

Supporting Information:

A $\text{Zn}(\text{ClO}_4)_2$ Electrolyte Enabling Long-Life Zinc Metal Electrodes for Rechargeable Aqueous Zinc Batteries

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Experimental Method

Material synthesis and characterization. The electrolytes were obtained by dissolving desired amount of $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, or $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ in deionized water. Trace precipitate showed up in $\text{Zn}(\text{ClO}_4)_2$ electrolyte which could be a result of slight hydrolysis of the salt, so that the mixture was settled and the clear liquid was used as the electrolyte. Zn concentration in the $\text{Zn}(\text{ClO}_4)_2$ electrolyte was measured with Agilent ICPOES730. VO_2 was synthesized by a similar procedure reported previously,¹ except for the utilization of microwave-assisted hydrothermal reaction rather than a conventional one. Typically, V_2O_5 and oxalate acid were dissolved in deionized water in a glass vessel and fitted in Monowave 200 synthesis system (Anton Paar). The temperature of the system was increased to 75 °C and stayed for 5 min, followed by the further increase of temperature to 180 °C and stayed for 10 min. After cooling to room temperature, the mixture was filtered and washed with deionized water and ethanol. X-ray diffraction (XRD) analysis was carried out on a PANalytical Empyrean diffractometer with Cu-K α or Co-K α radiation. Material morphologies were examined by a HITACHI SU8010 scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectroscopy (EDS) detector.

Electrochemistry. Zinc electrodes were cut into 13.5 mm diameter circles from zinc foil. VO_2 electrodes were prepared by mixing VO_2 with Super P and polyvinylidene fluoride (PVDF) in an 8:1:1 weight ratio in N-methyl-2-pyrrolidone (NMP). The slurry was casted onto carbon paper and dried. Zn stripping/plating (with Zn-Zn symmetric configuration), coulombic efficiency (copper foil as the cathode current collector), VO_2 cyclic voltammogram (CV), rate performance and cycling tests were carried out in 2032 coin cells with LANHE CT2001A battery cycler or Bio-logic VMP3 potentiostat/galvanostat. Electrochemical impedance spectroscopy (EIS) was obtained in T-shaped PFA Swagelok cells with Zn (11.5 mm diameter) as the working, counter and reference electrodes on the Bio-logic VMP3 potentiostat/galvanostat. The CV of the electrolyte was obtained in a beaker cell with Ti foil as the cathode and Zn foil as the anode on the Bio-logic VMP3 potentiostat/galvanostat.

Supporting Figures

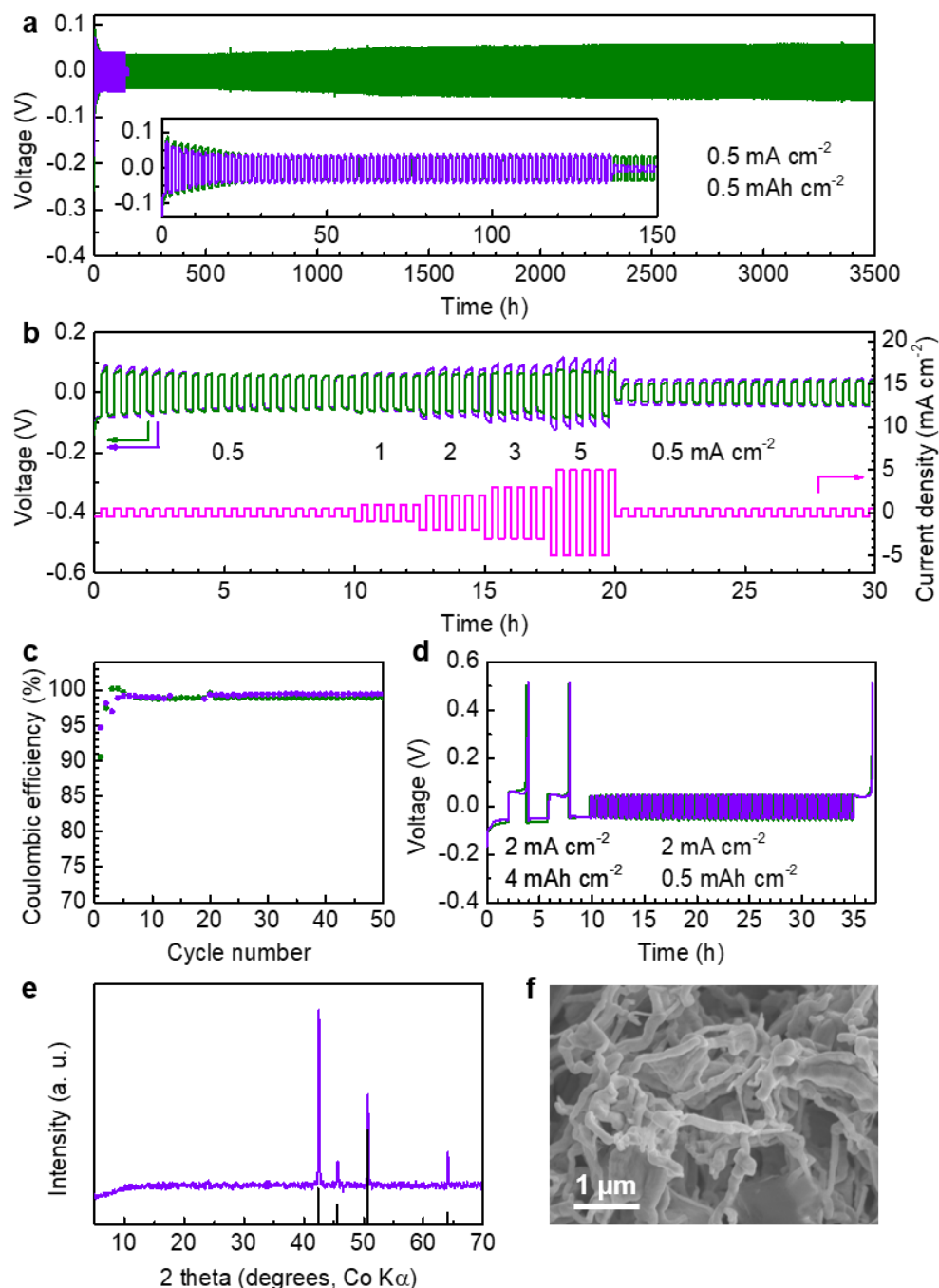


Figure S1. Zn stripping/plating behavior in symmetric cells at (a) 0.5 mA cm^{-2} current density and 0.5 mAh cm^{-2} capacity (inset shows the first 150 hour behavior) and (b) various current densities in $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ (purple) and $\text{Zn}(\text{ClO}_4)_2$ (green) electrolytes; CE tests with Cu current collectors in $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ (purple) and $\text{Zn}(\text{ClO}_4)_2$ (green) electrolytes: (c) full Zn stripping/plating CE and (d) partial Zn stripping/plating voltage profiles; (e) XRD (black peaks show the Zn diffractions) and (f) SEM image of the Zn electrode after deposition of 2 mAh cm^{-2} Zn at 0.5 mA cm^{-2} from the $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ electrolyte.

Discussion on the electrochemical performance comparison of $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ and $\text{Zn}(\text{ClO}_4)_2$ electrolytes:

Figure S1a-d above shows the electrochemical performance comparison between $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ and $\text{Zn}(\text{ClO}_4)_2$ electrolytes. The symmetric cell with $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ electrolyte short-circuits before 140 hours of Zn stripping/plating (Figure S1a). Similar early cell degradation has also been shown in previous publications.²⁻⁶ The cycle life is significant shorter than the over 3500 hours for $\text{Zn}(\text{ClO}_4)_2$. With the increase of current density, the overpotential increase in $\text{Zn}(\text{ClO}_4)_2$ is smaller than $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ (Figure S1b), suggesting the better rate capability of the former. When measuring coulombic efficiency (CE), the cell with $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ electrolyte shows partial cell degradation during the 15th ~ 20th cycle. An average CE of 99.4% was obtained using the data after 20th cycle, similar to the 99.0% CE for the $\text{Zn}(\text{ClO}_4)_2$ electrolyte (Figure S1c). Using the protocol proposed by Zhang *et al.*⁷ to evaluate CE also gives similar results for the two electrolytes, *i.e.* 99.3% for $\text{Zn}(\text{ClO}_4)_2$ and 98.6% for $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ (Figure S1d).

Figure S1e shows the XRD of the Zn electrode after depositing 2 mAh cm^{-2} Zn from $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ electrolyte, where only Zn diffractions are identified. The corresponding SEM image suggests the dendritic morphology of the deposited Zn (Figure S1f).

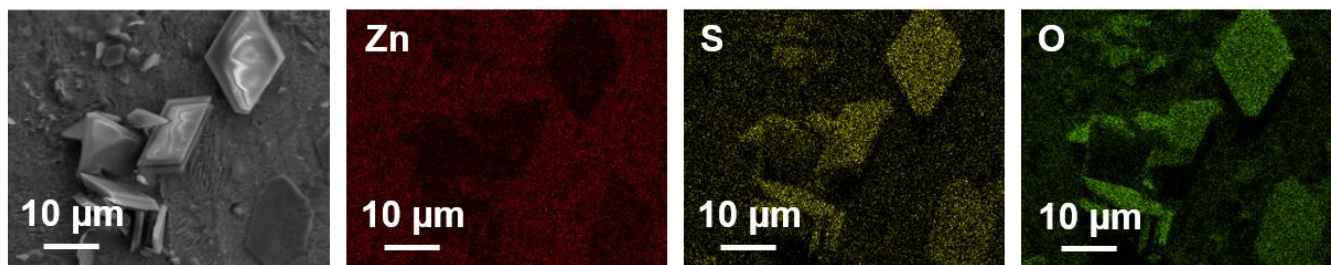


Figure S2. EDS mapping of the Zn electrode after 50 stripping/plating cycles in ZnSO_4 .

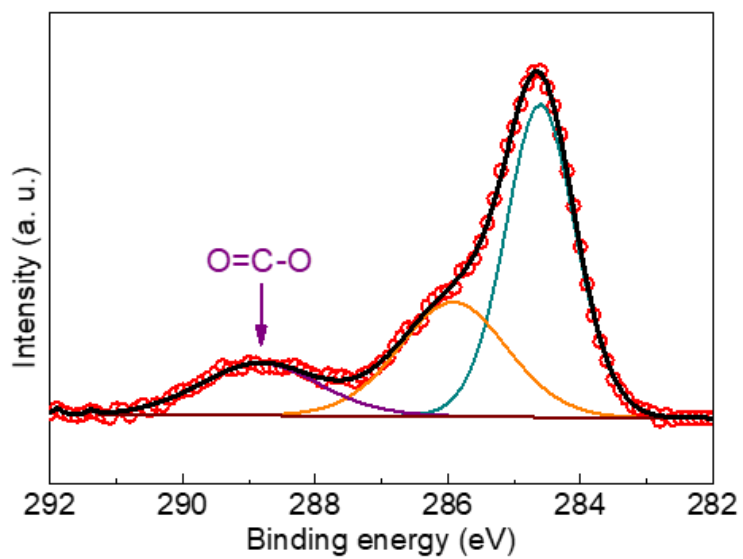


Figure S3. The fitting of C 1s XPS of the Zn electrode after one deposition in $\text{Zn}(\text{CH}_3\text{COO})_2$.

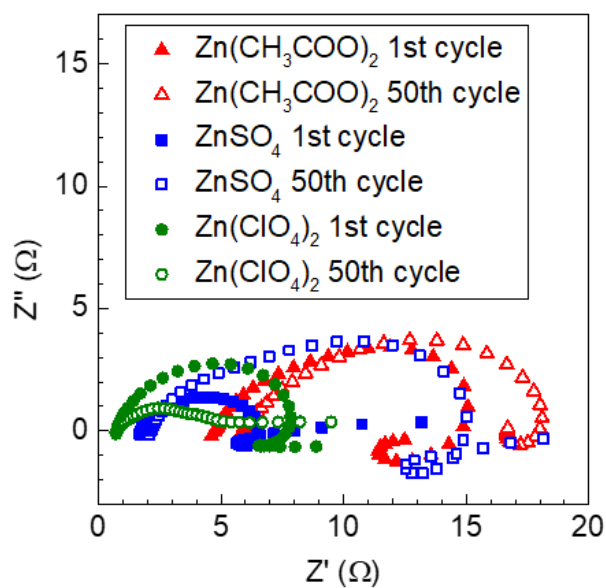


Figure S4. EIS of the Zn electrodes in ZnSO_4 (blue), $\text{Zn}(\text{CH}_3\text{COO})_2$ (red) and $\text{Zn}(\text{ClO}_4)_2$ (green) electrolytes at the first and 50th cycles.

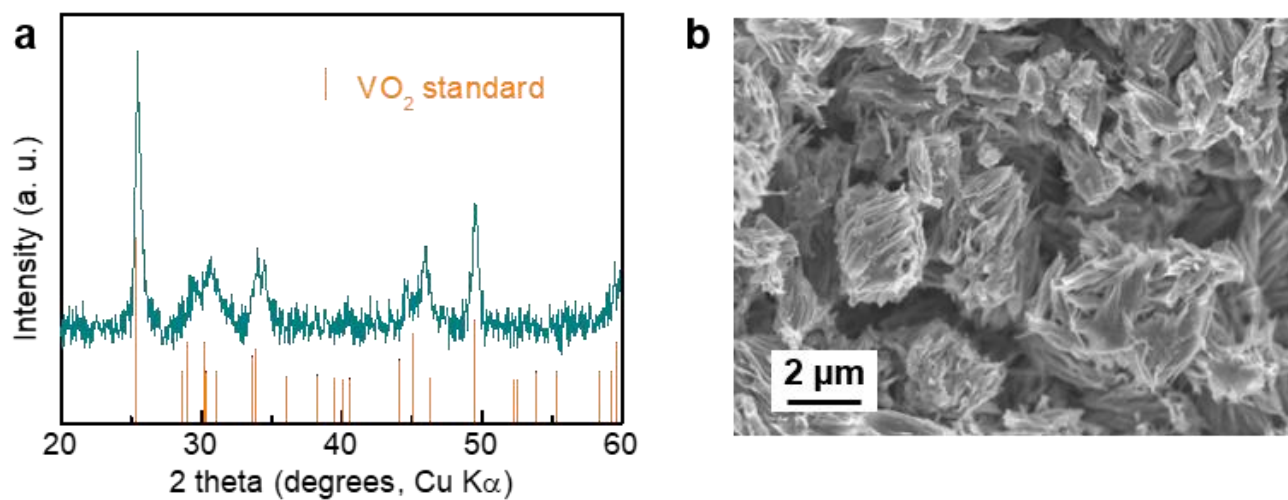


Figure S5. (a) XRD and (b) SEM image of VO_2 .

References

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