

Electronic Supplementary Material (ESI) for ChemComm.

## **A liquid-infiltrated Al<sub>2</sub>O<sub>3</sub> framework electrolyte enables aqueous zinc batteries**

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## Experimental Section

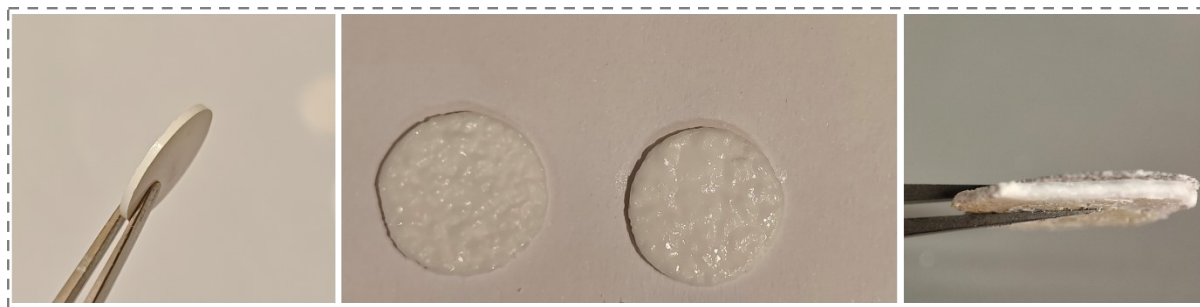
### Methods

**Materials synthesis.** The MnO<sub>2</sub>/carbon nanotube (CNT) was synthesized by following steps. First, 0.1 g carbon nanotubes were added to 60 mL of deionized water for ultrasonic dispersion for 15 minutes. Next, 0.486 g KMnO<sub>4</sub> was added and stirred for 30 min to prepare solution A. Then, 1.135 g Mn(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O was dissolved in 20 mL DI-water, and stirred for 15 min to make solution B. And then, solution B was added to the solution A, and stirred for 10 min to make solution C. After 60 min of ultrasound, the solution C was poured into a high-pressure reaction kettle lined with Teflon and kept at 120 °C for 12 hours. Finally, the product was removed and cleaned with deionized water three times, then freeze-dried for 72 hours.

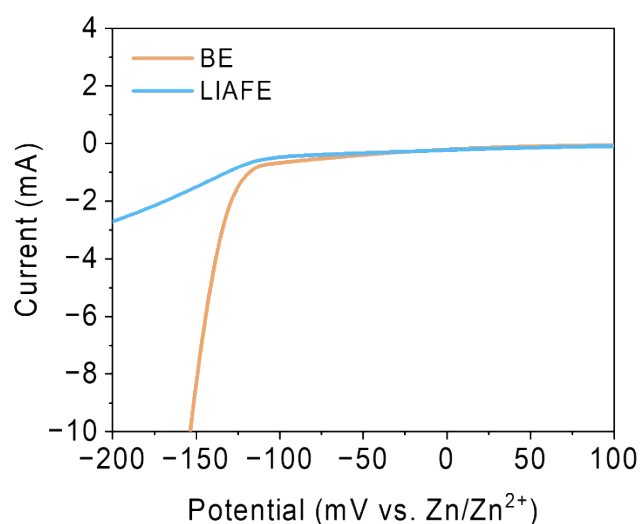
**Material characterization.** XRD measurements were performed on Anton Paar XRDynamic 500 diffractometers equipped with a Cu multilayer monochromator using Co-K $\alpha$  radiation ( $\lambda = 1.7902 \text{ \AA}$ ). On the diffracted beam side, the instrument was equipped with a Pixos 2000 (Si) detector. Diffraction patterns covering the range of  $2\theta$  from 5° to 80° were collected with a step size of 0.02°, using the  $\omega/2\theta$  reflection geometry. Scanning electron microscopy (SEM) images of Zn foils were conducted on a Zeiss microscope at an electron accelerating voltage of 10 kV with the images presented here made using the in lens detectors. Energy dispersive spectroscopy (EDS) (Oxford instrument) was performed on the same instrument.

**Electrochemical measurement.** Symmetric cells and asymmetric Zn/Cu cells with 2 M ZnSO<sub>4</sub> or LIAFE were assembled for cycling tests at various current densities. Cathodes were prepared by mixing MnO<sub>2</sub>/CNT, super P (TIMCAL), and PVDF (Arkema, HSV 900) in a mass ratio of 7:2:1. After adding NMP and stirring for 12 hours, coated on stainless steel mesh with active materials loading of 0.8-1 mg<sub>MnO<sub>2</sub></sub> cm<sup>-2</sup>. The cathodes were dried at 80 °C overnight in a vacuum oven and punched into dishes. The SP cathodes is prepared by mixing Super P and PVDF. Zinc foils with a thickness of 100  $\mu\text{m}$  were pressed into small pieces with a diameter of 12 cm to be used as anodes. Glassfiber (GF/D) were employed as separators. And the electrolytes for the cells with low mass loading contained 0.1 M MnSO<sub>4</sub>. The charge/discharge profiles of cells were tested on battery testing instruments (Land, China) at various current densities in the voltage ranges of 0.8-2.0 V. Both cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were carried out on Gamry electrochemical stations. CV profiles were collected at a scanning rate of 1 mV s<sup>-1</sup> under the voltage ranges of 0.8-1.8 V or 0.8-2.0 V. EIS was recorded at a frequency of 0.01 Hz-100 kHz.

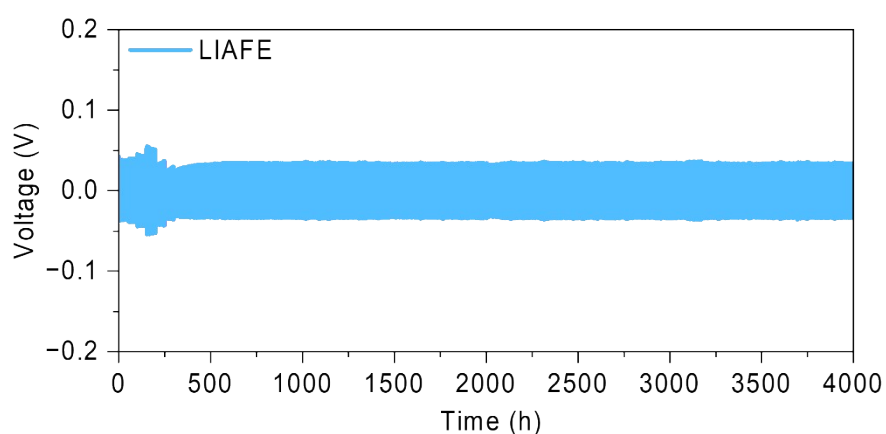
## Supplementary Figures



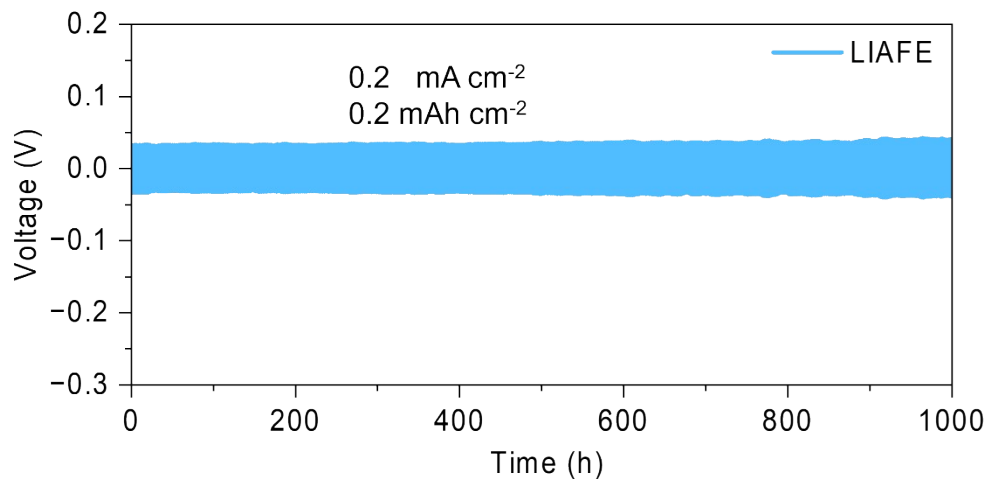
**Figure S1** After the basis electrolyte is applied to the surface of the tablet infiltrated for ten minutes, the basis electrolyte fully infiltrates the voids, forming the LIAFE.



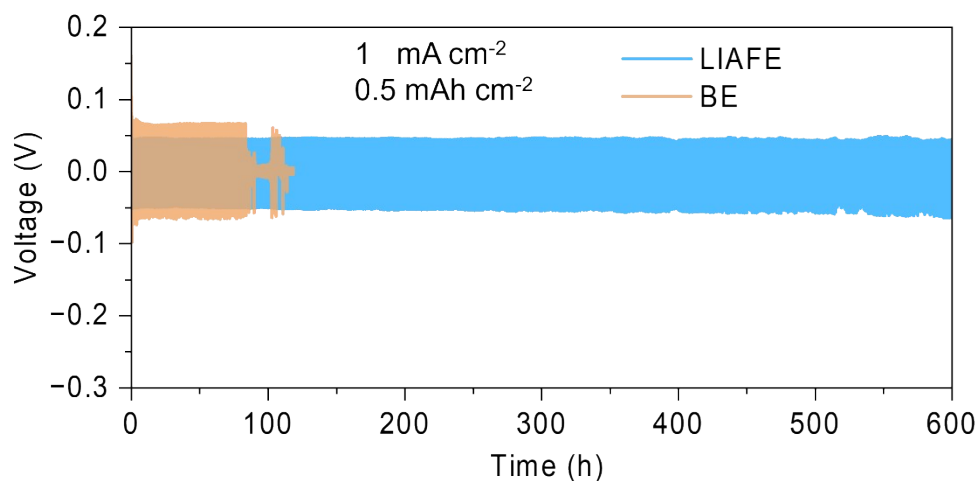
**Figure S2** The LSV profiles of Zn/Ti cells using BE and LIAFE as electrolytes.



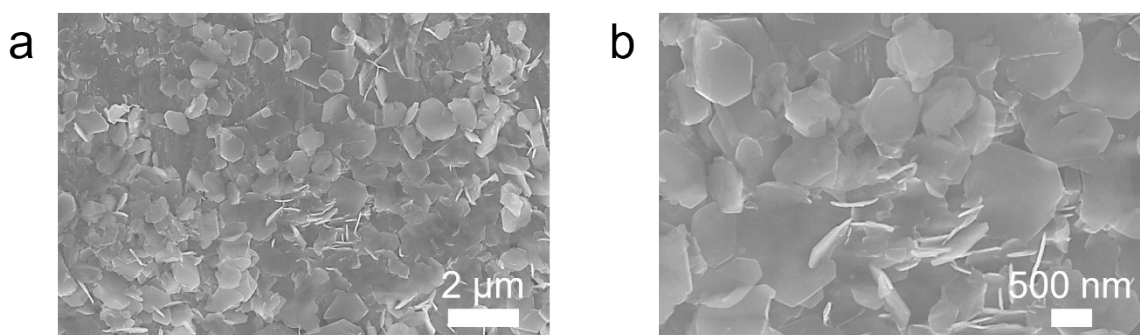
**Figure S3** Electrochemical performance of symmetric Zn/Zn cells with LIAFE. Rate performance at current density from 0.1 to 1 mA cm<sup>-2</sup> and the long-term cycling performances at 0.1 mA cm<sup>-2</sup>.



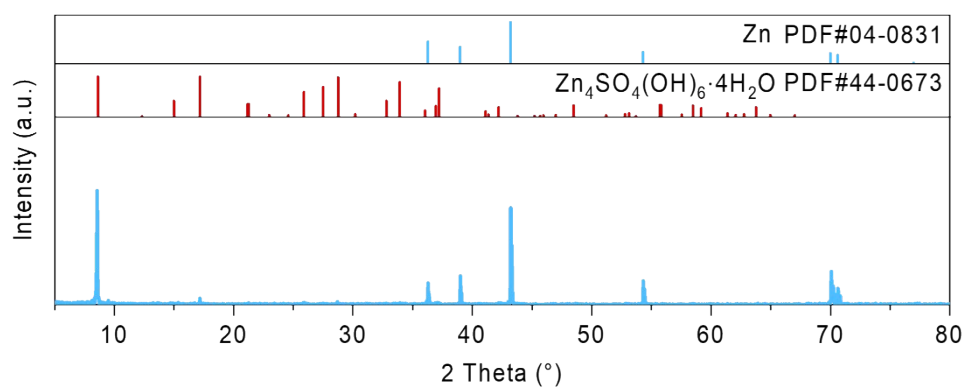
**Figure S4** Cycling performance of Zn/Zn cells with LIAFE at  $0.2 \text{ mA cm}^{-2}$ ,  $0.2 \text{ mAh cm}^{-2}$ .



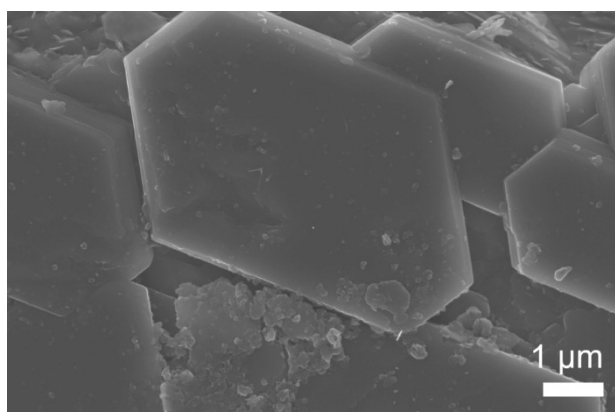
**Figure S5** Comparison of cycling performance of Zn/Zn cells with BE and LIAFE at  $1 \text{ mA cm}^{-2}$ ,  $0.5 \text{ mAh cm}^{-2}$ .



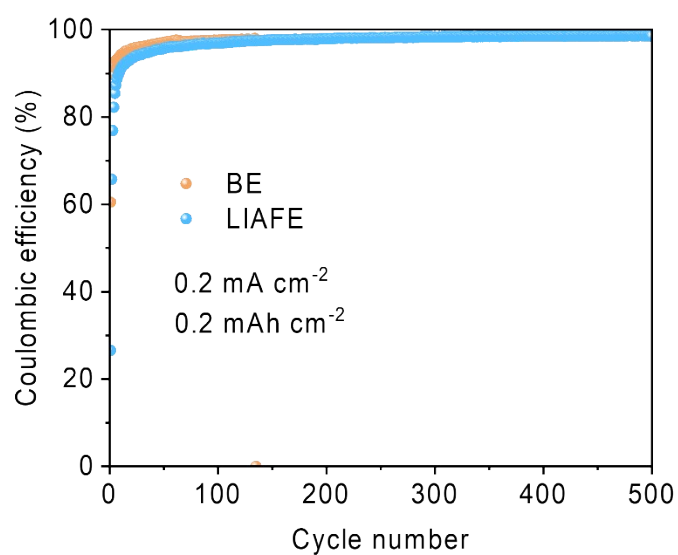
**Figure S6** (a) The SEM image of the zinc anode obtained from the cell using BE after cycling 100 hours at  $0.2 \text{ mA cm}^{-2}$ ; (b) with higher magnification.



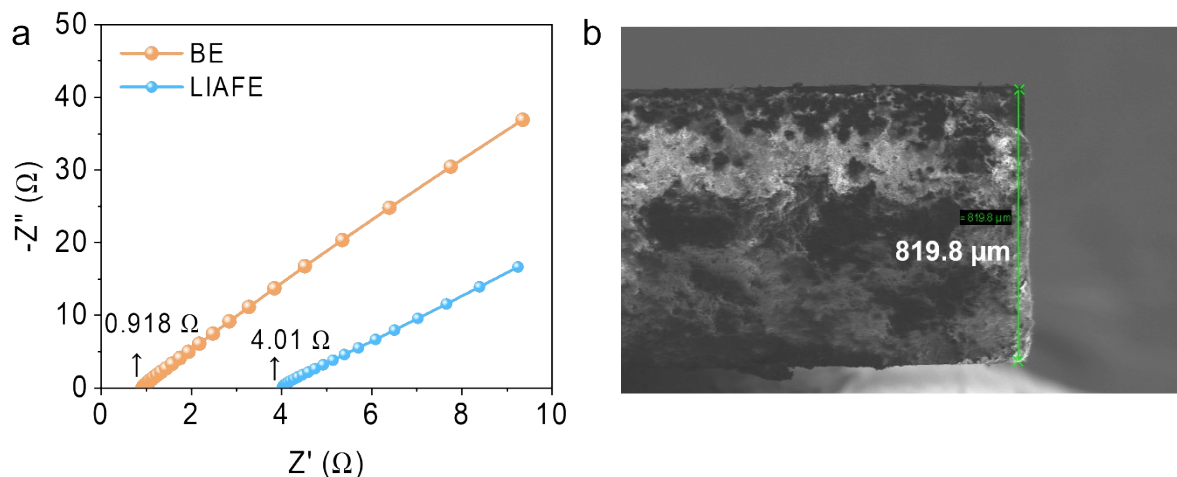
**Figure S7** The XRD patterns of Zn,  $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot 4\text{H}_2\text{O}$ , and the cycled zinc anode with BE.



**Figure S8** Larger magnification SEM images of zinc anodes obtained from the Zn/Zn cell with LIAFE after 2500 hours cycle.



**Figure S9** Comparison of the coulombic efficiency of Zn/Cu cells with BE and LIAFE at a current density of  $0.2 \text{ mA cm}^{-2}$  with a fixed capacity of  $0.2 \text{ mAh cm}^{-2}$  at a cut-off voltage of  $0.5 \text{ V}$ .



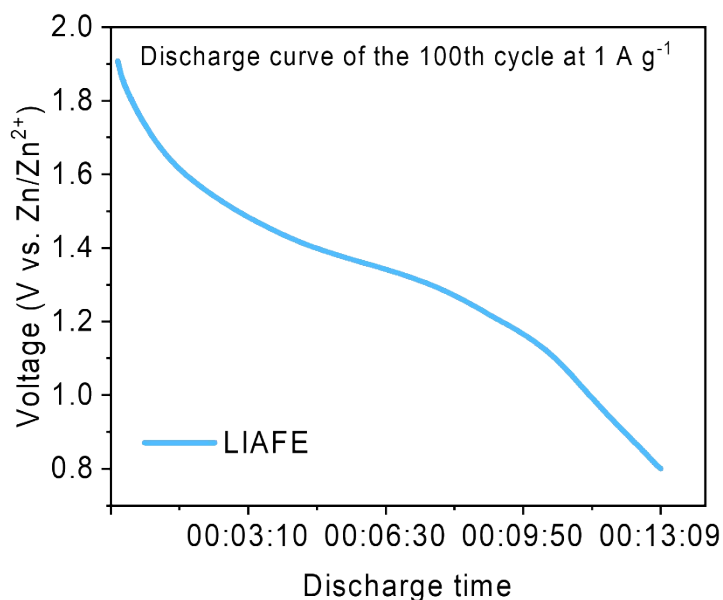
**Figure S10** (a) The ohmic resistance measured by conducting EIS on stainless-steel symmetric battery with BE and LIAFE; (b) the cross-section SEM image of the solid tablet.

The calculation process of ionic conductivity is as follows,

$$\text{For BE electrolytes, } \sigma = \frac{l}{RA} = \frac{0.07}{0.918 \times 3.14 \times 0.775 \times 0.775} = 40 \text{ mS/cm}$$

$$\text{For LIAFE electrolytes, } \sigma = \frac{l}{RA} = \frac{0.082}{4.01 \times 3.14 \times 0.775 \times 0.775} = 11 \text{ mS/cm}$$

Where, R is ohmic resistance, A is the area of stainless-steel spacer. L is the distance between two electrodes, with 0.07 cm for the BE separator and 0.082 cm for the LIAFE solid tablets.



**Figure S11** The 100<sup>th</sup> cycle curve of discharge time for the full cell using LIAFE at 1 A g<sup>-1</sup>.

**Table S1** Comparison of electrochemical performance of this work with published works.

Work	Ionic conductivity (mS cm <sup>-1</sup> )	Impedance ( $\Omega$ )	Specific Capacity (mAh g <sup>-1</sup> )	Coulombic efficiency (%)	300 cycles retention (%)	Ref
LIAFE	11	98	219.4	99.6	99	This work
PPCu1C-ZMIL5	24.3	850	124.6	99	85	Ref.1
PVA@SR gel	14.2	300	141.7	99.4	97	Ref.2
Janus separator	23.9	80	197	99.6	~96	Ref.3
lean-water hydrogel	2.6	/	92	99.8	~94	Ref.4
GG/SA	25.4	39	140	/	~92	Ref.5
PEO composite	23	/	92	96	80.2	Ref.6
KCR electrolyte	33.2	50	120	/	~88	Ref.7
PAM-LDH	19.2	150	232.4	/	~90	Ref.8
CT3G30	32.3	250	230.1	99.9	99.2	Ref.9

## Reference

1. J. Hu, Y. Qu, F. Shi, J. Wang, X. He, S. Liao and L. Duan, *Adv. Funct. Mater.*, 2022, **32**, 2209463.
2. A. Chen, C. Zhao, J. Gao, Z. Guo, X. Lu, J. Zhang, Z. Liu, M. Wang, N. Liu, L. Fan, Y. Zhang and N. Zhang, *Energy Environ. Sci.*, 2023, **16**, 275-284.
3. X. Zhang, J. Li, K. Qi, Y. Yang, D. Liu, T. Wang, S. Liang, B. Lu, Y. Zhu and J. Zhou, *Adv. Mater.*, 2022, **34**, 2205175.
4. Y. Wang, Q. Li, H. Hong, S. Yang, R. Zhang, X. Wang, X. Jin, B. Xiong, S. Bai and C. Zhi, *Nat. Commun.*, 2023, **14**, 3890.
5. J. Wang, Y. Huang, B. Liu, Z. Li, J. Zhang, G. Yang, P. Hiralal, S. Jin and H. Zhou, *Energy Stor. Mater.*, 2021, **41**, 599-605.

6. D. Wang, X. Guo, Z. Chen, Y. Zhao, Q. Li and C. Zhi, *ACS Appl. Mater. Interfaces*, 2022, **14**, 27287-27293.
7. Y. Huang, J. Liu, J. Zhang, S. Jin, Y. Jiang, S. Zhang, Z. Li, C. Zhi, G. Du and H. Zhou, *RSC Adv.*, 2019, **9**, 16313-16319.
8. P. Dedetemo Kimilita, Y. Yoshimi and N. Sonoyama, *J. Electrochem. Soc.*, 2022, **169**, 080527.
9. M. Chen, J. Chen, W. Zhou, X. Han, Y. Yao and C.-P. Wong, *Adv. Mater.*, 2021, **33**, 2007559.