

## Supplementary Information for

### **Bilateral *in-situ* functionalization towards Ah-scale aqueous zinc metal batteries**

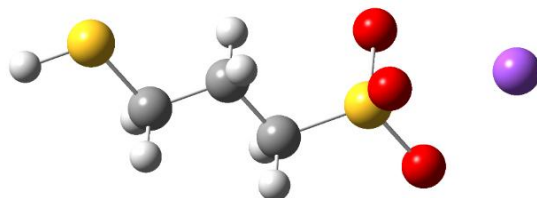
Yexin Song,<sup>1</sup> Manjing Chen,<sup>1</sup> Ziyang Zhong,<sup>1</sup> Zhexuan Liu,<sup>1\*</sup> Shuquan Liang,<sup>1</sup> Guozhao Fang<sup>1,2\*</sup>

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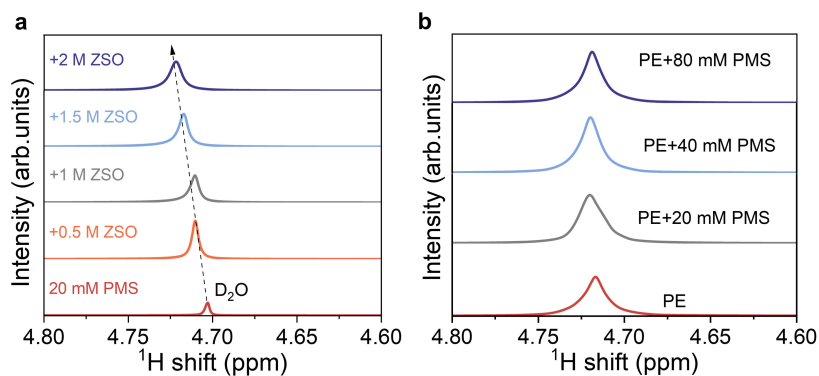
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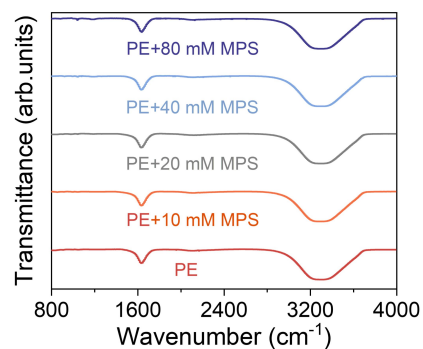
## Figures and Tables



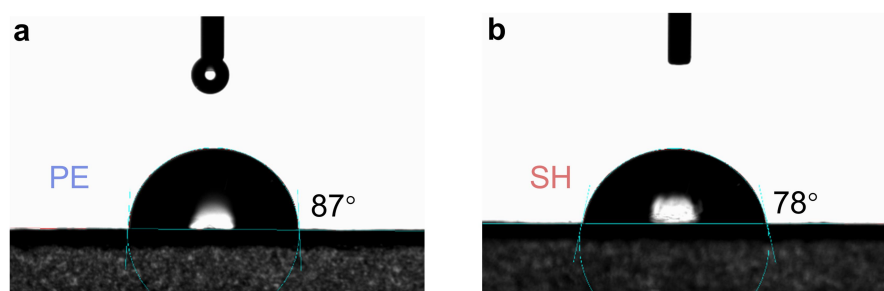
**Supplementary Fig. 1** The structure of PMS. (White means H; Yellow means S; Grey means C; Red means O; Purple means Na<sup>+</sup>)



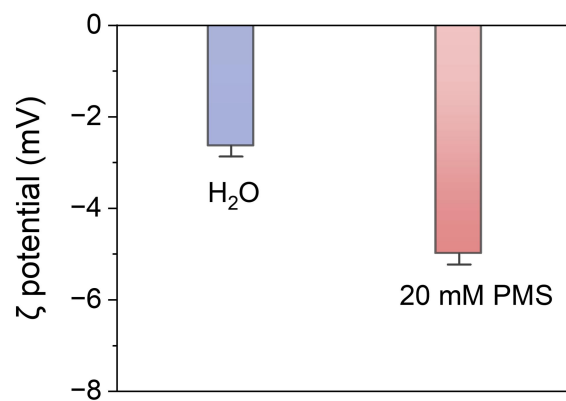
**Supplementary Fig. 2** The <sup>1</sup>H shift of D<sub>2</sub>O from 4.8 ppm to 4.6 ppm. (a) In the electrolytes with different ZnSO<sub>4</sub> salt concentrations and (b) in PE with different PMS concentration.



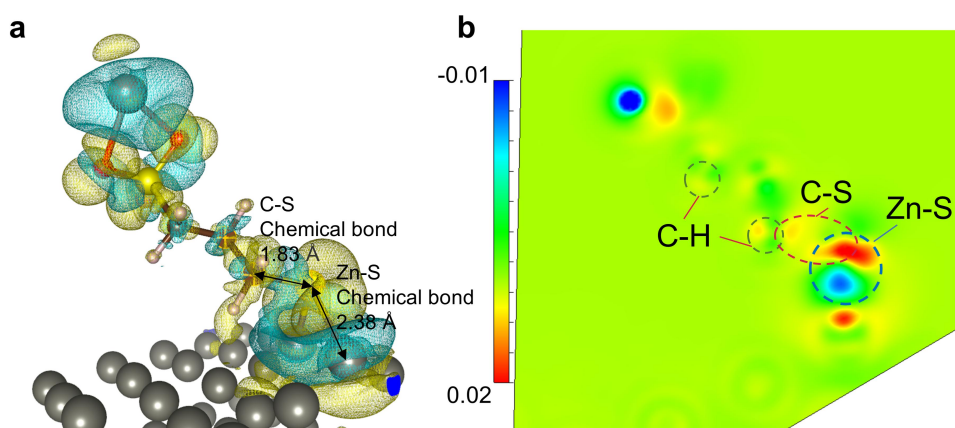
**Supplementary Fig. 3** The FTIR spectra of different PMS concentration in PE.



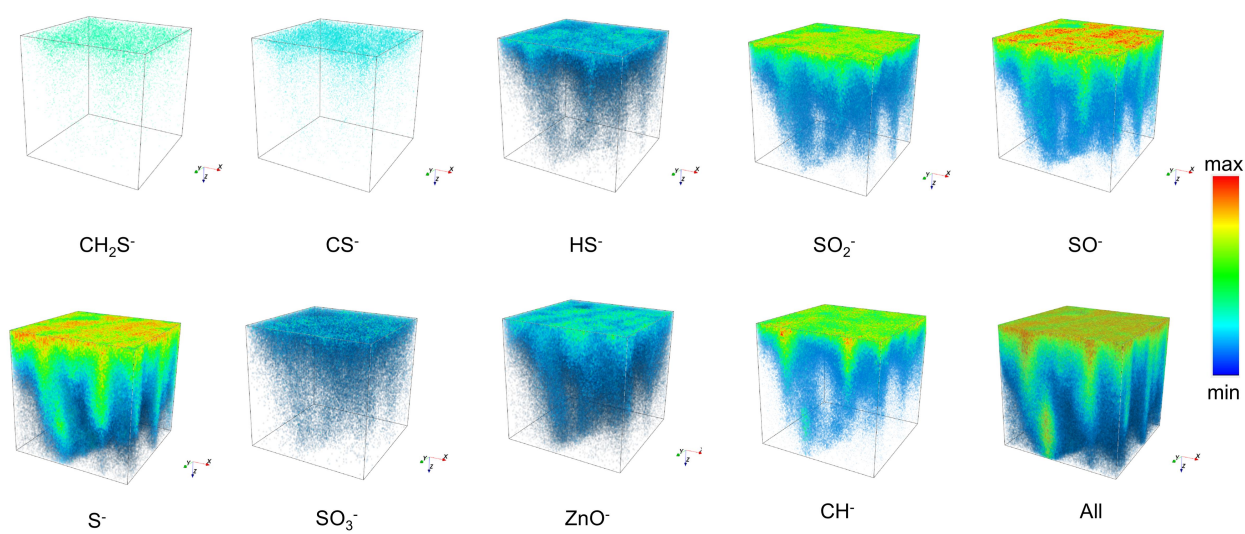
**Supplementary Fig. 4** Static contact angle measurements of Zn negative electrodes in (a) PE and (b) SH electrolytes.



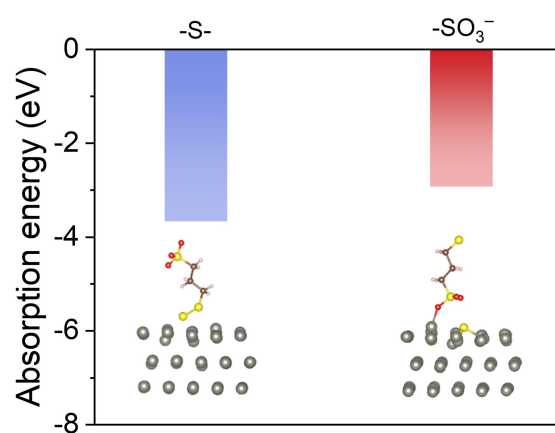
**Supplementary Fig. 5**  $\zeta$  potential of Zn powder in aqueous solution before and after the addition of PMS.



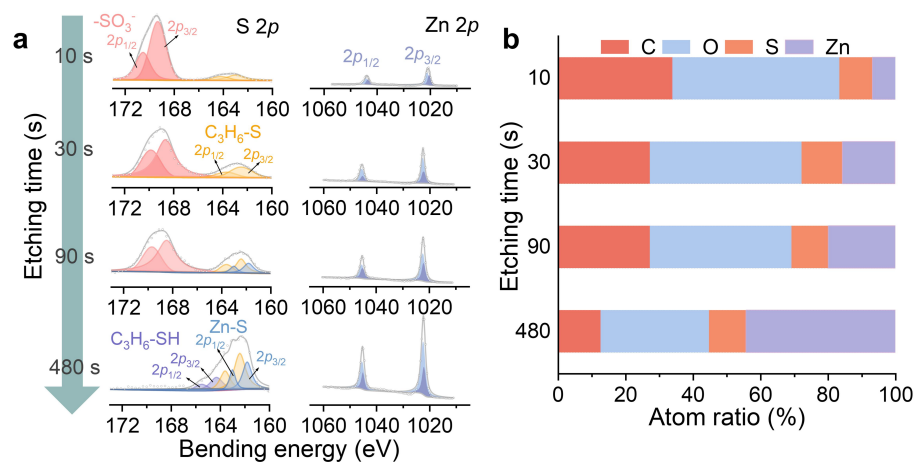
**Supplementary Fig. 6** (a) Charge density difference of adsorbed PMS molecule at the interface of Zn. (b) 2D plot of interfacial charge densities.



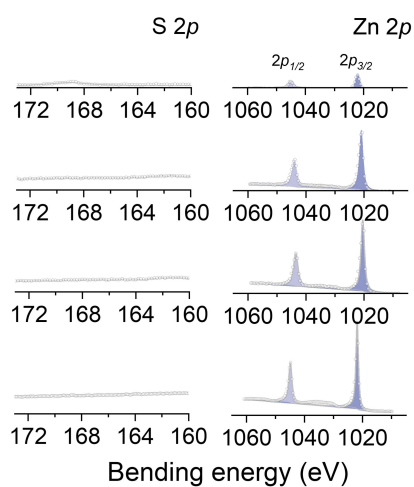
**Supplementary Fig. 7** Different species in Three-dimensional view of distributions for PMS on Zn negative electrode in the negative TOF-SIMS sputtered volumes.



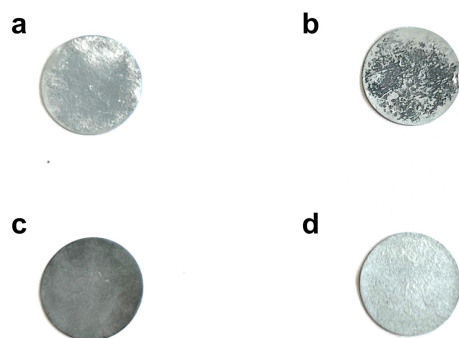
**Supplementary Fig. 8** Zn-S absorption with  $-\text{S}-$  and  $-\text{SO}_3^-$ .



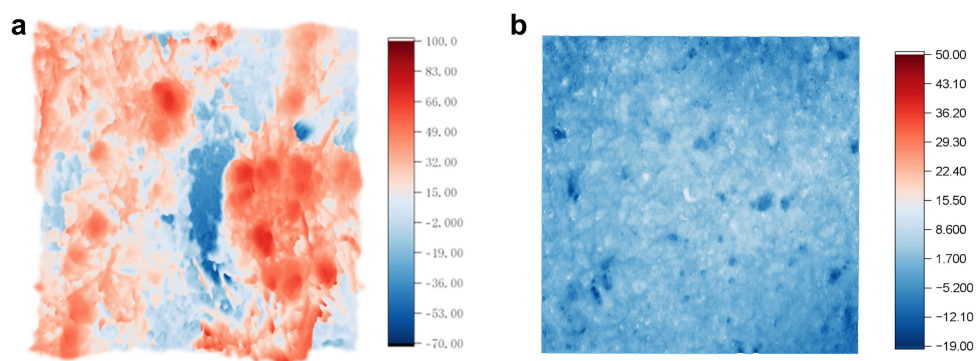
**Supplementary Fig. 9** (a) XPS depth profiles of Zn foil surface after soaking in PMS solution. (b) The corresponding atom ratios.



**Supplementary Fig. 10** XPS depth profiles of Zn foil surface after soaking in pure water.

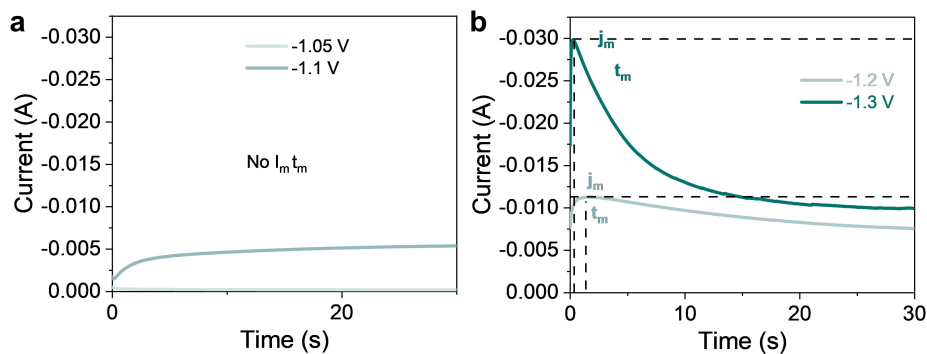


**Supplementary Fig. 11** Optical images of Zn negative electrodes (a) stripping side, (b) plating side in PE electrolyte and (c) stripping side, (d) plating side in SH electrolyte after plating at  $2 \text{ mA cm}^{-2}$  with a capacity of  $10 \text{ mAh cm}^{-2}$ .



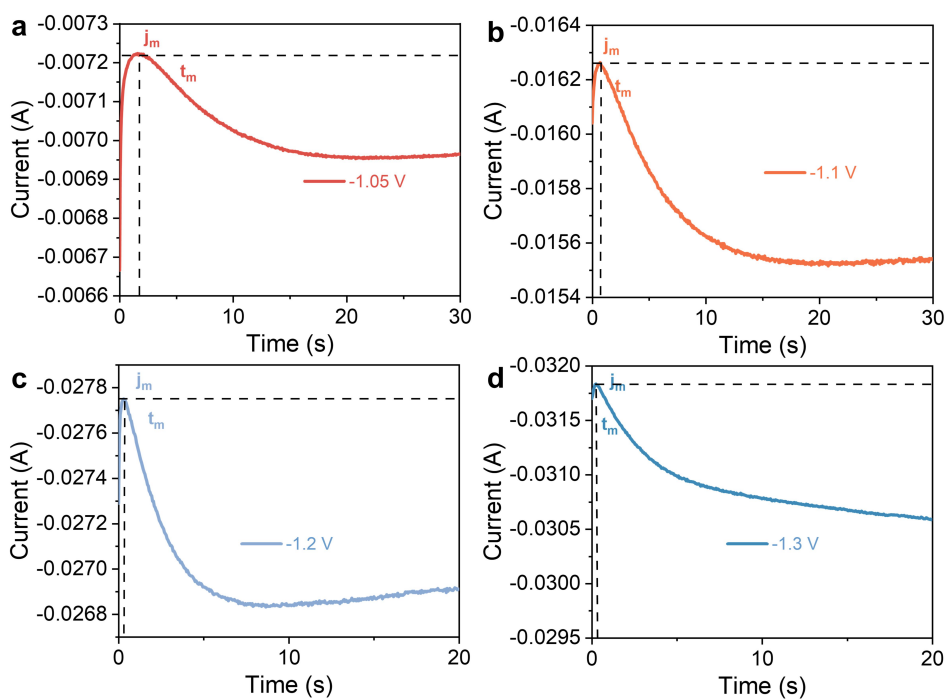
**Supplementary Fig. 12** Top-view LCSM images of a) bare Zn and b) Zn-SH electrodes after Zn deposition. Unit is  $\mu\text{m}$ .

(a) After the deposition of  $10 \text{ mAh cm}^{-2}$  Zn in the PE electrolyte, the surface appears rough with varying degrees of pits and protrusions. (b) In contrast, the surface of  $10 \text{ mAh cm}^{-2}$  Zn deposited in the SH electrolyte is relatively flat.

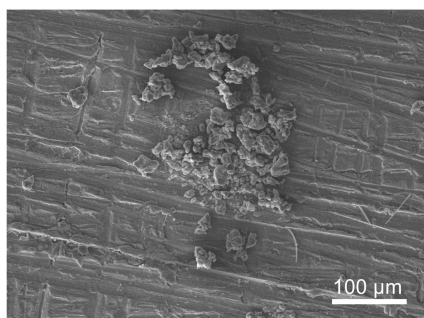


**Supplementary Fig. 13** Current-time transients obtained at a given potential in PE.

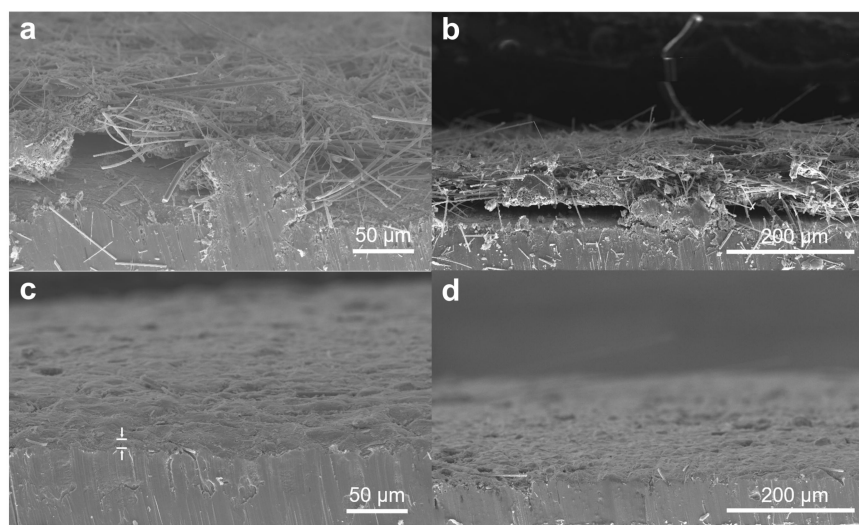
Notes: under the voltage of  $\leq -1.05$  V, no response current appears. Under the voltage of  $-1.1$  V, no obvious nucleation process appears even though there has a response current.



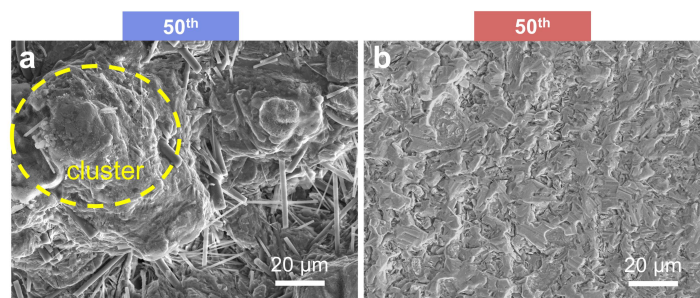
**Supplementary Fig. 14** Current-time transients obtained at a given potential in SH.



**Supplementary Fig. 15** SEM image of Zn negative electrode after  $0.1 \text{ mAh cm}^{-2}$  deposition in PE.



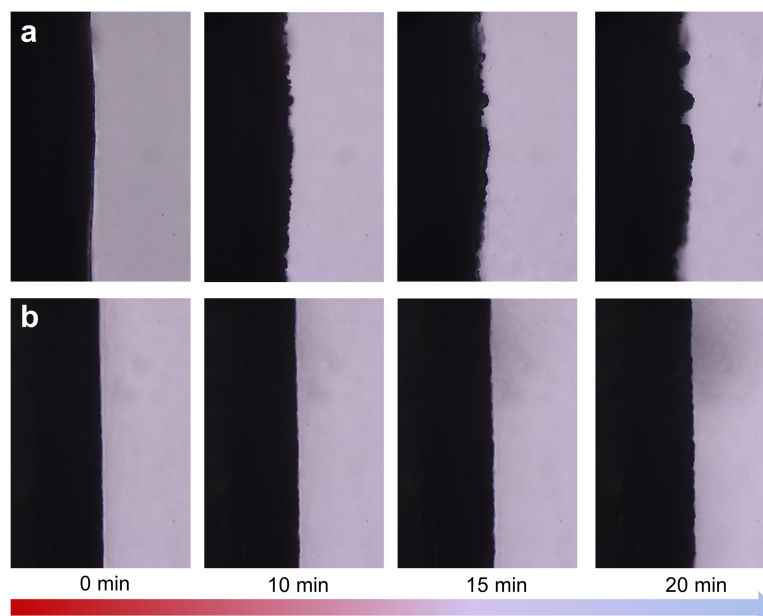
**Supplementary Fig. 16** Cross-sectional SEM images of (a, b) bare Zn and (c, d) Zn-SH electrodes after Zn deposition.



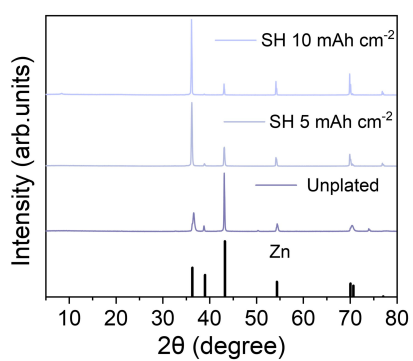
**Supplementary Fig. 17** SEM images of (a) bare Zn and (b) Zn-SH electrodes after 50 cycles.



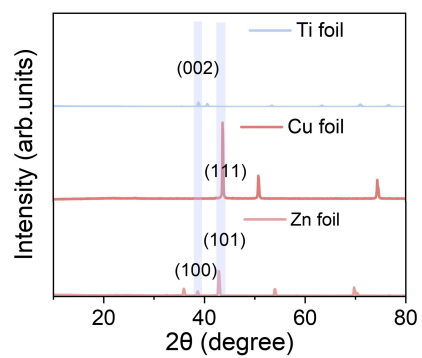
**Supplementary Fig. 18** The photographs of optical microscope.



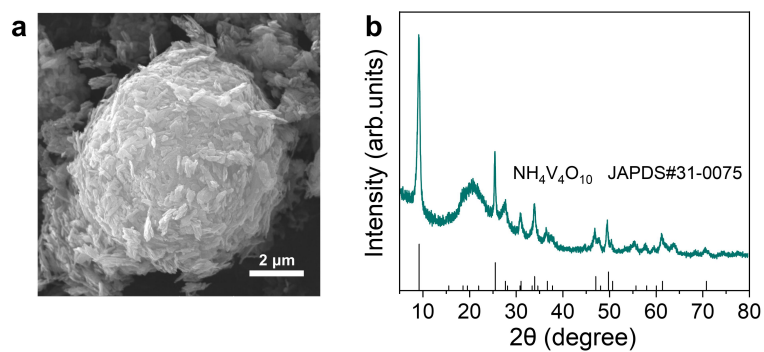
**Supplementary Fig. 19** *Operando* optical microscope images of the Zn plating process in (a)PE and (b) SH electrolyte at  $3 \text{ mA cm}^{-2}$ .



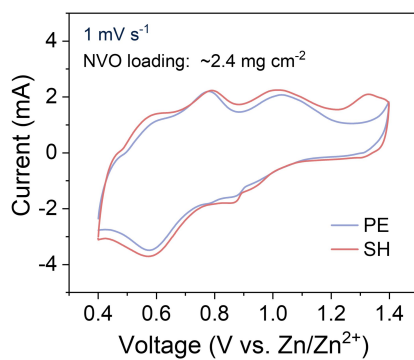
**Supplementary Fig. 20** XRD patterns of Zn negative electrodes in the unplated state and after 5 and  $10 \text{ mAh cm}^{-2}$  deposition in the SH electrolyte.



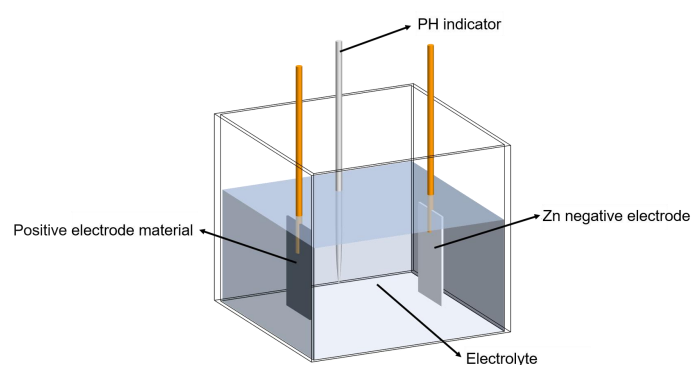
**Supplementary Fig. 21** XRD patterns of Ti foil, Cu foil and Zn foil.



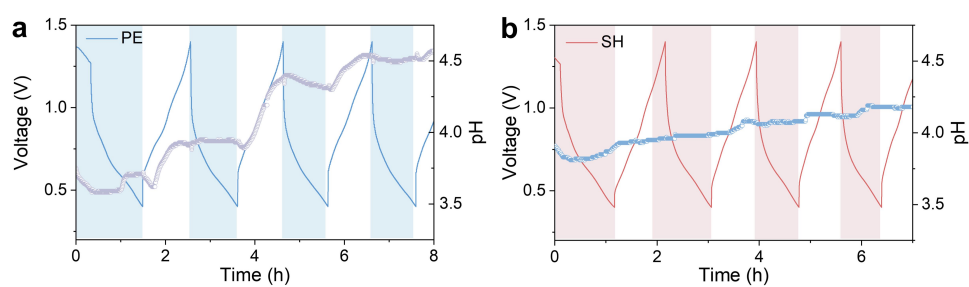
**Supplementary Fig. 22** (a) SEM image of the  $\text{NH}_4\text{V}_4\text{O}_{10}$  particle and (b) the XRD pattern of the  $\text{NH}_4\text{V}_4\text{O}_{10}$  positive electrode.



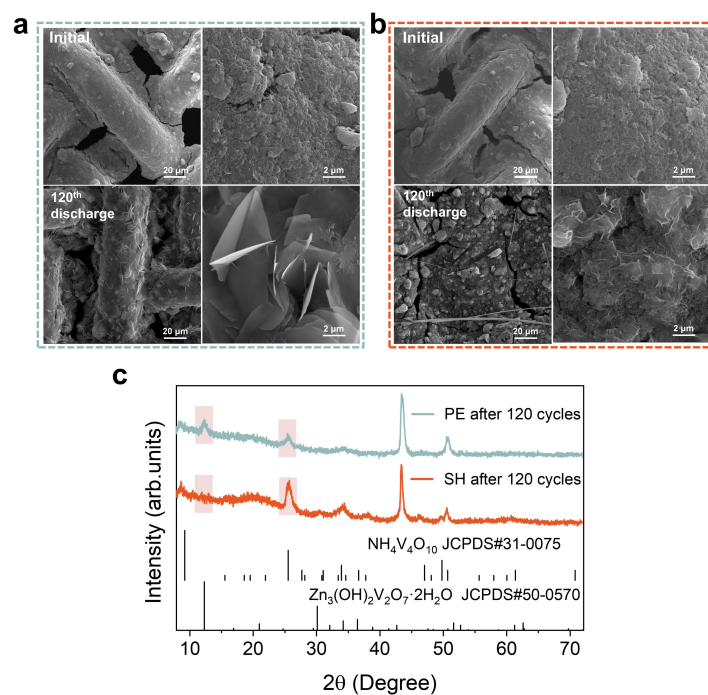
**Supplementary Fig. 23** CV curves of full cells at a scan rate of  $1\ \text{mV s}^{-1}$ .



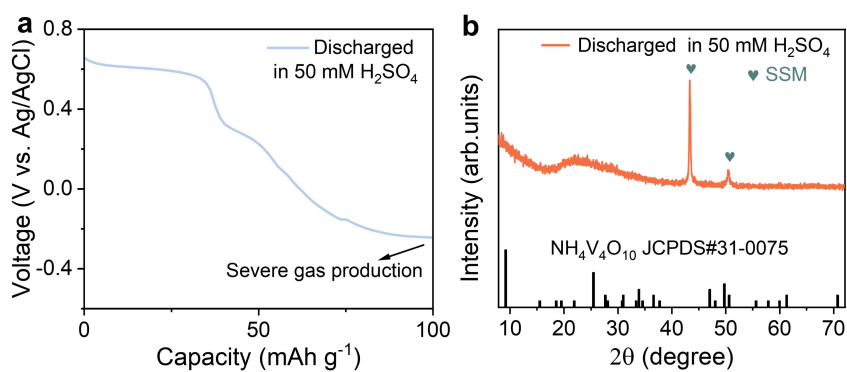
**Supplementary Fig. 24** Schematic diagram of *in-situ* pH measurement device.



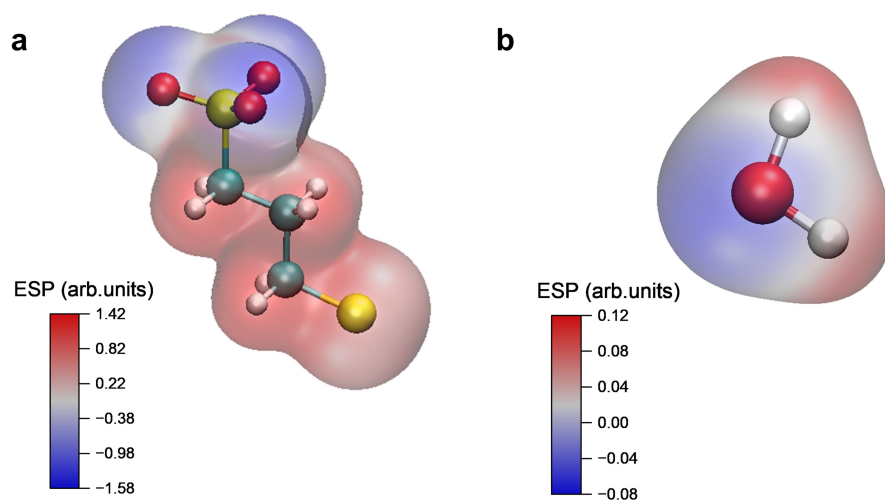
**Supplementary Fig. 25** *In-situ* pH results near positive electrode in (a) PE and (b) SH electrolyte at  $0.2 \text{ A g}^{-1}$ .



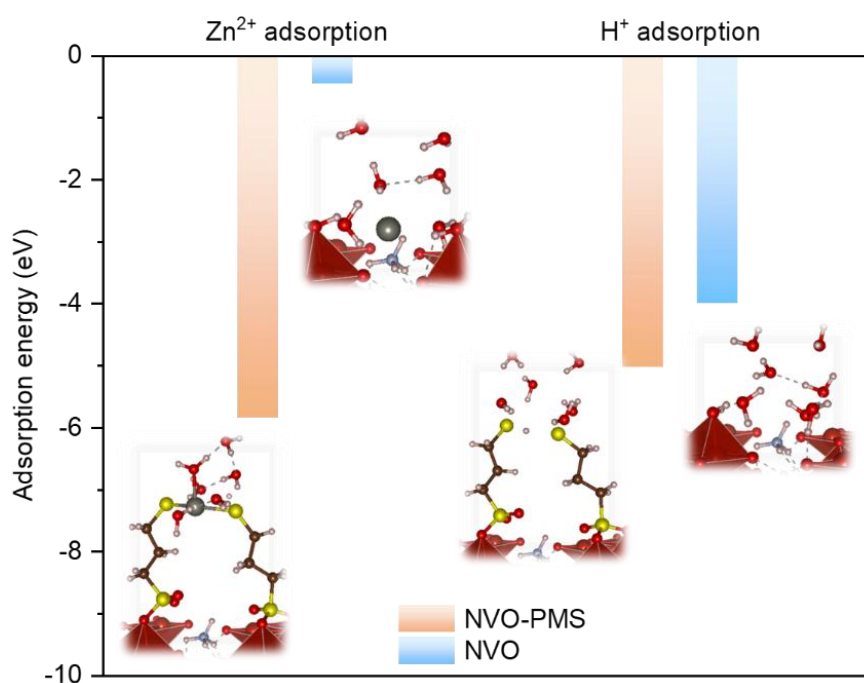
**Supplementary Fig. 26** Surface morphology of NVO initial and after 120 cycles in (a) PE and (b) SH electrolyte. (c) *Ex-situ* XRD patterns of NVO in PE and SH electrolyte after 120 cycles.



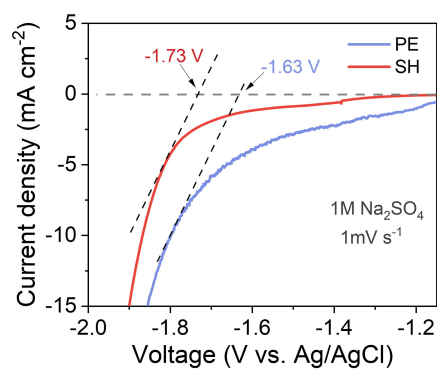
**Supplementary Fig. 27** (a) Discharge curve of NVO positive electrode in a three-electrode battery system with 50 mM H<sub>2</sub>SO<sub>4</sub> electrolyte. (b) XRD of NVO after discharge reaction.



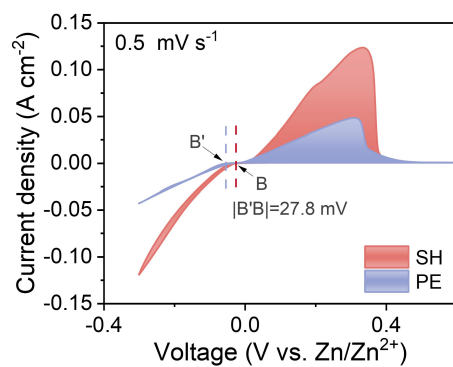
**Supplementary Fig. 28** The electrostatic potential differences between a) PMS molecules and b) water molecules.



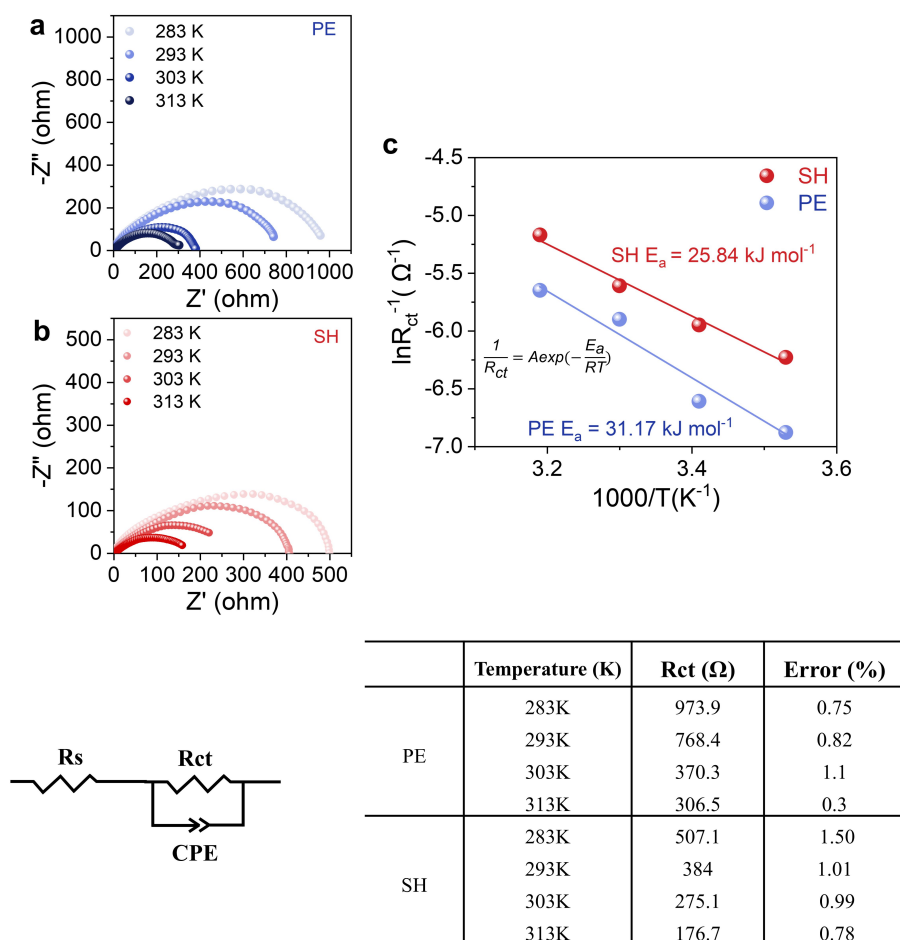
**Supplementary Fig. 29** Adsorption energy with  $\text{Zn}^{2+}$  or  $\text{H}^+$  of the NVO cathode interface with adsorbed PMS or  $\text{H}_2\text{O}$ .



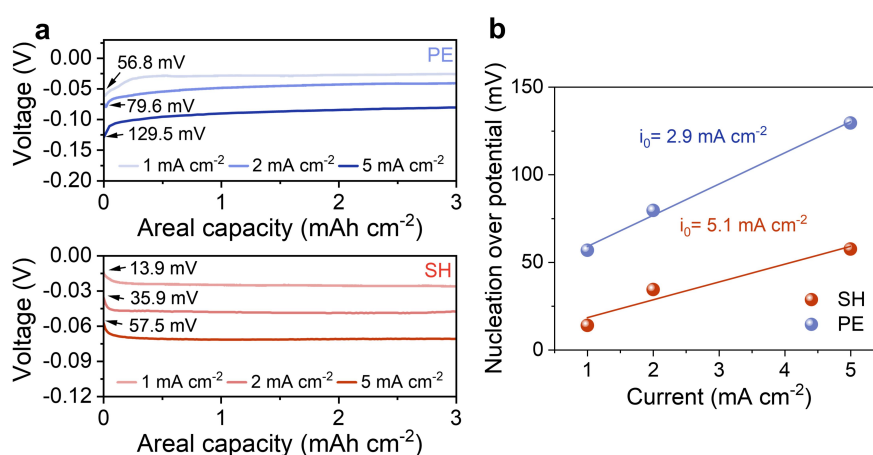
**Supplementary Fig. 30** LSV curves of the Zn negative electrodes in PE and SH.



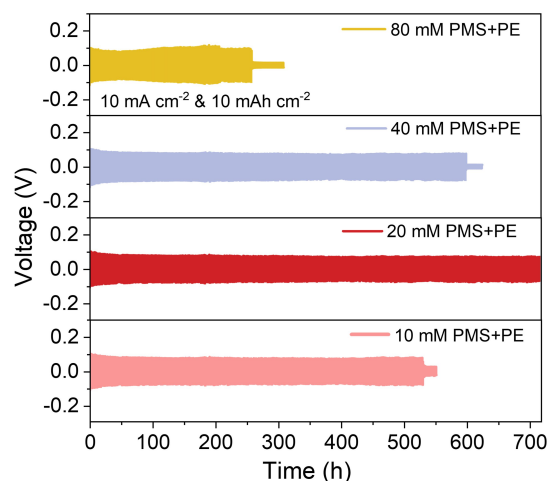
**Supplementary Fig. 31** CV curves of Zn||Cu half cells in PE and SH at  $0.5 \text{ mV s}^{-1}$ .



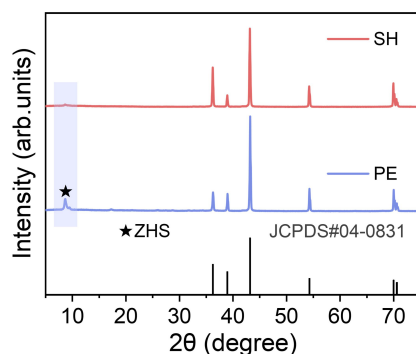
**Supplementary Fig. 32** Nyquist plots of Zn||Zn symmetric cells at different temperatures in (a) PE and (b) SH. (c) Corresponding Arrhenius curves and comparison of activation energies.



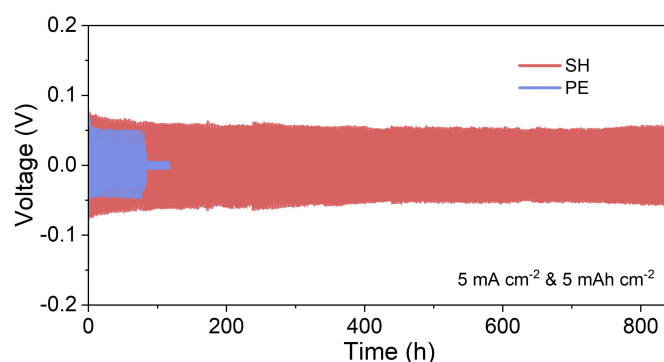
**Supplementary Fig. 33** (a) Galvanostatic nucleation overpotential of Zn negative electrode in the SH and PE electrolyte. (b) The calculated exchange current density.



**Supplementary Fig. 34** Cycle performance of Zn||Zn symmetric cells with different PMS concentration in PE.

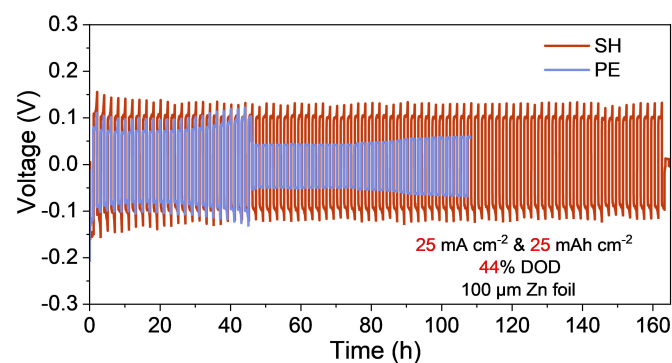


**Supplementary Fig. 35** XRD patterns of the Zn negative electrode after 50 cycles in SH and PE at  $10 \text{ mA cm}^{-2}$  and  $10 \text{ mAh cm}^{-2}$ .

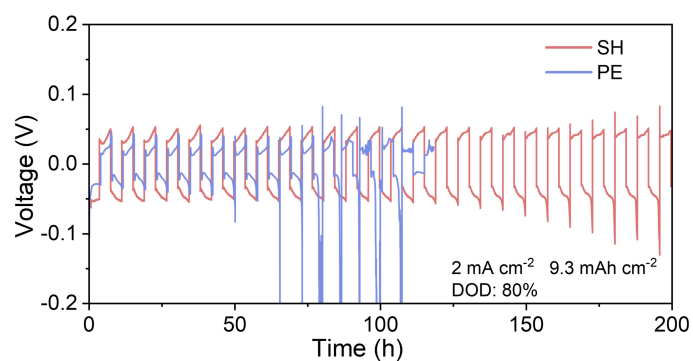


**Supplementary Fig. 36** Galvanostatic Zn plating/stripping process in PE and SH electrolyte at a current density of  $5 \text{ mA cm}^{-2}$  with a capacity of  $5 \text{ mAh cm}^{-2}$ .

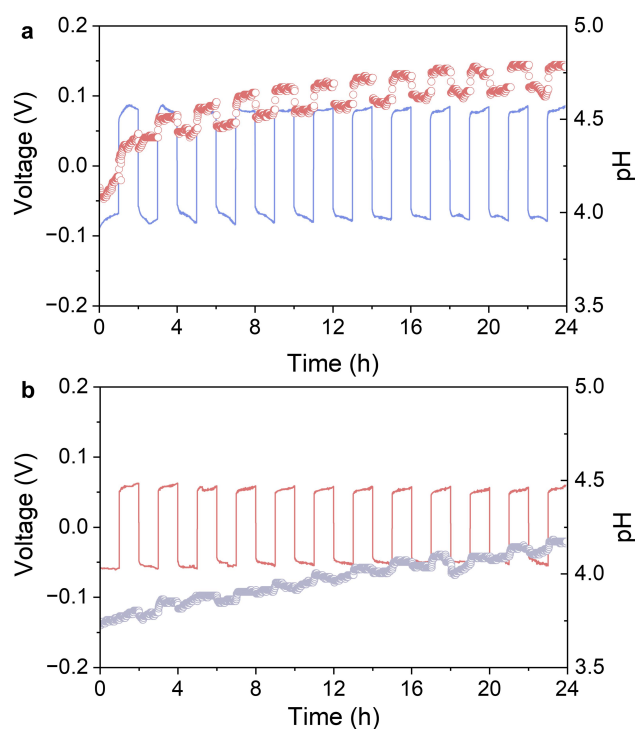
The two symmetric Zn||Zn cells exhibit a similar voltage hysteresis at the current density of  $5 \text{ mA cm}^{-2}$  and areal capacity of  $5 \text{ mAh cm}^{-2}$ . After just 94 h cycling in PE, a sudden decrease in polarization voltage was observed in the symmetric cell, which is ascribed to the emergence of a short circuit, potentially resulting from uncontrolled growth of dendrites. In contrast, the symmetric cell in the SH electrolyte shows a prolonged lifespan over 810 h and its accumulated plated capacities can reach  $2.1 \text{ Ah cm}^{-2}$ . ( $5 \text{ mA cm}^{-2} \times 845 \text{ h}/2$ )



**Supplementary Fig. 37** Cycle performance of Zn||Zn symmetric cells with a high Zn utilization rate of 44% DOD<sub>Zn</sub>.

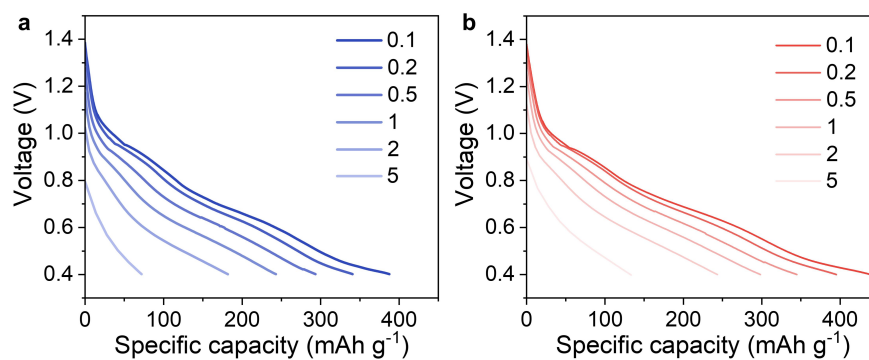


**Supplementary Fig. 38** Cycle performance of Zn//Zn symmetric cells with a higher Zn utilization rate of 80% DOD<sub>Zn</sub>. The Zn foil was used in a thickness of 20  $\mu\text{m}$ , corresponding to a theoretical capacity of 11.63 mAh cm<sup>-2</sup>.

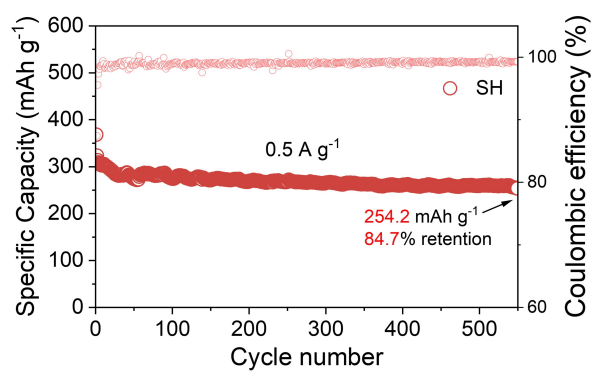


**Supplementary Fig. 39** *In-situ* pH results near first discharge side of Zn||Zn symmetrical cells in (a) PE and (b) SH electrolyte.

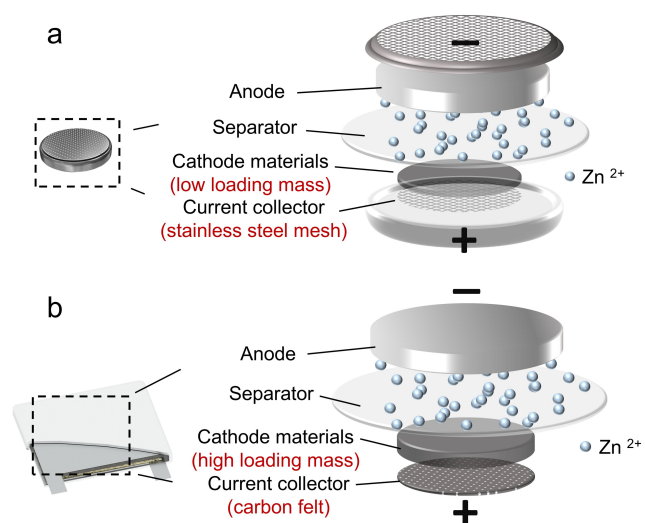
In the PE electrolyte, the exposure of the Zn negative electrode surface leads to the generation of hydrogen gas due to a concurrent proton-related electron reaction during Zn deposition ( $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ ). This phenomenon was visually evident through the significant pH transitions observed during the charging and discharging phases, further corroborating that the stepwise nature of pH changes is attributed to the side reactions involving protons at the Zn negative electrode surface. However, in the SH electrolyte, this stepwise pH fluctuation was markedly suppressed, exhibiting a more pronounced buffering effect and demonstrating its advantage in pH stability.



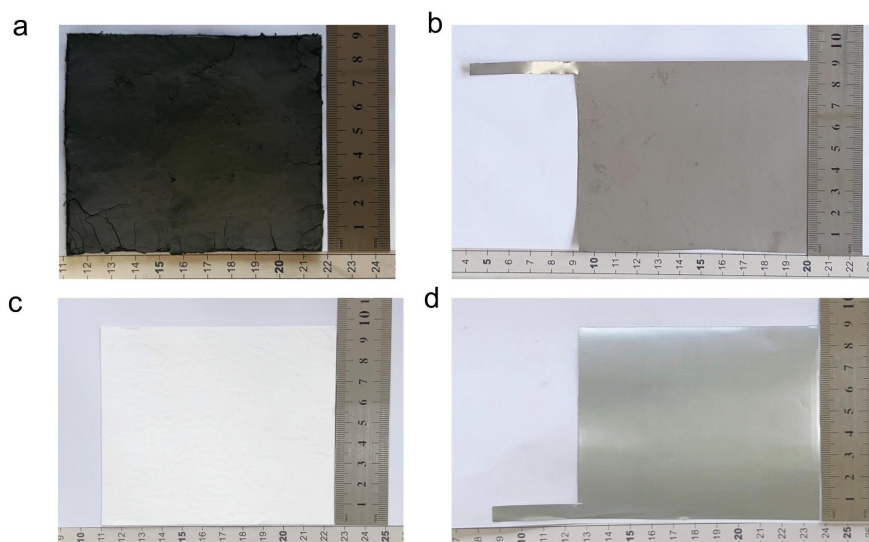
**Supplementary Fig. 40** Galvanostatic discharge profiles of Zn ||NVO cells at various current densities in (a) PE and (b) SH electrolytes.



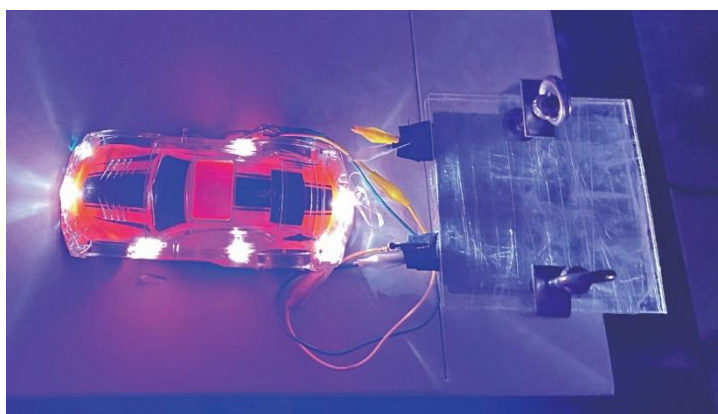
**Supplementary Fig. 41** Cycle performance of Zn ||NVO cells at 0.5 A g<sup>-1</sup> in SH electrolytes.



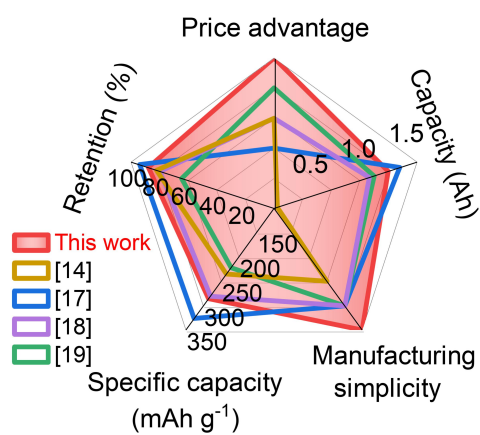
**Supplementary Fig. 42** Diagram of a coin cell and a pouch cell.



**Supplementary Fig. 43** The components of pouch cell. (a) Positive electrode, (b) Ti foil, (c) Glassfiber, (d) Zn foil. The detailed parameter is illustrated the **Supplementary Table S2**.



**Supplementary Fig. 44** The digital photographs of a lighted toy car.



**Supplementary Fig. 45** Comparison with typical reported pouch cells.

**Supplementary Table 1.** The atomic content of different elements of PMS-intercalated  $\text{NH}_4\text{V}_4\text{O}_{10}$  at discharged state in TEM (discharge to 0.4 V).

| Element | Line Type | Wt%    | Wt% Sigma | Atomic % |
|---------|-----------|--------|-----------|----------|
| C       | K series  | 3.20   | 0.20      | 7.07     |
| N       | K series  | 2.20   | 0.23      | 4.16     |
| O       | K series  | 35.77  | 0.29      | 59.29    |
| S       | K series  | 0.13   | 0.04      | 0.11     |
| V       | K series  | 48.32  | 0.28      | 25.16    |
| Zn      | K series  | 10.38  | 0.16      | 4.21     |
| Total:  |           | 100.00 |           | 100.00   |

**Supplementary Table 2.** The parameters of every component in the ampere-hour  $\text{Zn}||\text{NVO}$  pouch cell.

| Mass of the components                     | Values   | Electrochemical parameter | Values                    |
|--------------------------------------------|----------|---------------------------|---------------------------|
| Positive electrode                         | 5.657 g  | Specific capacity         | 311.2 mAh g <sup>-1</sup> |
| Carbon felt (1 mm)                         | 2.775 g  | Cell average voltage      | 0.68 V                    |
| Electrolyte                                | 30.520 g | Capacity                  | 1.2 Ah                    |
| Separator                                  | 2.836 g  | Energy                    | 0.874 Wh                  |
| Package                                    | 4.317 g  |                           |                           |
| Zn negative electrode (100 $\mu\text{m}$ ) | 15.990 g |                           |                           |
| Pouch-cell weight                          | 62.113 g |                           |                           |

**Supplementary Table 3.** Summarized properties of our and some previously reported pouch cell used Vanadium-positive electrode ZABs.

| Type               | Configuration                                                                                                        | Current density          | Capacity (Ah) | Capacity retention (%) | Cycling number | Ref.      |
|--------------------|----------------------------------------------------------------------------------------------------------------------|--------------------------|---------------|------------------------|----------------|-----------|
| Additive           | PMS//NH <sub>4</sub> V <sub>4</sub> O <sub>10</sub>                                                                  | 3                        | ~1.2          | ~84                    | 150            | This work |
|                    |                                                                                                                      | 5                        | ~0.48         | ~85                    | 683            | This work |
| Positive electrode | Nanofibre@Zn//Al <sub>x</sub> V <sub>2</sub> O <sub>5</sub>                                                          | 0.1 A g <sup>-1</sup>    | 0.27          | ~82.0                  | 30             | 1         |
| Organic liquid     | DME//V <sub>2</sub> O <sub>5</sub>                                                                                   | 0.1 A g <sup>-1</sup>    | 0.2           | ~91                    | 50             | 2         |
| Positive electrode | CaV <sub>4</sub> O <sub>9</sub> -V <sub>5</sub> O <sub>12-X</sub> ·6H <sub>2</sub> O                                 | 1.25 mA cm <sup>-2</sup> | 0.037         | ~82.6                  | 50             | 3         |
| Negative electrode | Etching Zn//NH <sub>4</sub> V <sub>4</sub> O <sub>10</sub>                                                           | 1 A g <sup>-1</sup>      | 0.124         | ~91.2                  | 80             | 4         |
| Organic liquid     | EG//V <sub>2</sub> O <sub>5</sub>                                                                                    | 0.1 A g <sup>-1</sup>    | 0.73          | ~76.4                  | 110            | 5         |
| Negative electrode | Zeolite Zn//VO <sub>2</sub>                                                                                          | unknown                  | 0.02          | ~89.7                  | 100            | 6         |
| Additive           | SPS//V <sub>2</sub> O <sub>5</sub>                                                                                   | 1 mA cm <sup>-2</sup>    | 0.02          | ~82.8                  | 200            | 7         |
| Organic liquid     | TBP//V <sub>2</sub> O <sub>5</sub>                                                                                   | unknown                  | 0.11          | ~74.9                  | 250            | 8         |
| Additive           | MPS//V <sub>2</sub> O <sub>5</sub>                                                                                   | 1 mA cm <sup>-2</sup>    | 0.042         | ~86.6                  | 250            | 9         |
| Organic liquid     | HMPA//V <sub>2</sub> O <sub>5</sub>                                                                                  | 1 mA cm <sup>-2</sup>    | 0.07          | ~64                    | 300            | 10        |
| Separator          | CCM//NaV <sub>3</sub> O <sub>8</sub> ·1.5 H <sub>2</sub> O                                                           | 0.5 A g <sup>-1</sup>    | 0.014         | ~85.7                  | 300            | 11        |
| Additive           | NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> //Zn <sub>0.25</sub> V <sub>2</sub> O <sub>5</sub> ·nH <sub>2</sub> O | 0.5 A g <sup>-1</sup>    | 0.031         | ~67.8                  | 400            | 12        |
| Organic            | THF//Zn <sub>0.25</sub> V <sub>2</sub> O <sub>5</sub> ·nH <sub>2</sub> O                                             | 6 C                      | 0.065         | ~100                   | 500            | 13        |

|                    |                                                                           |                              |       |       |     |               |
|--------------------|---------------------------------------------------------------------------|------------------------------|-------|-------|-----|---------------|
| liquid             |                                                                           |                              |       |       |     |               |
| Negative electrode | Ti-Zn//NH <sub>4</sub> V <sub>4</sub> O <sub>10</sub>                     | 1 A g <sup>-1</sup>          | 0.034 | ~85   | 500 | <sup>14</sup> |
| Organic liquid     | GBL//VO <sub>2</sub>                                                      | 0.25 A g <sup>-1</sup>       | 0.23  | ~77.3 | 400 | <sup>15</sup> |
| Additive           | Ims//NaV <sub>3</sub> O <sub>8</sub> ·1.5 H <sub>2</sub> O                | 1 A g <sup>-1</sup>          | 0.33  | ~91.4 | 115 | <sup>16</sup> |
| Organic liquid     | SL//VOH                                                                   | 0.1 A g <sup>-1</sup>        | 1.32  | ~100  | 64  | <sup>17</sup> |
| Negative electrode | 3D-NC@Zn//VO <sub>2</sub>                                                 | 0.1 A g <sup>-1</sup>        | 1.12  | ~64.7 | 200 | <sup>18</sup> |
| Hydrogel           | Chi gel//Zn <sub>x</sub> V <sub>2</sub> O <sub>5</sub> ·nH <sub>2</sub> O | 0.2 A g <sup>-1</sup>        | 0.9   | ~84   | 200 | <sup>19</sup> |
| Organic liquid     | SL//V <sub>2</sub> O <sub>5</sub>                                         | 0.056 A g <sup>-1</sup><br>1 | 1.0   | ~80   | 390 | <sup>20</sup> |

## Supplementary References

- 1 Wan, F. et al. A universal compensation strategy to anchor polar organic molecules in bilayered hydrated vanadates for promoting aqueous Zinc-ion storage. *Adv. Mater.* **33**, 2102701 (2021).
- 2 Dong, Y. et al. Cell-nucleus structured electrolyte for low-temperature aqueous zinc batteries. *J. Energy Chem.* **83**, 324-332 (2023).
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