Electronic Supplementary Information (ESI)

Enhanced Reversibility and Electrochemical Window of Zn-ion Batteries with Acetonitrile/Water-in-Salt Electrolytes

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Experimental Section

1. Materials preparation

δ-MnO_2 was synthesized using a hydrothermal method. Briefly, 6 mmol $KMnO_4$ and 1 mmol $MnSO_4 \cdot H_2O$ were dissolved into 70 mL distilled water. After stirring, the solution was transferred into a 100 mL Teflon contained autoclave and heated at 180 °C for 12 hours. When the autoclave cooled down to room temperature, the PH was adjusted to 7, and the powder sample was filtered and collected. Next, the powder was dried at 100 °C overnight. The aqueous electrolyte was 15 M (molality, mol kg^{-1}) zinc trifluoromethanesulfonate ($Zn(CF_3SO_3)_2$) system. The acetonitrile/water-in-salt (AWIS) hybrid electrolytes were prepared by adding acetonitrile (AN) in the aqueous electrolyte with different H_2O/AN volume ratios (2:1, 1:1, and 1:2), which was named as H_2O/AN-1, H_2O/AN-2, and H_2O/AN-3, respectively (Table SI-1). H_2O/AN ratio in the AWIS hybrid electrolyte was optimized in the Zn|Zn symmetric cells, of which the cycling stability was shown in Figure S1. It can be found that H_2O/AN-3 with an H_2O/AN volume ratio of 1:1 exhibited the smallest overpotential and the most extended lifespan. Therefore, H_2O/AN-3 was used for further investigation and referred to as the hybrid electrolyte.

Table SI-1. The composition and PH of different electrolytes investigated in this work.

Electrolyte	$Zn(CF_3SO_3)_2$ (g)	H_2O (ml)	AN (ml)	PH
Aqueous electrolyte	32.7	6	0	6.68
H_2O/AN-1	32.7	4	2	-
H_2O/AN-2	32.7	2	4	-
H_2O/AN-3	32.7	3	3	6.75

2. Structural characterizations

The crystal structure of the Zn foils before and after cycling was examined by Powder X-ray diffraction (XRD, Bruker D8-Advance X-ray diffractometer) using Cu Kα radiation (1.54056 Å). The morphology was observed by using a scanning electron microscope (SEM, Tescan MIRA3 FEGESEM). The electrolytes were characterized by using an inVia Raman Microscope coupled with a 785 nm diode laser (Renishaw).

3. Electrochemical measurements

As the active material, δ-MnO_2 was mixed with carbon nanotube-PVDF-NMP blend (LB107-54, Cnano Technology), and the weight ratio of active material, carbon nanotube, and PVDF is 7:2:1. Subsequently, the slurry was pasted on a titanium foil and dried in a vacuum oven at 60 °C overnight. Next, the as-prepared electrode was cut into 12 mm round plates. The mass loading of MnO_2 was around 1 mg on each disk. Galvanostatic charge/discharge test was carried out on a Neware BTS 4000 battery tester. The galvanostatic charge-discharge measurement of Zn-MnO_2 was performed at 0.1C (1C = 300 mA g^{-1}, based on MnO_2) within a voltage range of 0.8-1.8V, 0.8-2.0V, and 0.8-2.2V. Electrochemical impedance spectroscopy (EIS) measurement was conducted on Biologic SP-150 Potentiostat/Galvanostat Station in a frequency range of 200 kHz to 0.01 Hz with a voltage amplitude of 5 mV.

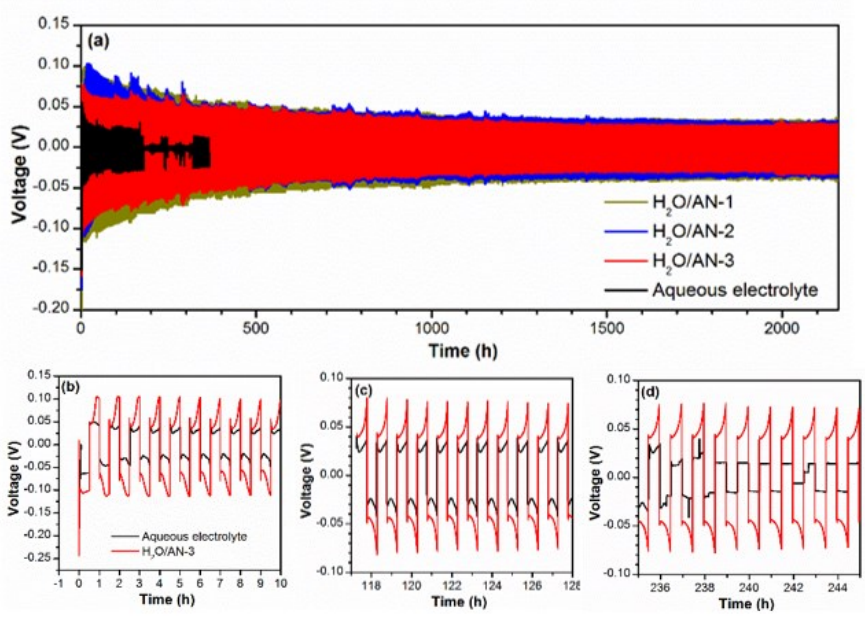

Figure S1. (a) Effect of different electrolytes on the cycling stability of Zn|Zn symmetric cells measured at a current density of 1 mA cm^{-2} with a constant capacity of 1mAh cm^{-2}; (b-d) comparsion of charge/discharge profiles of aquesou electrolye with H_2O/AN-3 (hybrid electrolyte) at different times.

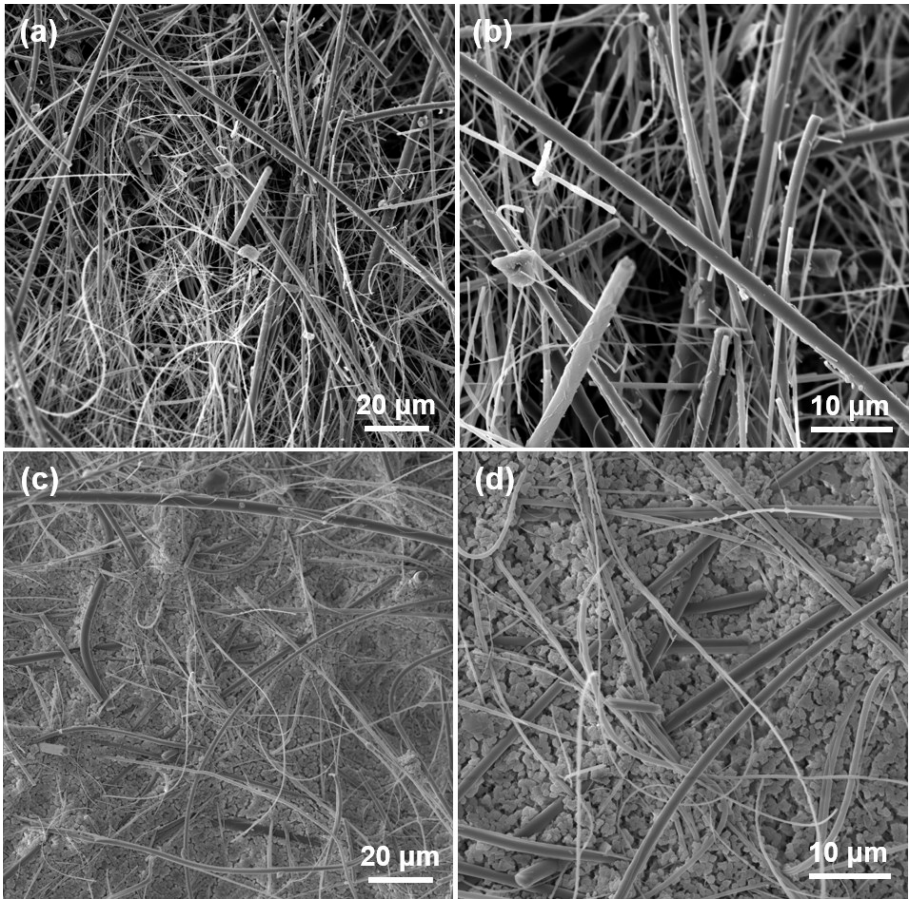

Figure S2. SEM images of the glass-fiber separators recovered from the Zn-Zn symmetric cells with (a, b) the hybrid electrolyte (H_2O/AN-3) and (c, d) the aqueous electrolyte.

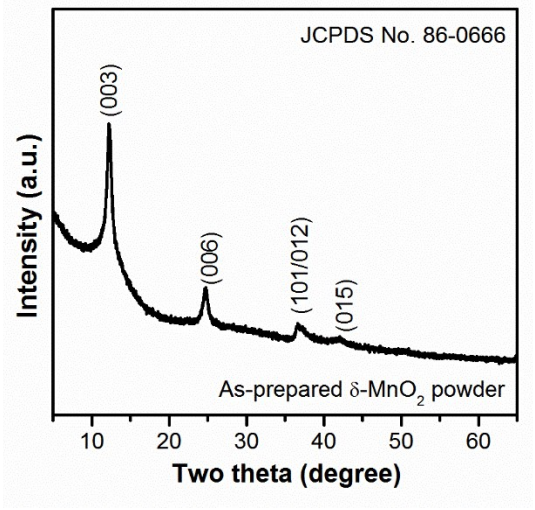

Figure S3. XRD pattern of the δ-MnO_2 powder.

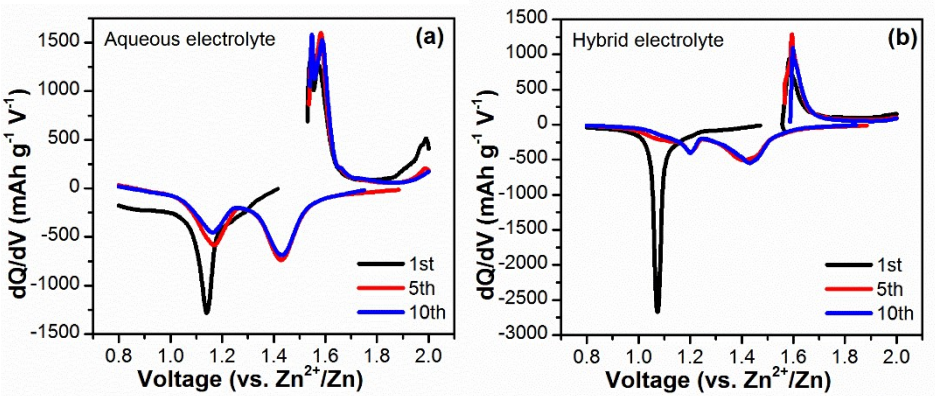

Figure S4. dQ/dV curves of Zn-MnO_2 cells with the (a) aqueous electrolyte and (b) hybrid electrolyte in the 1st, 5th, and 10th cycles (0.8-2.2V).

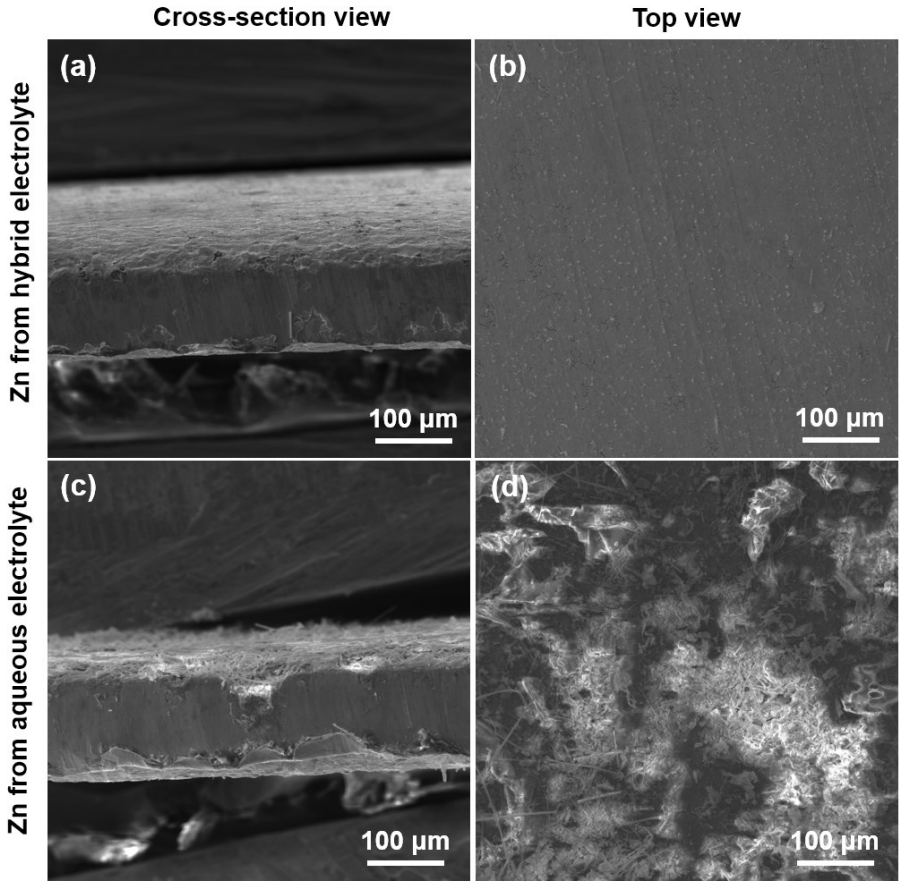

Figure S5. SEM images of Zn metal anodes recovered Zn-MnO_2 cells with the (a, b) hybrid electrolyte and (c, d) aqueous electrolyte after cycling (0.8-2.2 V).

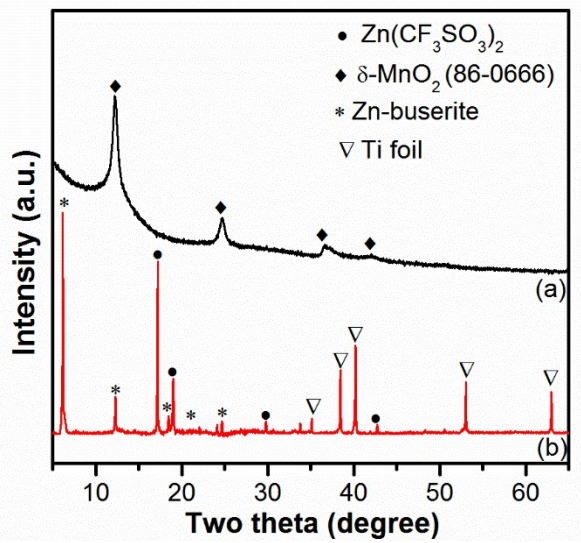

Figure S6. XRD patterns of (a) the as-prepared MnO_2 powder and (b) the MnO_2 electrode at the discharge state in the hybrid electrolyte (0.8-2.0V). (Zn-buserite is indexed according to Nat. Commun., 2017, 8, 405).

Table SI-2. EIS parameters obtained by fitting the data with the equivalent circuit in Figure 1b.

Sample	R_0 (Ω)	R_{SEI} (Ω)	R_{CT} (Ω)
Hybrid electrolyte	17.8	10.0	135.2
Aqueous electrolyte	0.2	12.0	236.0