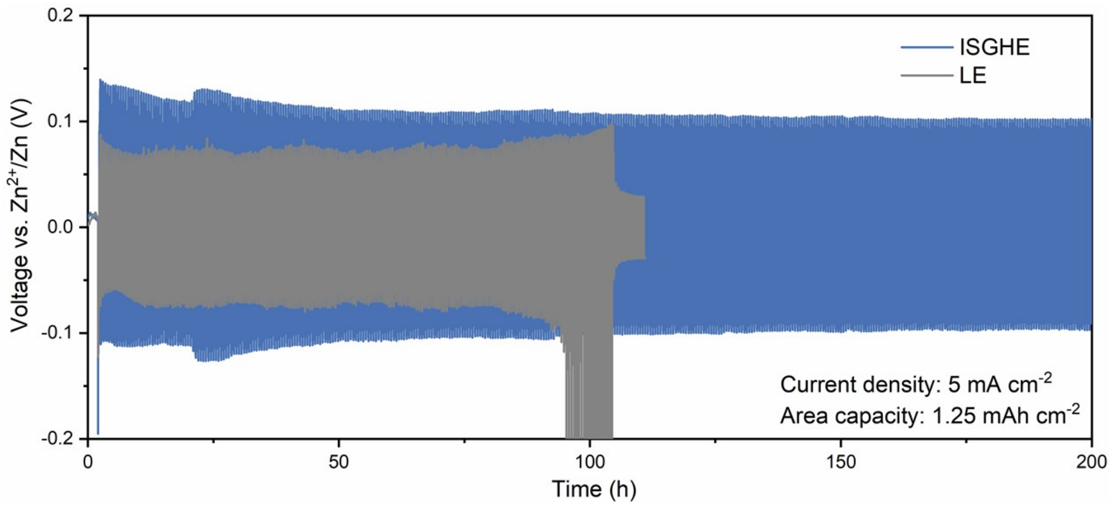

Fig. S8 Long-term galvanostatic cycling performance of Zn||Zn symmetric cells based on ISGHE and LE at 5 mA cm^{-2} and 1.25 mAh cm^{-2}.

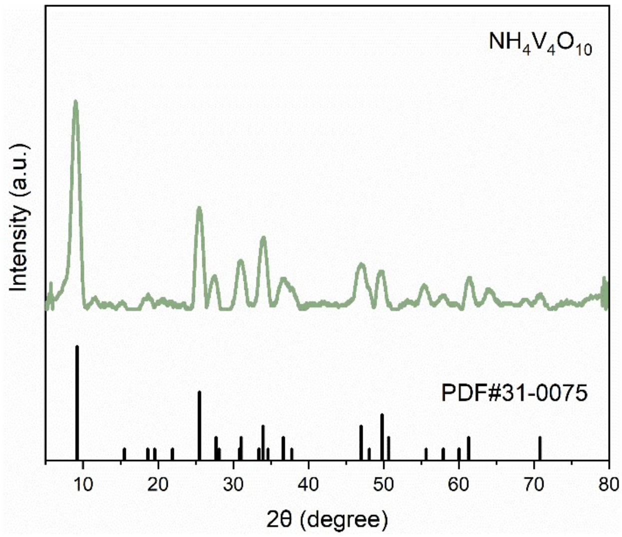

Fig. S9 XRD pattern of $NH_4V_4O_{10}$.

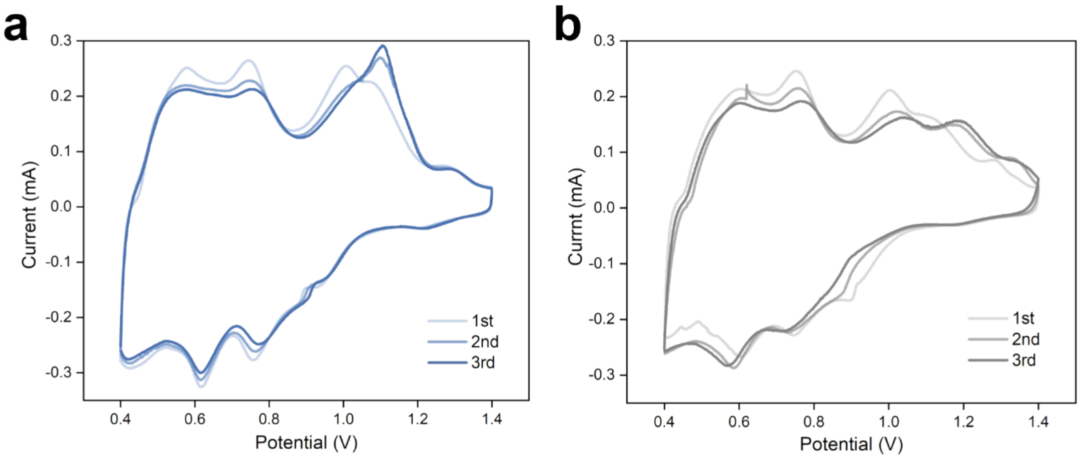

Fig. S10 CV curves of the initial three cycles of Zn||NVO cells based on (a) ISGHE and (b) LE at a scan rate of 0.1 mV s^{-1}.

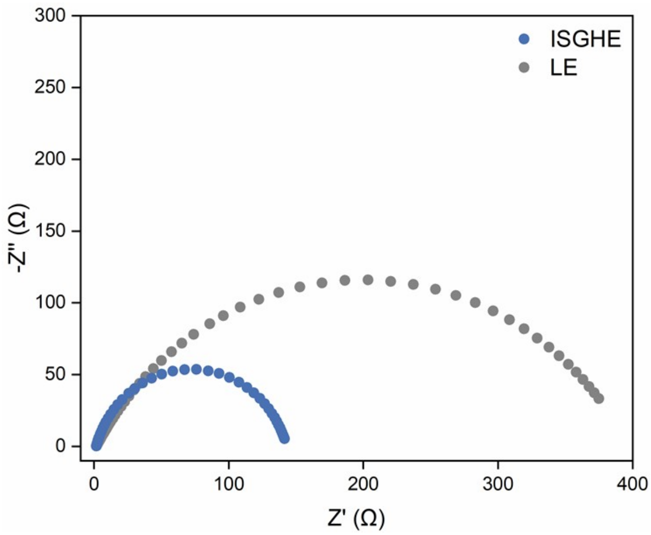

Fig. S11 EIS plots of Zn||NVO full cells based on ISGHE and LE in the frequency range of 100 kHz to 0.01 Hz.

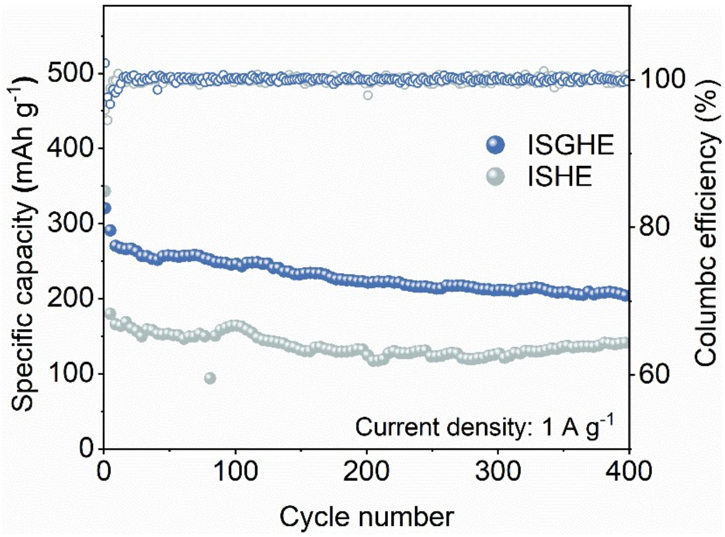

Fig. S12 Long-term cycling performance of Zn||NVO full cells based on ISGHE and ISHE at a current density of 1 A g^{-1}.

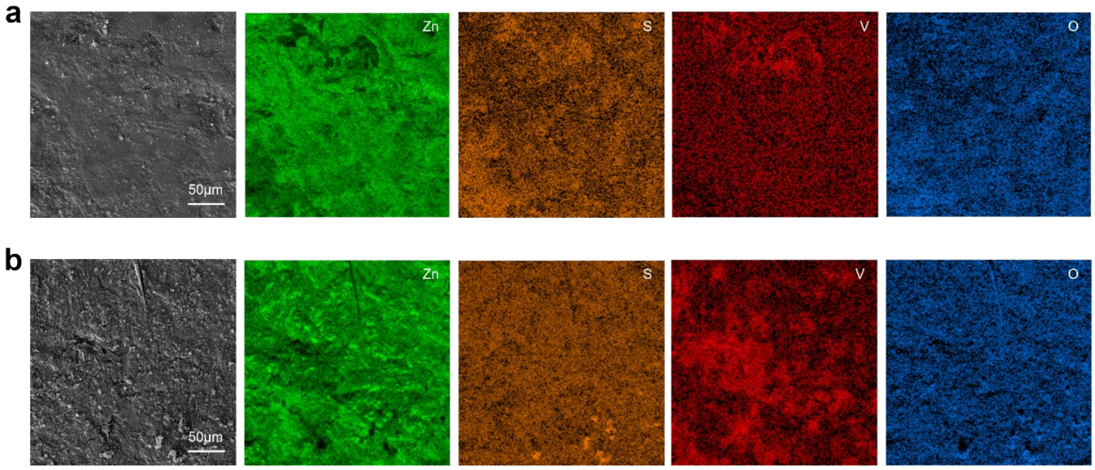

Fig. S13 SEM/EDS images of Zn anodes in Zn||NVO batteries based on (a) ISGHE and (b) LE after 50 cycles at 1 A g^{-1}.

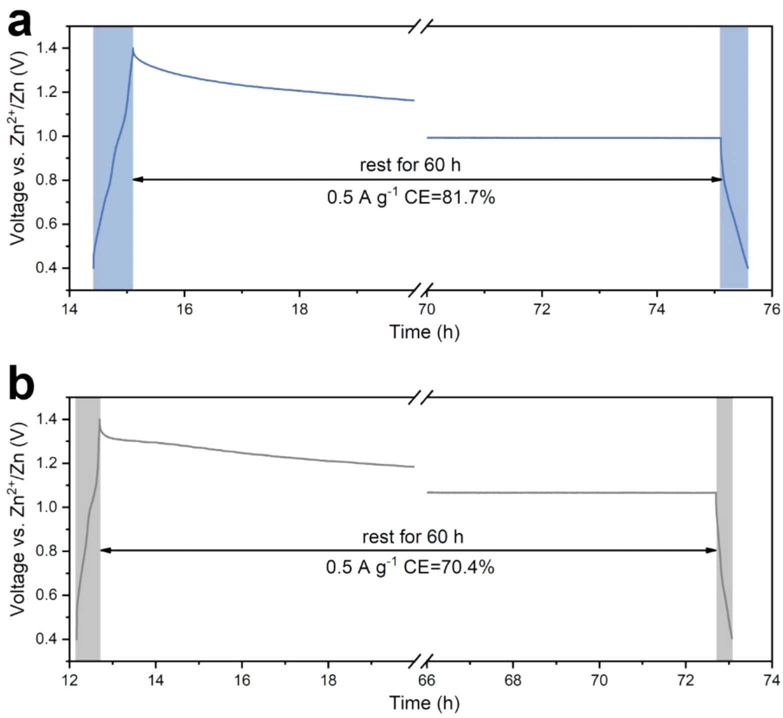

Fig. S14 Resting tests of Zn||NVO full cells based on (a) ISGHE and (b) LE.

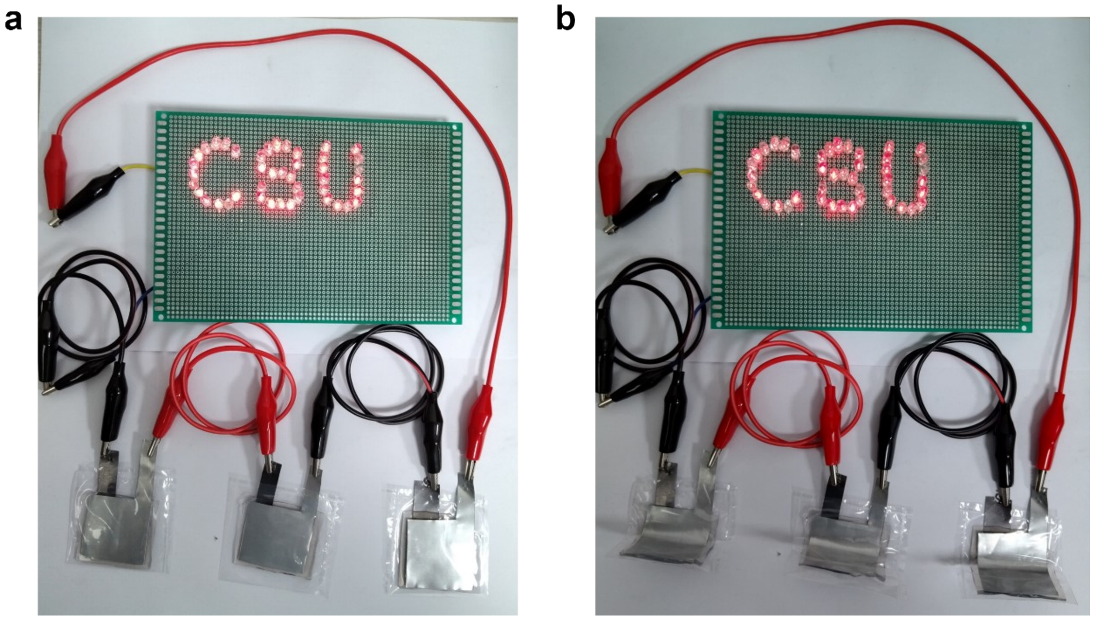

Fig. S15 Optical images of three ISGHE-based pouch cells powering an array of light bulbs at (a) flat and (b) bended states.

Reference

1. H. Li, Z. Liu, G. Liang, Y. Huang, Y. Huang, M. Zhu, Z. Pei, Q. Xue, Z. Tang, Y. Wang, B. Li and C. Zhi, *ACS Nano*, 2018, **12**, 3140-3148.
2. Y. Tang, C. Liu, H. Zhu, X. Xie, J. Gao, C. Deng, M. Han, S. Liang and J. Zhou, *Energy Storage Mater.*, 2020, **27**, 109-116.