Supporting Information

Highly Stable Zinc Iodine Single Flow Battery with Super High Energy Density for Stationary Energy Storage

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This paper is dedicated to the 70th anniversary of DICP

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Experimental Section

Experimental reagents

Analytical grade zinc bromide (Israel Chemicals), potassium chloride (DAMAO Chemical Reagent Factory, Tianjin, China), Nafion dispersion (5wt %, Dupont, H type) and porous polyolefin separator (0.1 µm average pore size, 58% ±7.5% porosity, 900 µm thickness) were used as received. The Nafion 115 membrane was purchased from Dupont. All the electrolytes that mentioned were prepared with deionized water.

Preparation of the composite porous polyolefin ion conducting membrane

Nafion solution with a concentration of 5% in isopropanol was casted on the porous polyolefin separator with the doctor blade of 250 µm (Elcometer 3545 adjustable Bird Coater, Scraper, Elcometer 3545/8) to prepare the composite porous polyolefin ion conducting membrane. Then the composite porous polyolefin ion conducting membrane was dried at room temperature for several hours until the solvent was completely evaporated.

Single cell and stack assembly

The structure of single flow battery is the same as the ZIFB that we have reported. For the positive side, electrolyte was pump into the positive compartments and then sealed with the volume about 7.2 mL (3 mm electrode) or 14.2 mL (5 mm electrode). The calculation of the energy density was based on the electrolyte volume of the positive electrolyte. The effective area of the electrode was 48 cm^2 (6 cm ×8 cm). The battery performance was evaluated by Arbin 2000 at room temperature with the current density range from 20 mA/cm^2 to 80 mA/cm^2. The charge-discharge process was terminated by the capacity limit. The cell stack was assembled by pressing 5 single cell. For each single cell, the area of electrode was about 425 cm^2 with the thickness of 3 mm or 6 mm. And some necessary parts such as: carbon plastic bipolar plates, PVC frames and gaskets were self-made.

Cyclic voltammetry

The cyclic voltammetry measurements was conducted via a typical three-electrode system as we mentioned previously. The electrolyte composition was 0.1M I_3^- and 0.1M I^- in 1M KCl. Glassy carbon electrode (radius 2.5mm) and graphite plate (3cm×3cm) were selected as the working electrode and counter electrode respectively. Saturated calomel electrode (pre-soaked in saturated potassium chloride) was used as the reference electrode. The electrochemical measurements were recorded by an electrochemical station (Gamry reference 3000).

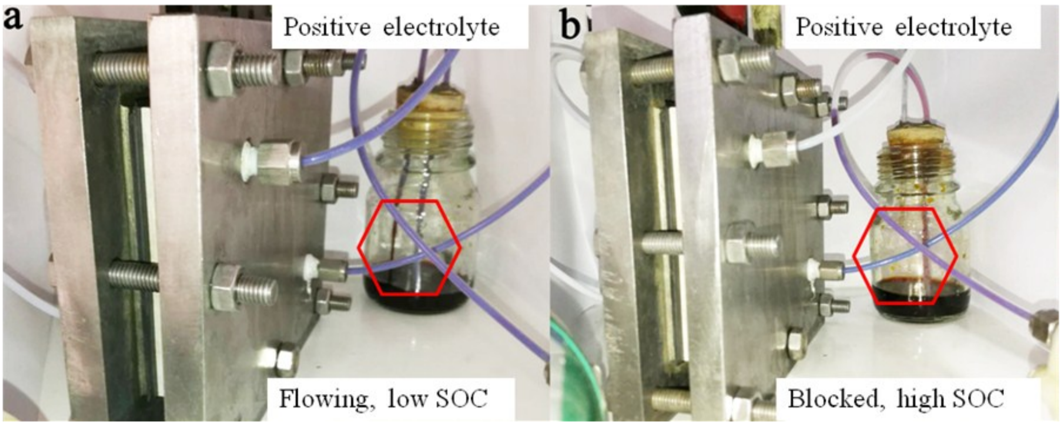

Figure S1. The photographs of the ZIFB at low (a) and high SOC (b).

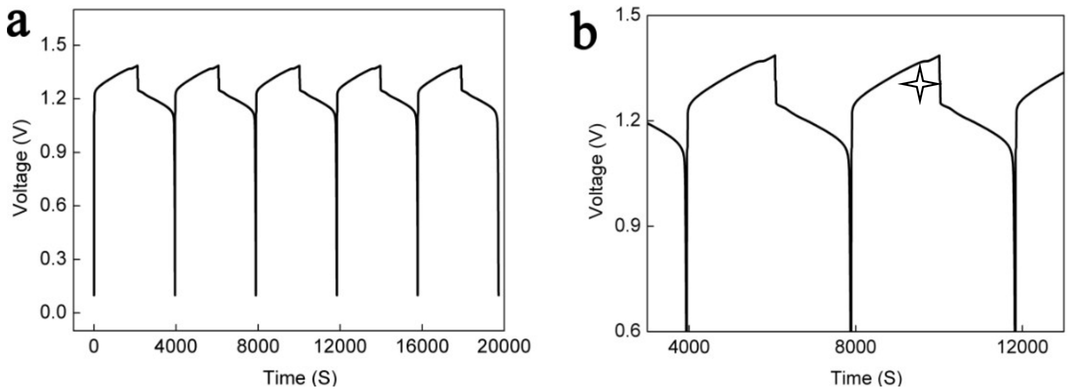

Figure S2. a) The representative voltage profile of the battery assembled with porous polyolefin separator at the current density of 40 mA/cm^2. b) Figure S1a after magnifying.

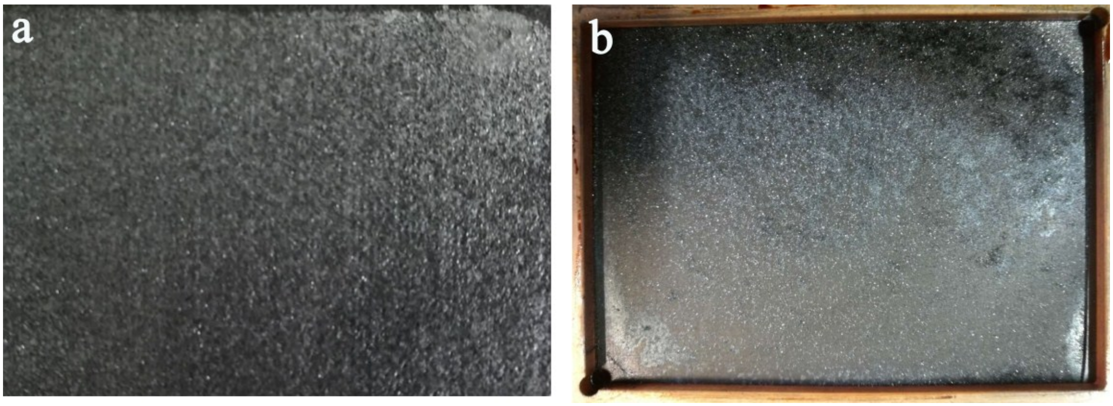

Figure S3. Surface morphology of the positive graphite felt (a) and current collector (b) on the positive side after charging to a high SOC.

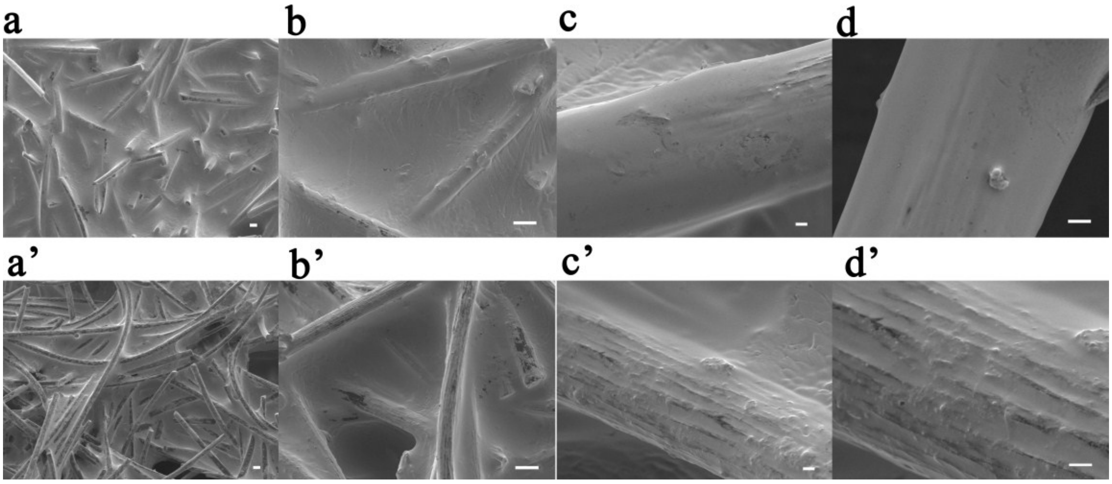

Figure S4. The morphology of I_2 deposition at nearly 100% SOC. (a-d) The surface morphology of positive graphite felt that near the membrane side. (Scale bar: 10 μm, 10 μm, 1 μm, 1 μm) (a'-d')The surface morphology of the positive graphite felt that near the bipolar plate side. (Scale bar: 10 μm, 10 μm, 1 μm, 1 μm)

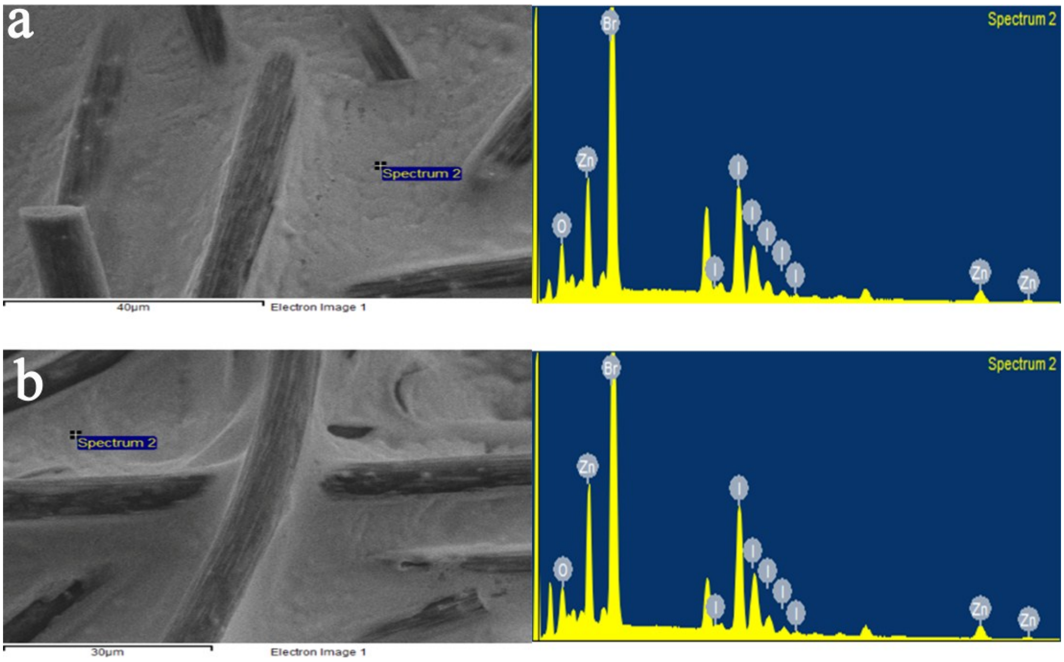

Figure S5. Microstructural analysis of positive electrode after being charged. a) Surface morphology of positive graphite felt on the membrane side (Scale bar: 40μm) and the corresponding energy-dispersive X-ray spectroscopy spectra of the marked area in image. (b) Surface morphology of positive graphite felt on the bi-polar plate side (Scale bar: 40μm) and the corresponding energy-dispersive X-ray spectroscopy spectra of the marked area in image.

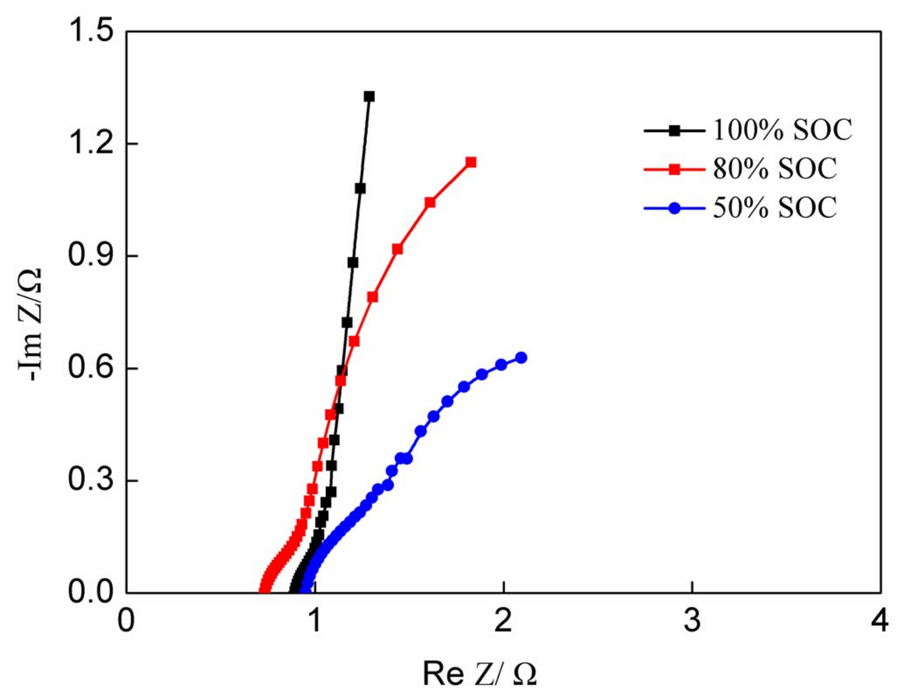

Figure S6. Impedance spectrum of the ZISFB at different SOC.

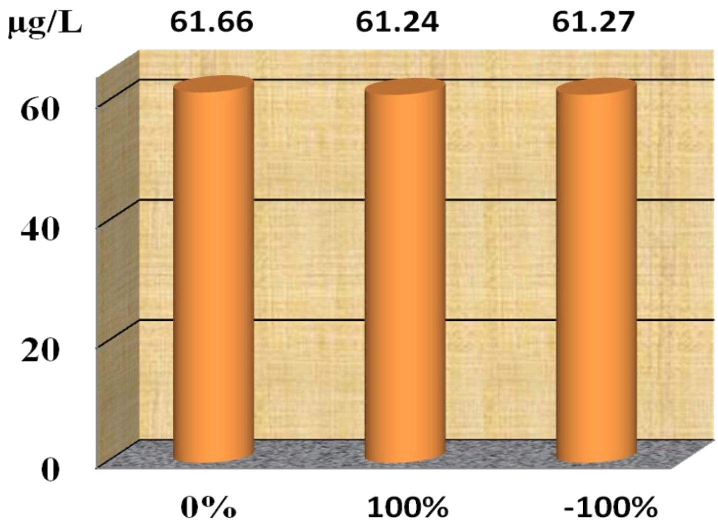

Figure S7. The concentration of I^- in the negative electrolyte at different SOC.

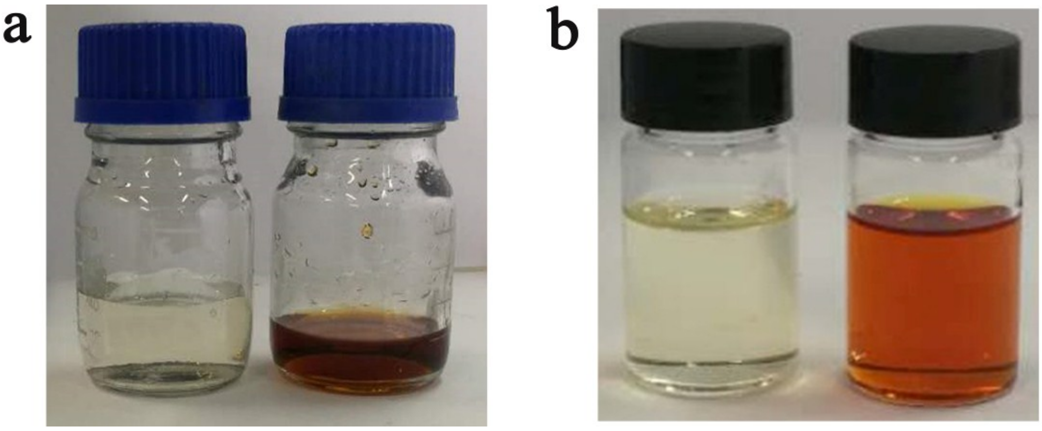

Figure S8. (a) The positive (right) and negative (left) electrolyte volume of ZIFB after a long cycling. (b)The comparison of the electrolyte before (left) and after (right) oxidizing by the oxygen in the air.

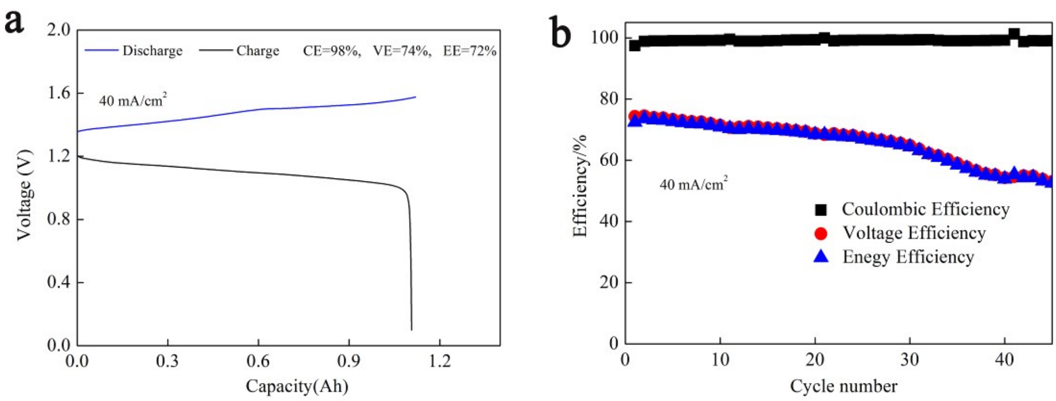

Figure S9. (a) The representative charge-discharge curve of the battery assembled with Nafion 115 membrane at the current density of 40 mA/cm^2. (b) The cycling performance of the battery at 40 mA/cm^2.

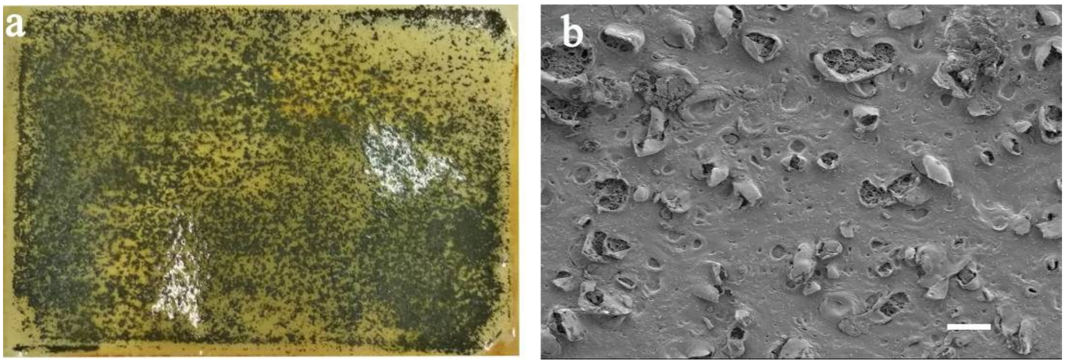

Figure S10. (a) The photography of Nafion 115 membrane after the battery test. (b) The surface morphology of the Nafion 115 membrane after cycling（scale bar 10μm）.

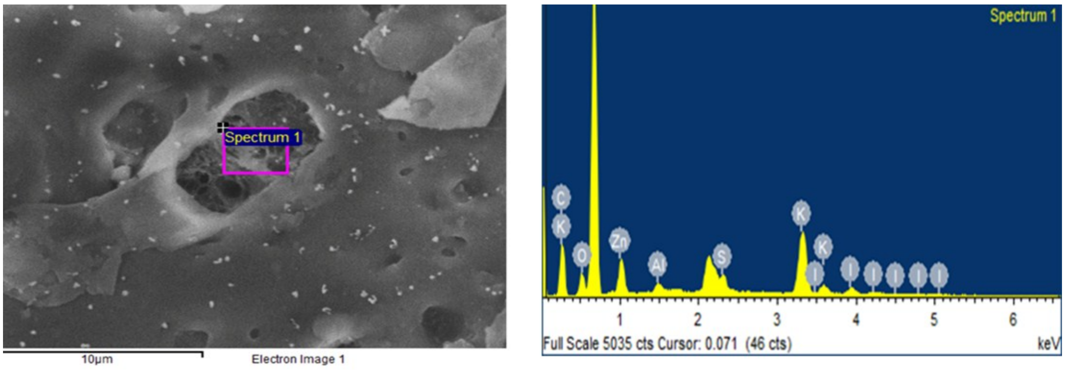

Figure S11. The surface morphology of the Nafion 115 membrane after the battery test and EDS spectra of the marked area.

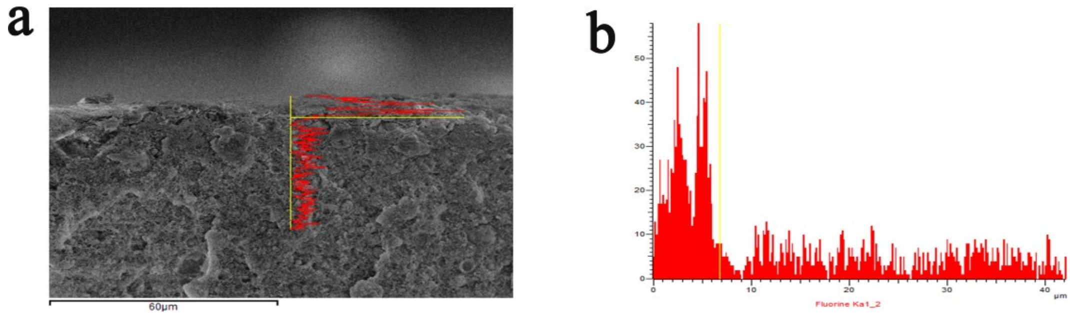

Figure S12. (a)The EDS spectra of “F” element in the cross-section of composite membrane. (b) The magnified spectra of “a”.

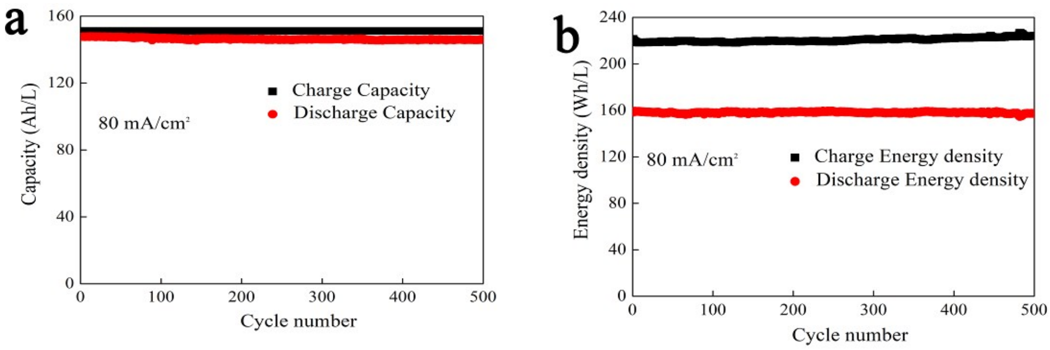

Figure S13. The capacity (a) and energy density (b) retention versus cycle number at the current density of 80 mA/cm^2.

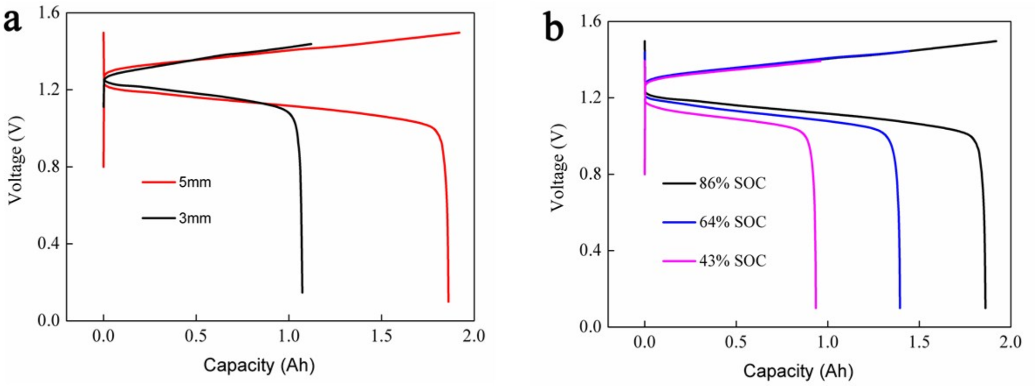

Figure S14. (a) The performance of the battery assembled with different thickness electrode at the current density of 40 mA/cm^2. (b) Assembled with 5mm electrode, the battery performance with different SOC at the current density of 40 mA/cm^2.

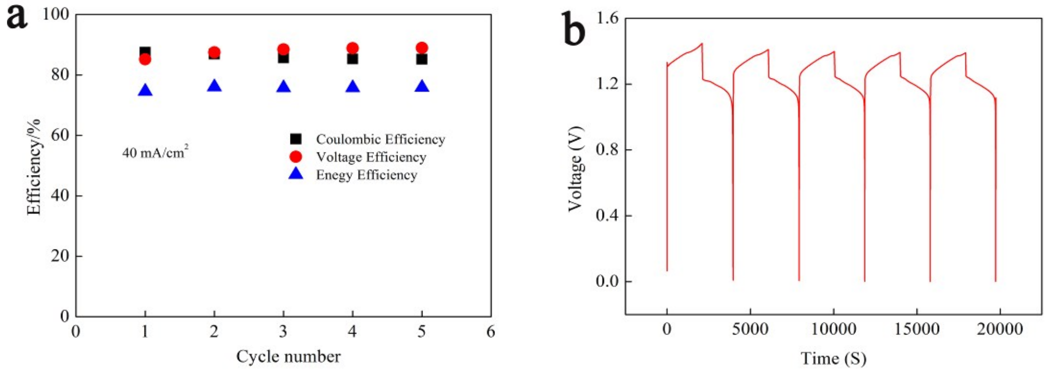

Figure S15. (a) The performance of the battery assembled with the composite porous polyolefin ion conducting membrane with the Nafion layer on the negative side. (b) The representative voltage curve of the battery.

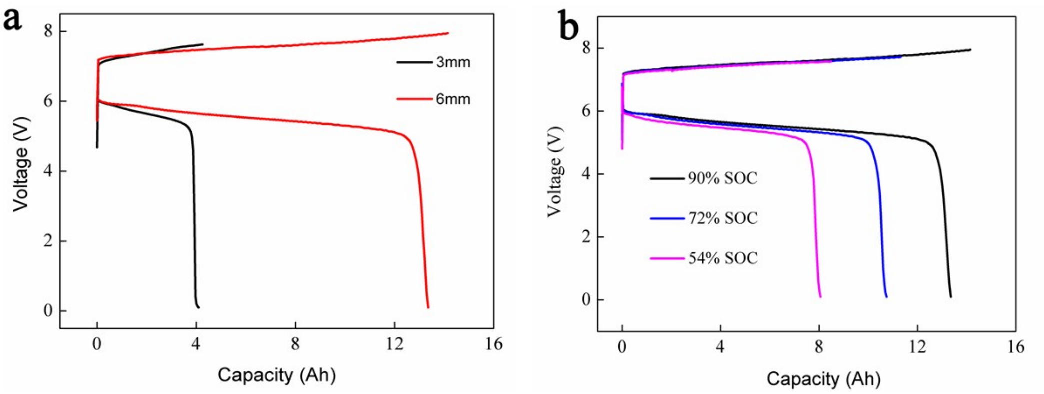

Figure S16. (a) The performance of the cell stack assembled with different thickness electrode at the current density of 80 mA/cm^2. (b) Assembled with 6 mm electrode , the stack performance with different SOC at the current density of 80 mA/cm^2.

Table S1. Compositions of the electrolytes with different concentration.

Electrolyte	Electrolyte (mol/L)		
	KI	$ZnBr_2$	KCl
3 M	3	1.5	2
6 M	6.0	3.0	0
7.5 M	7.5	3.75	0

Table S2. The parameters of 3D porous graphite felt electrode.

Porosity	Specific area	Thickness of the graphite felt	Density of the graphite felt
90%	10 m^2/g	1.8mm(pressing)	0.1g/cm^3

The specific area of graphite felt: 10 m^2/g
The porosity of the graphite felt: 90%
The thickness of the graphite felt in the ZISFB:1.8 mm (pressing)
The density of I_2: 4.93 g/cm^3
The molecular weight of I_2: 253.8
The pore volume of graphite felt:
The pore volume of graphite felt of 1cm^2: 1cm^2*0.18cm*0.9=0.162cm^3

The theoretical areal load capacity of graphite felt:
0.162cm^3/cm^2*4.93g/cm^3/254g/mol*26.8Ah/mol*2=168mAh/cm^2

The theoretical thickness of the I_2 deposition:
The area of 1cm^2 graphite felt (3mm electrode): 10m^2/g*0.03g =0.3m^2
The thickness of I_2 deposition: 0.162cm^3/3000cm^2= 0.54 um