Supporting Information

Enhancing Performance and Longevity of Solid-State Zinc-Iodine Batteries with Fluorine-Rich Solid Electrolyte Interphase

Yongxin Huang[1], Yiqing Wang[1], Xiyue Peng[1], Tongen Lin [1, 2], Xia Huang[1], Norah S. Alghamdi [1,3,4], Masud Rana[1], Peng Chen[1], Cheng Zhang[1,*], Andrew K. Whittaker[1], Lianzhou Wang[1,2] and Bin Luo [1,*]

[1] Australian Institute for Bioengineering and Nanotechnology (AIBN), The University of Queensland QLD 4072, Australia

[2] School of Chemical Engineering, The University of Queensland St Lucia, QLD 4072, Australia

[3] School of Chemistry and Molecular Biosciences, Faculty of Science, The University of Queensland St Lucia, QLD 4072, Australia

[4] Department of Chemistry, Faculty of Science, Imam Mohammad Ibn Saud Islamic University (IMSIU), Riyadh, 11564 Saudi Arabia

Emails: b.luo1@uq.edu.au, c.zhang3@uq.edu.au

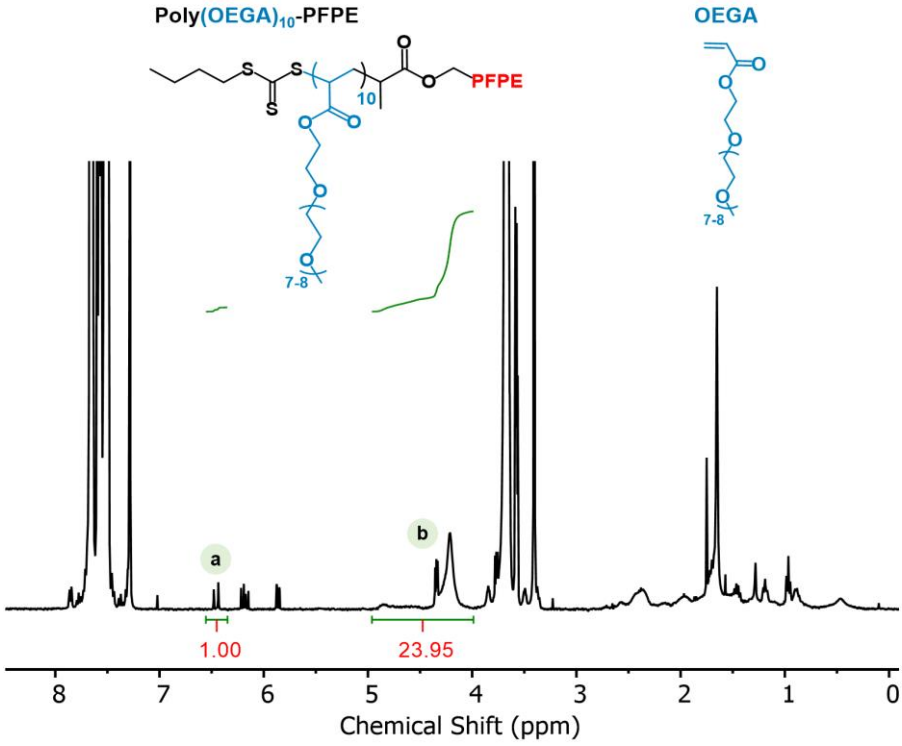

Figure S1. 1H NMR spectra of the crude Poly(OEGA)10-PFPE polymers in CDCl3. a, unreacted monomer peak (1H, CH2=); b, unreacted monomer (2H, CH2O-) + polymer peak (2H, CH2O-). $Conversion\ \% = (\int b - 2\int a)/\int b \times 100$.

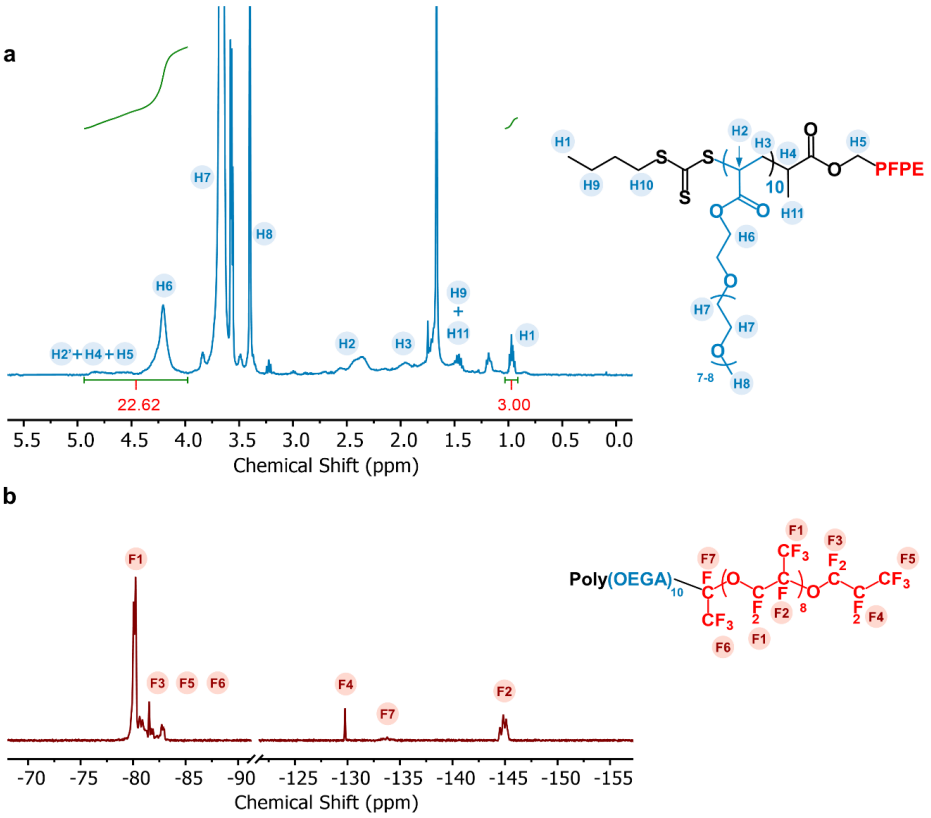

Figure S2. (a) ^{1}H and (b) ^{19}F NMR spectra of PF in deuterated chloroform ($CDCL_3$) with corresponding chemical structure.

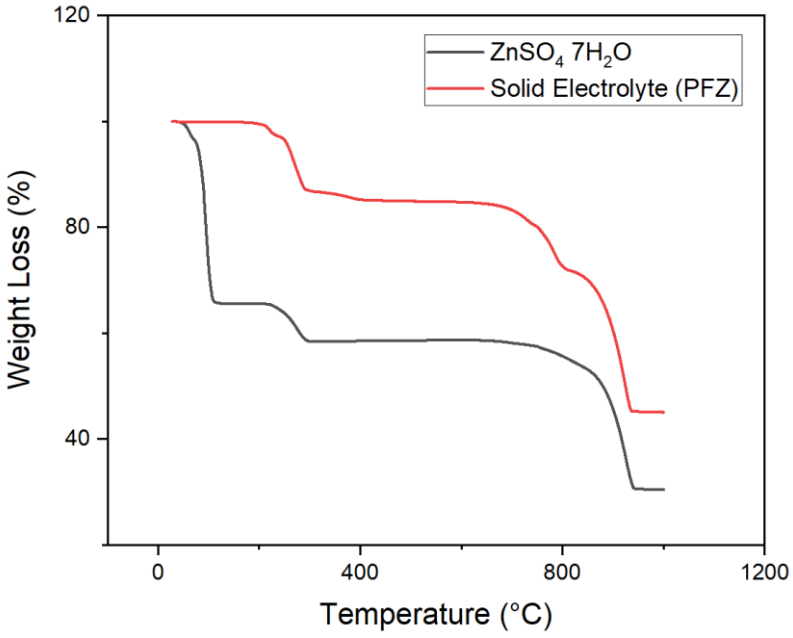

Figure S3. Thermal gravimetric analysis (TGA) for zinc salt and PFZ.

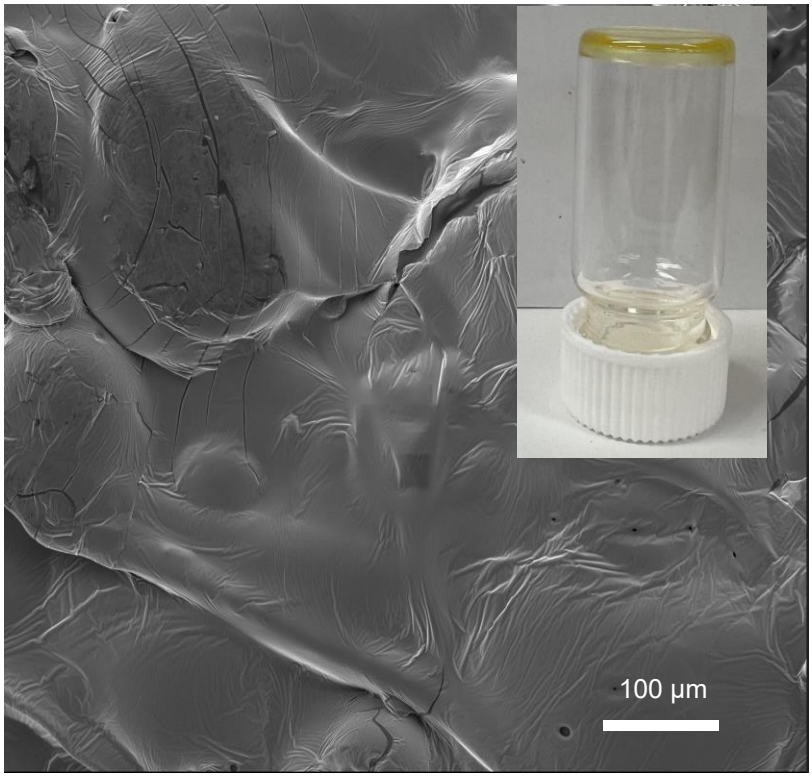

Figure S4. PFZ after overnight drying at 100°C and SEM image of PFZ.

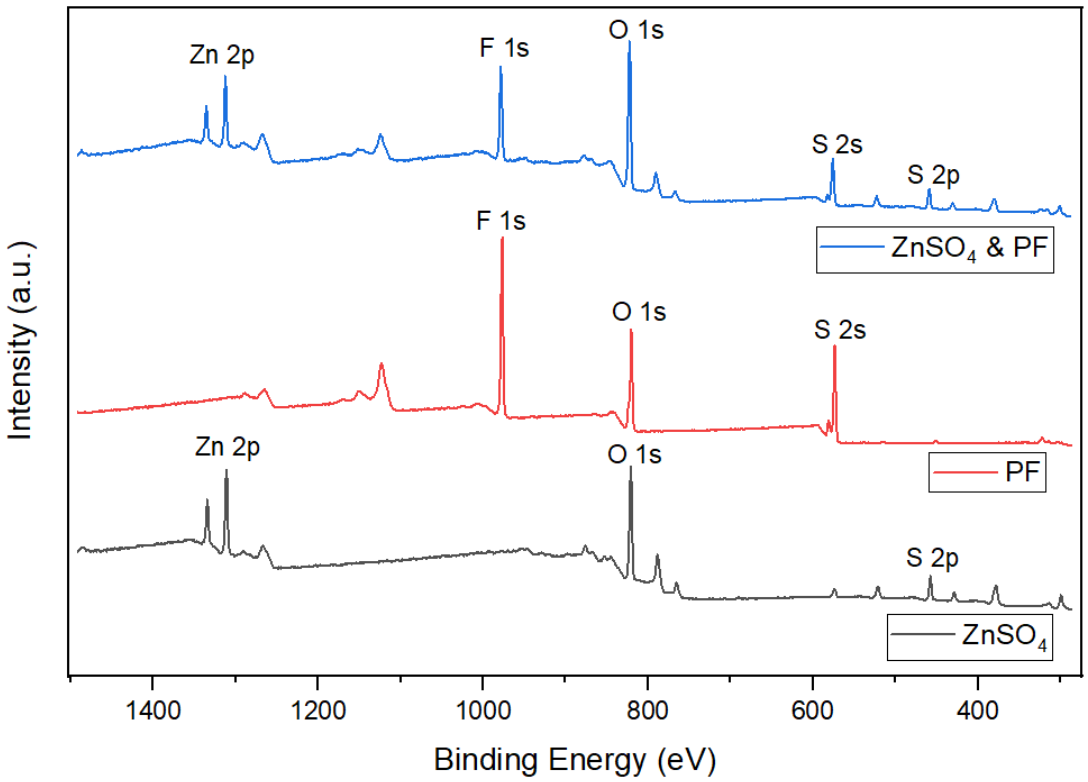

Figure S5. XPS spectra of the $ZnSO_4$, PF and $ZnSO_4$ & PF (PFZ).

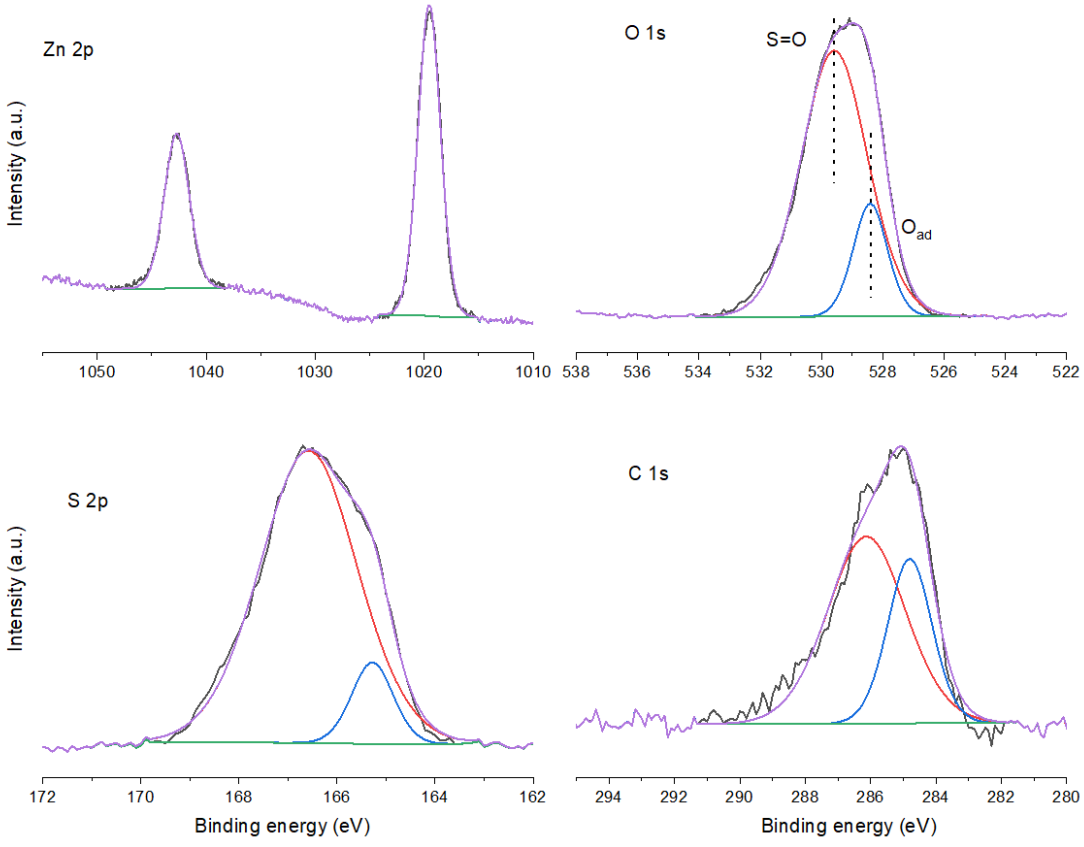

Figure S6. XPS spectra of $ZnSO_4$.

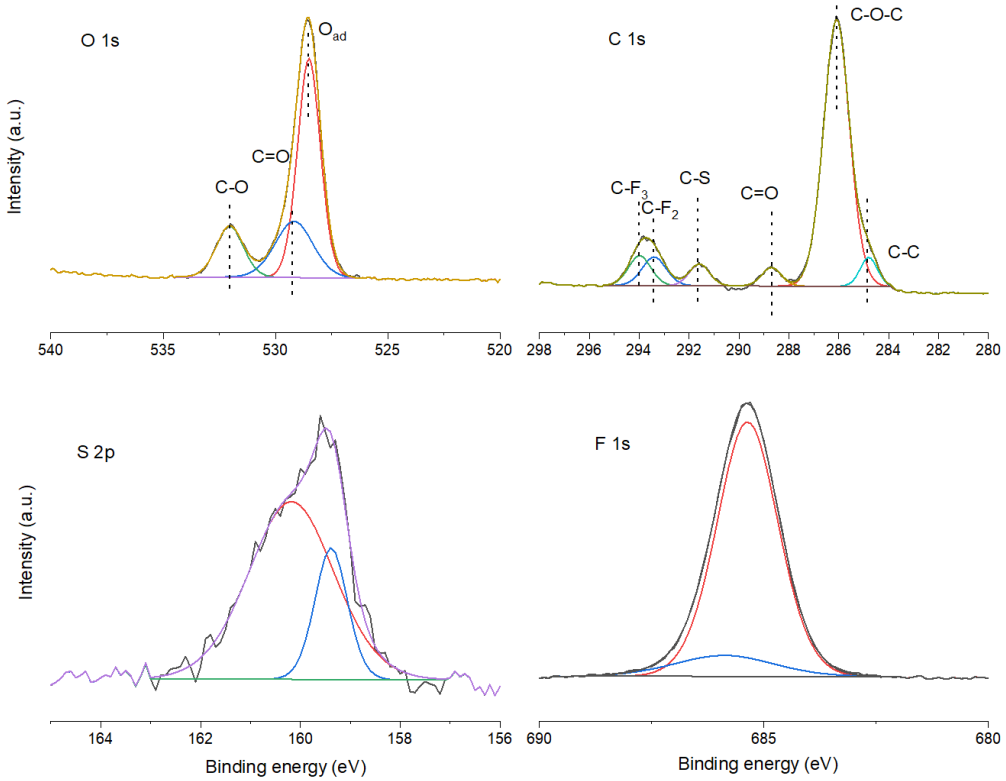

Figure S7. XPS spectra of the PF [1-3].

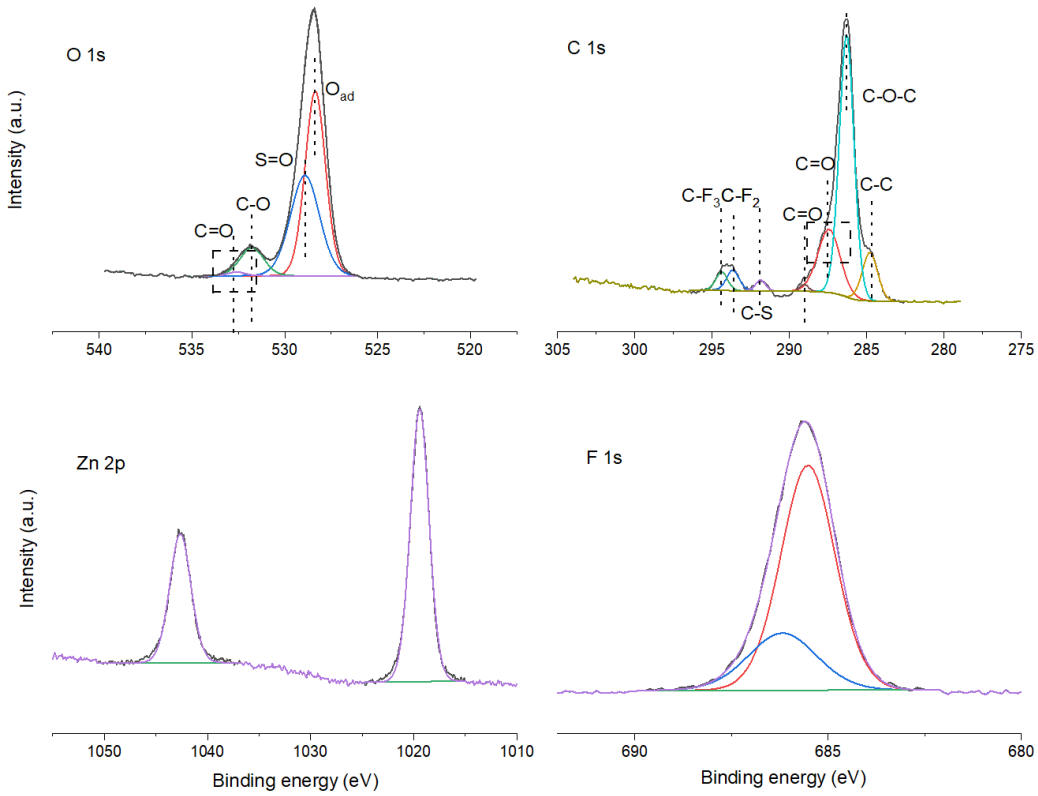

Figure S8. XPS spectra of the PFZ.

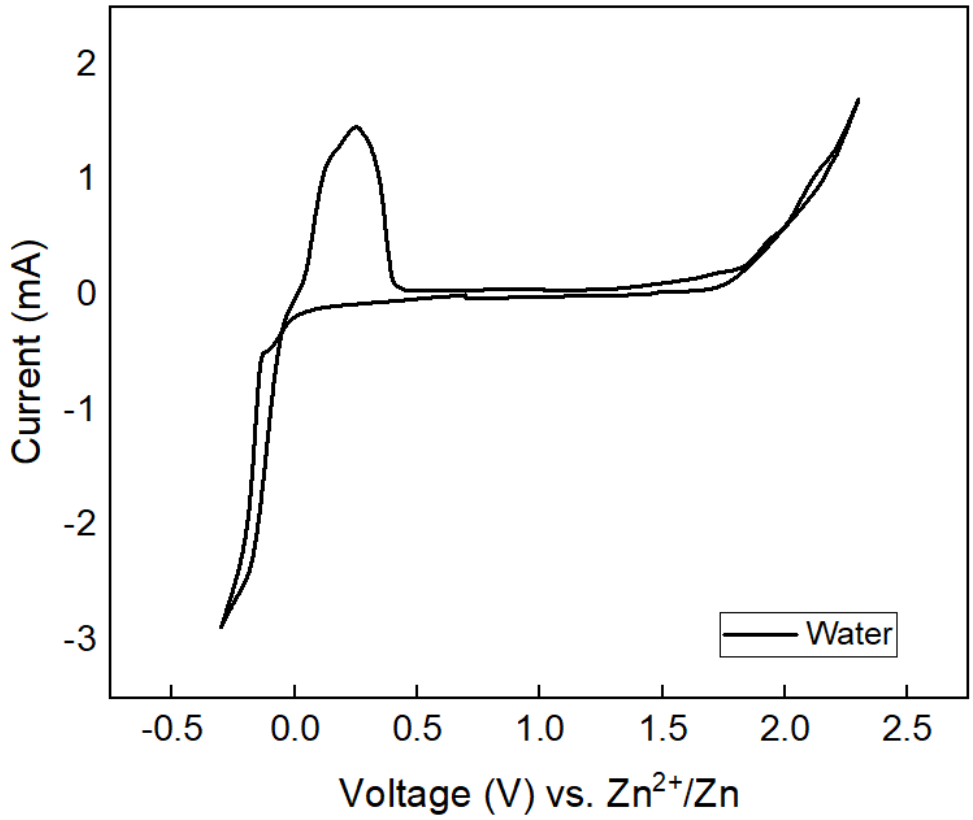

Figure S9. The electrochemical stability window of water.

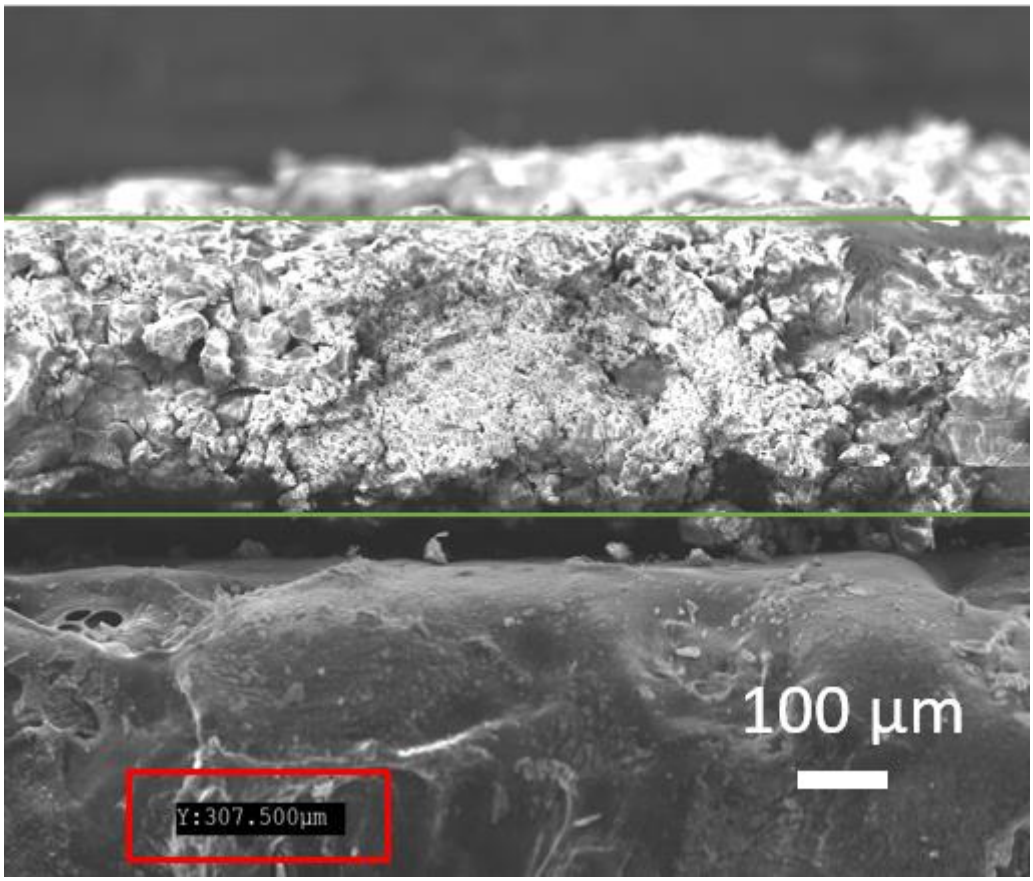

Figure S10. Y: The thickness of PFZ which got from SEM image of the electrolyte's crossing section.

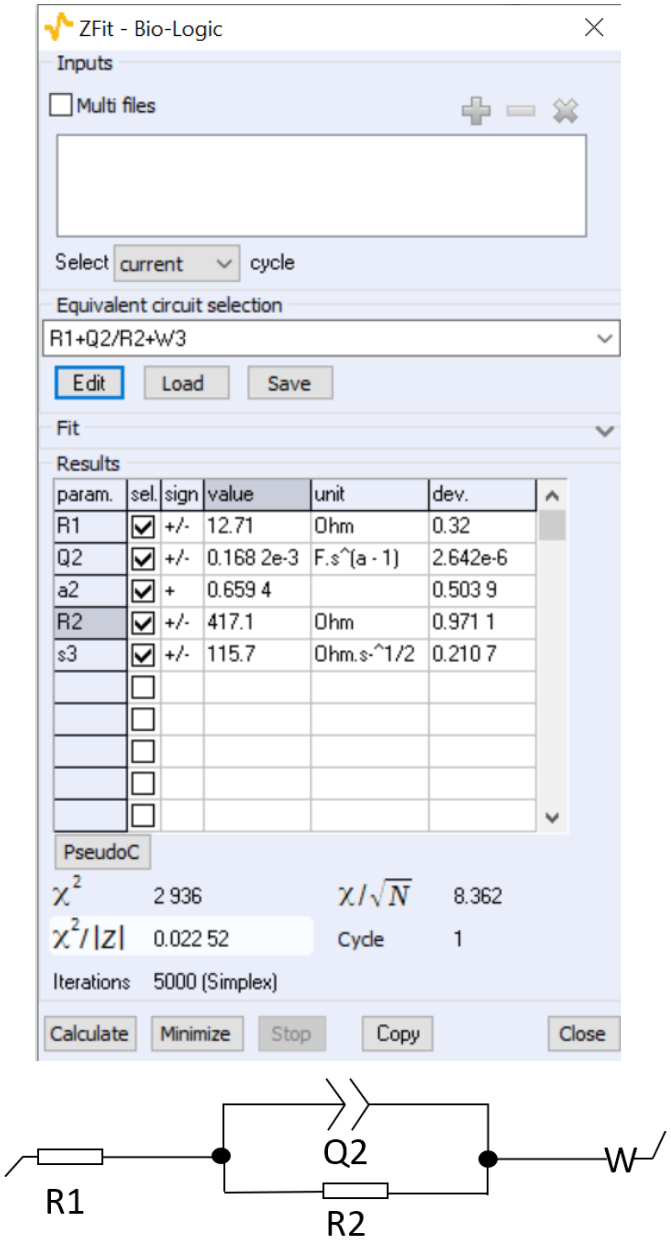

Figure S11. Bio-logic's simulation results.

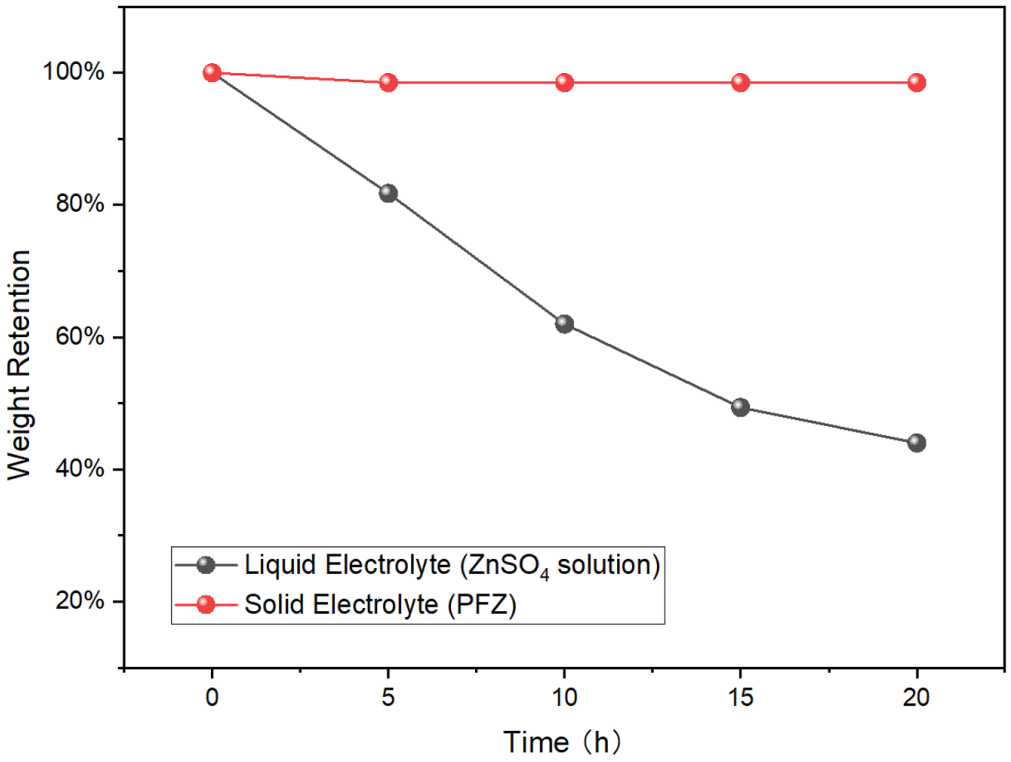

Figure S12. The weight retention of aqueous $ZnSO_4$ solution electrolyte and PFZ electrolyte in the air atmosphere at 50 °C.

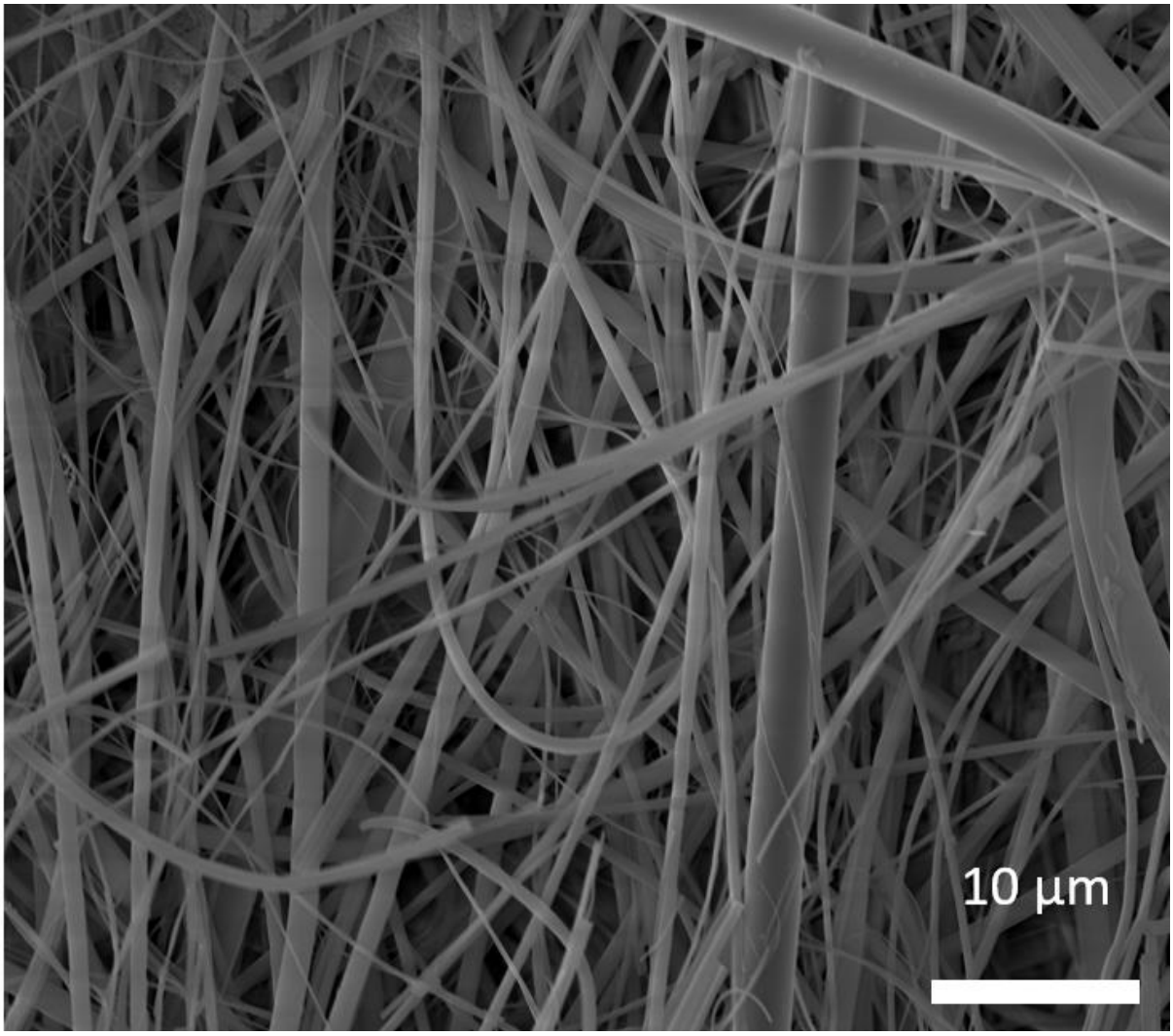

Figure S13. SEM image of glass fiber (GF).

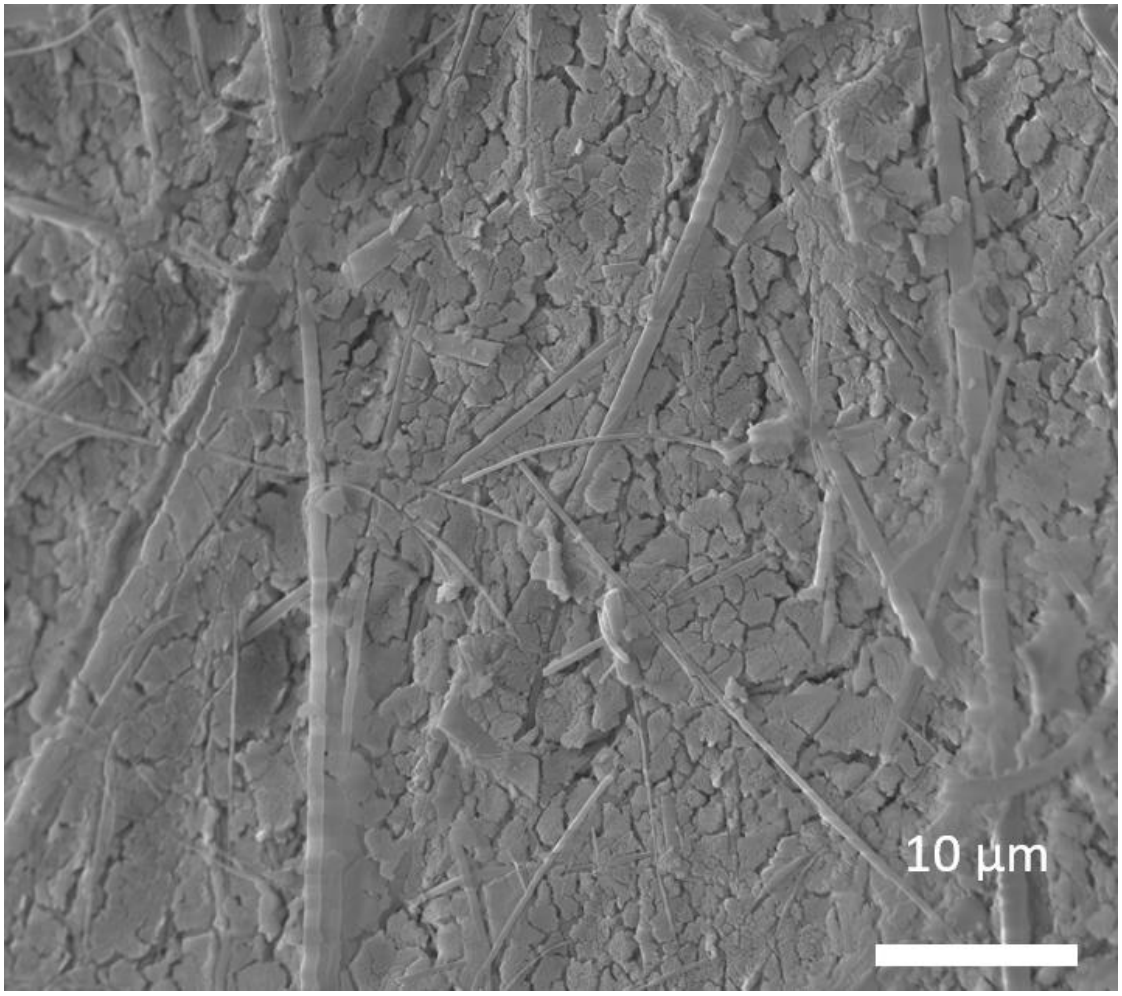

Figure S14. SEM image of GF after absorbing PFZ and cycling 100 cycles.

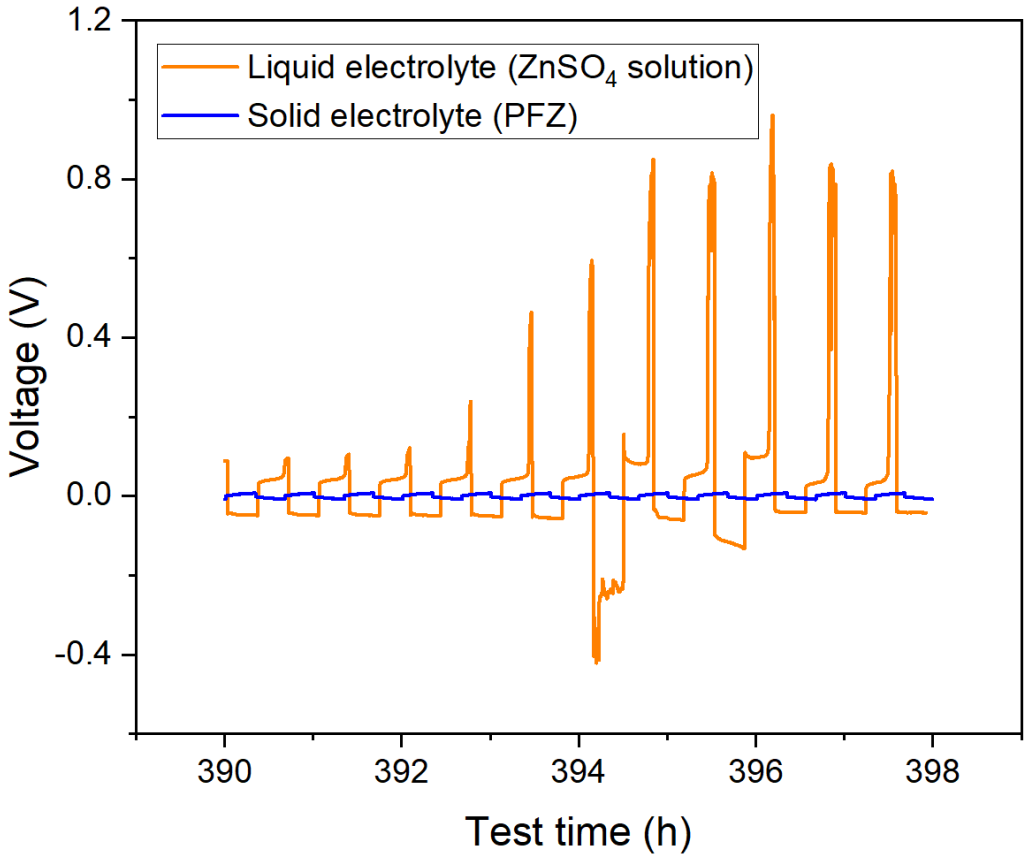

Figure S15. Detail of the galvanostatic Zn plating and stripping in Zn//$ZnSO_4$//Zn and Zn//PFZ//Zn symmetrical batteries at current densities of 0.2 mA cm^{-2} during the 390th hour to 398th hour.

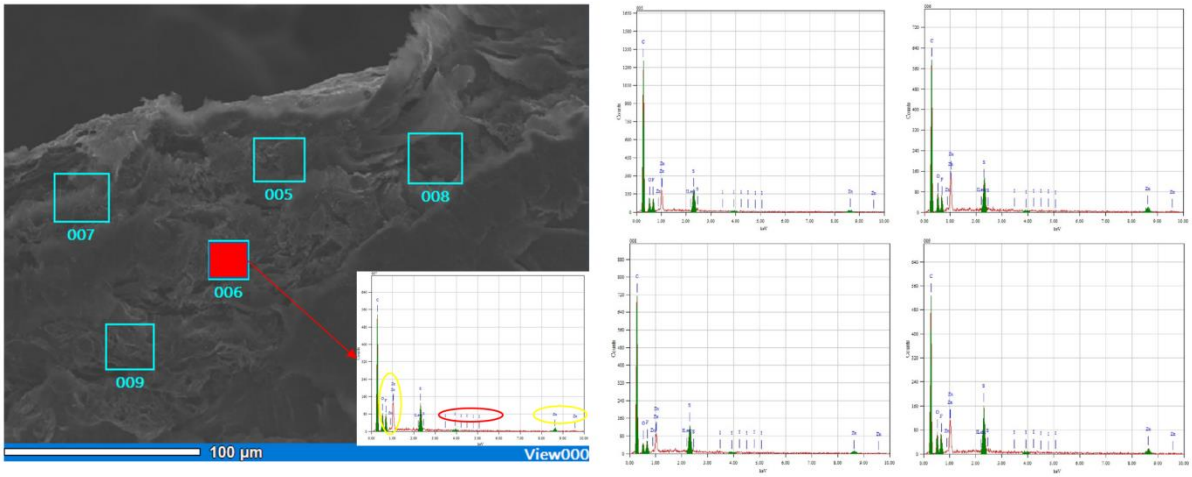

Figure S16. SEM image of the cross-section of CMK-N@I_2 cathode and its elemental analysis.

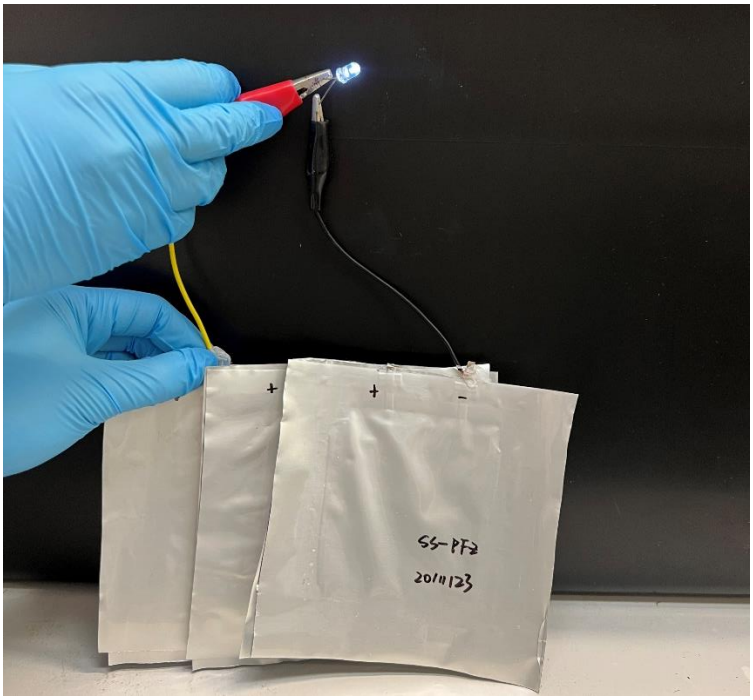

Figure S17. Photograph for 3 in-series connected soft-packed pouch cell to light up an LED.

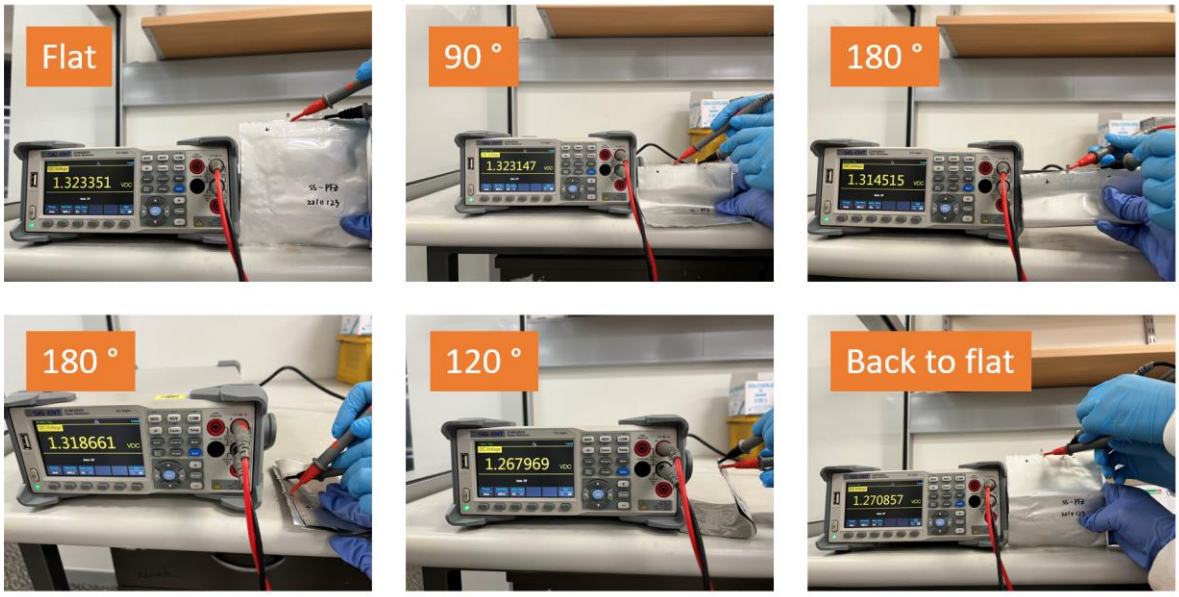

Figure S18. Photograph for the open-circuit voltage of a soft-packed pouch cell in different folding angles.

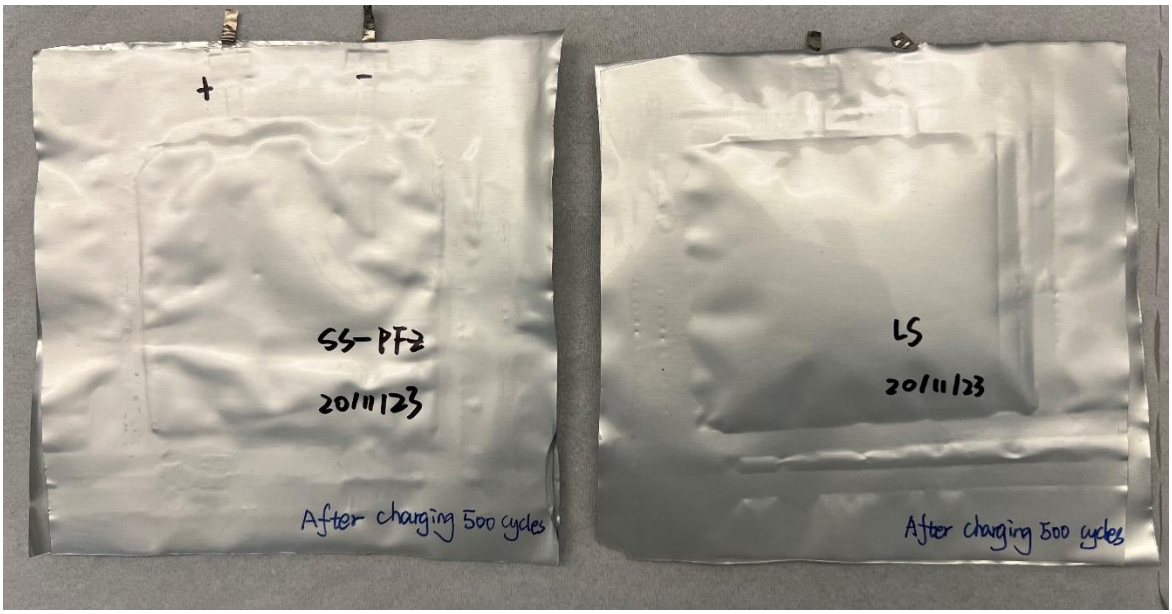

Figure S19. Optical image of pouch cell after 500 cycling states to demonstrate the hydrogen-free property using PFZ (left). The right image is the liquid electrolyte performance.

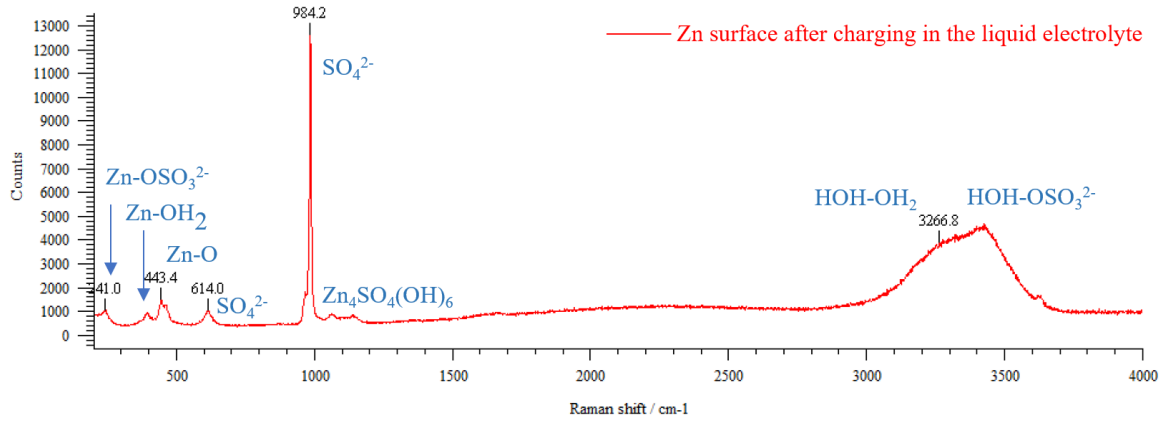

Figure S20. Raman spectroscopy of Zn anode cycled in 2 M $ZnSO_4$ aqueous solution.

Table S1. Estimated molar ratio of EO/Zn^{2+} in PFZ.

$N_{,EO}$	DP*	m_{PF} (mg)	n_{PF} (mmol)	n_{EO} (mmol)	n_{Zn2+} (mmol)	Molar ratio EO/Zn^{2+}
8.5	10.0	30	0.0043	0.36	2	2/11

*DP: degree of polymerization

Table S2. Detailed structural characteristics of the polymer PF.

	Conversion (%)	**Fluorine content (wt %)**[a]	$M_{n,\,NMR}$ **(g/mol)**[b]
PF	89.0	19.2	7000

[a]The weight percentage of fluorine in the samples. [b]The $M_{n,\,NMR}$ for the polymers was calculated by considering the integrals of the peaks due to protons H3 (2H) and the protons H1 (3H) as shown in Figure S1a.

Table S3. Changes in I_3^- *concentration* of solutions in the H-shape right tanks *over* time using different separators (Glass Fiber separator and PFZ).

Glass Fiber	**Stay time**	**0 min**	**1 min**	**10 mins**	**30 mins**	**60 mins**	**120 mins**
	Concentration (mol/L)	1.98 x 10^{-4}	0.27	0.31	0.42	0.55	0.56
PFZ	**Stay time**	**0 min**	**1 min**	**60 min**	**12 hours**	**24 hours**	**36 hours**
	Concentration (mol/L)	1.98 x 10^{-4}	6.82 x 10^{-4}	2.43 x 10^{-3}	3.08 x 10^{-3}	3.24 x 10^{-3}	3.45 x 10^{-3}

Reference

[1] M. Tou, R. Michalsky, *Joule* **2017**, *1*.

[2] M.E. Turano, R.G. Farber, E.C.N. Oskorep, R.A. Rosenberg, D.R. Killelea, *J. Phys. Chem. C* **2020** *124*, 1382.

[3] N. Ktari, S. Nunige, A. Azioune, M. Piel, C. Connan, F. Kanoufi, C. Combellas, Managing, *Chem. Mater.* **2010,** *22*, 5725.