

Supplementary Information

Trace Sc³⁺-electrolyte additive enabling stable Zn metal anodes for aqueous zinc-ion batteries

Chun Chen,^{a,b,c} Liansheng Li^{b,c} Zuxin Long,^{b,c} and Qinghua Liang^{a,b,c,*}

- a. School of Rare Earth, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China
- b. Key Laboratory of Rare Earth, Chinese Academy of Sciences, Ganzhou, Jiangxi 341000, P. R. China
Ganjiang Innovation Academy, Chinese Academy of Sciences, Ganzhou, Jiangxi 341000, P. R. China

*Corresponding authors.

E-mail: qhliang@gia.cas.cn

Experimental Section

Preparation of Electrolytes. Deionized water (DI) obtained from an ultrapure water system was used to prepare all aqueous electrolytes. $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ purchased from Aladdin Ltd., Shanghai was dissolved in deionized water to prepare the pristine 2.0 M ZnSO_4 electrolyte. A stoichiometric amount of scandium sulfate ($\text{Sc}_2(\text{SO}_4)_3$) (0.005 M, 0.01 M, 0.02 M) purchased from Aladdin Ltd., Shanghai was dissolved into 2.0 M ZnSO_4 electrolytes to prepare Sc^{3+} -containing electrolytes. The V_2O_5 nanobelt was prepared according to the method reported in the previous report.¹ The V_2O_5 nanobelt cathode was prepared by grinding and mixing V_2O_5 nanobelt, Super-P, and carboxy methyl cellulose (CMC) at a weight ratio of 7:2:1 for 10 mins. The mixture was dispersed with a quantity of deionized water to prepare the slurry under stirring at room temperature for 12 h. The prepared slurry was cast onto graphite paper and then dried in a vacuum oven at 90 °C for 12 h. The active carbon (AC) cathodes for Zn-ions hybrid capacitors (ZHCs) consisting of commercial AC, Super P, and CMC with a mass ratio of 7: 2: 1, were prepared by a similar procedure of V_2O_5 cathode preparation. The stainless-steel foil was used as the current collector for the AC cathode.

Material Characterizations. The phase structures of Zn electrodes were characterized by a Bruker D8 Advance X-ray diffractometer (Cu-K α , $\lambda = 1.5418 \text{ \AA}$). The morphology of the plated Zn cycled under different test conditions was observed by scanning electron microscopy (SEM).

Electrochemical measurements. Cyclic voltammetry (CV) measurement of Zn plating/stripping was measured in a two-electrode cell, where Ti foil serves as the working electrode, and Zn plane acts as the counter electrode. Electrochemical impedance spectroscopy (EIS) of the Zn||Zn symmetric cell was recorded by a CHI660E electrochemical workstation from 100 kHz to 0.01 Hz at open-circuit voltage with an amplitude voltage of 5 mV under different temperatures. The nucleation overpotential was tested by Zn||Cu asymmetric cell at a current density of 2.0 mA cm⁻². The Zn||Zn symmetric cells were assembled by sandwiching the glass fibre (Whatman GF/A) between two commercial Zn foil (100 μm , 12 mm in diameter) in CR2032 coin-type cells filled with 60 μL ZnSO_4 or ZnSO_4/Sc electrolytes. Zn||Cu asymmetric cells

were assembled by Zn foil (100 μm , 12 mm in diameter), Cu foil (12 mm in diameter), and glass fibre. Zn||V₂O₅ full cells filled with 70 μL electrolytes were assembled using Zn foil (10 μm , 10 mm in diameter) as the anode, V₂O₅ nanobelt paper as the cathode, and glass fibre as the separator.

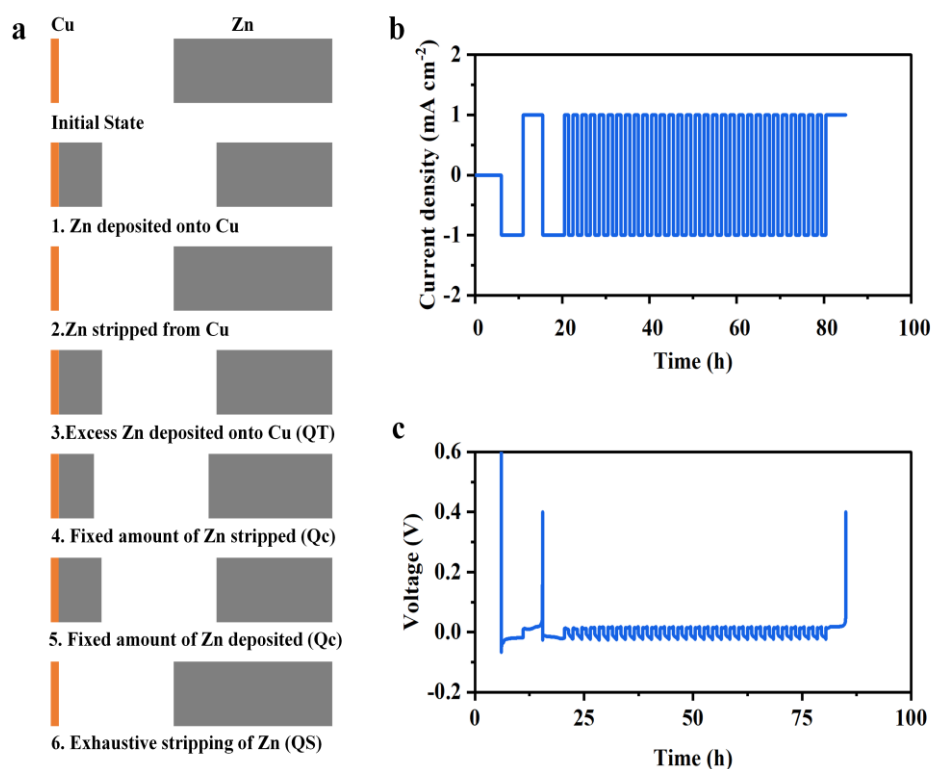


Fig. S1 (a) The schematic illustration of an accurate method for testing the CE of Zn||Cu cell.¹ The Cu substrate is applied with one single Zn plating/stripping cycle at a current density of 1.0 mA cm⁻², where the cycle is done by plating 5.0 mA h cm⁻² of Zn and then fully stripping the Zn to 0.4 V. Subsequently, 5.0 mA h cm⁻² charges of Zn were plated on Cu substrate again at a current density of 1.0 mA cm⁻² then stripping/plating cycling ($Q_C=1.0$ mA h cm⁻²) for 30 cycles at 1.0 mA cm⁻². During the final stripping process, the deposited Zn was stripped until the voltage exceeded 0.4 V. (b) The corresponding current density and (c) voltage-time plot.

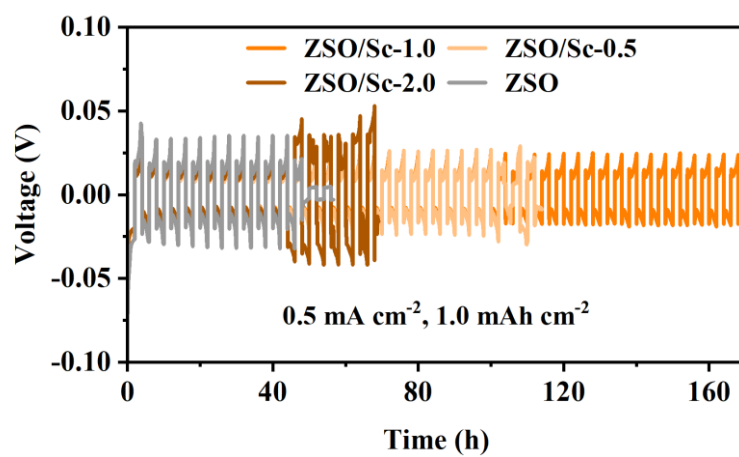


Fig.S2 The long-term galvanostatic cycle performances of the Zn||Zn symmetric cells using different electrolytes at 0.5 mA cm^{-2} and 1.0 mA h cm^{-2} .

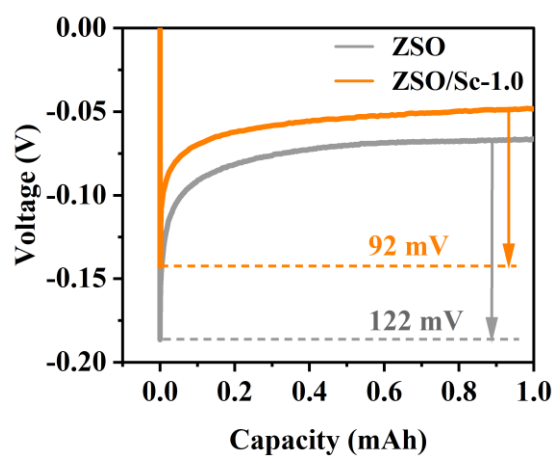


Fig. S3 The nucleation overpotentials of Zn deposition on the Zn plate in the ZSO and ZSO/Sc-1.0 electrolytes at a current density of 2.0 mA cm^{-2} .

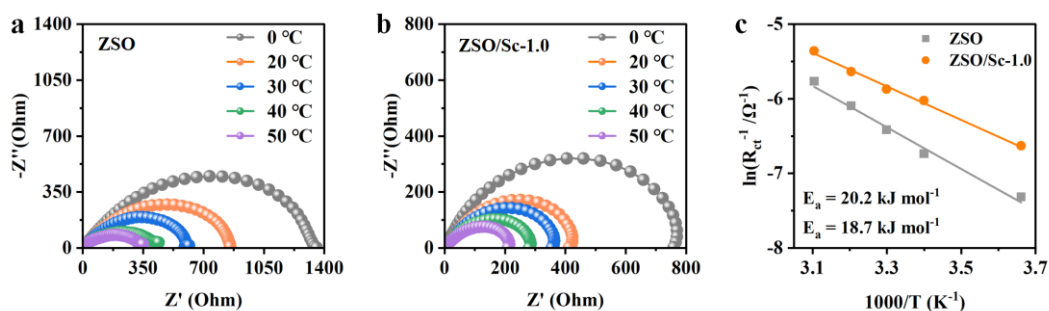


Fig. S4 EIS results of the Zn||Zn symmetrical cells assembled by ZSO (a) and ZSO/Sc-1.0 electrolytes (b) at different temperatures recorded from 100 kHz to 0.01 Hz at the open-circuit voltage. (c) The temperature-dependent reciprocal resistances in ZSO and ZSO/Sc-1.0 electrolyte. Arrhenius equation ($\ln(R_{ct}^{-1}) = \ln A - E_a/RT$) was used to calculate E_a , where R_{ct} is the charge transfer resistance, E_a is the activation energy, T is the absolute temperature, and R is the gas constant. The R_{ct} is obtained from the semicircle of the Nyquist plots of Zn||Zn symmetric cells tested at different temperatures. The E_a is calculated by linearly fitting $\ln(1/R_{ct})$ versus $1000/T$.

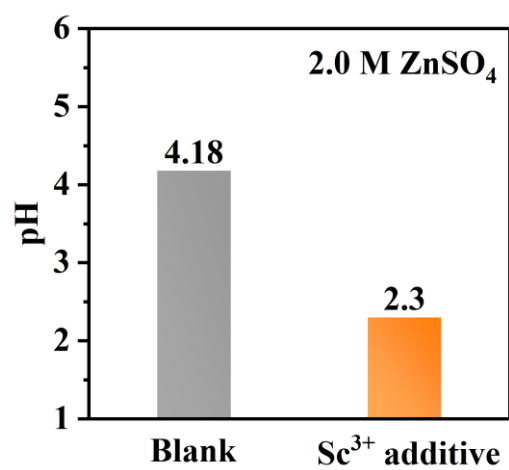


Fig. S5 The pH values of the ZSO and ZSO/Sc-1.0 electrolytes tested at 24.8 °C.

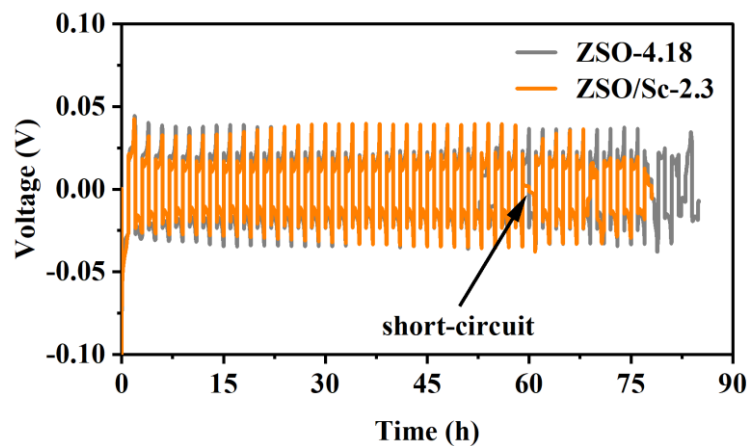


Fig. S6 The long-term galvanostatic Zn stripping/plating of the Zn||Zn symmetric cells using ZnSO₄ electrolytes with different pH values. The ZSO-2.3 electrolyte was prepared by adding a certain amount of 0.1M H₂SO₄ solution.

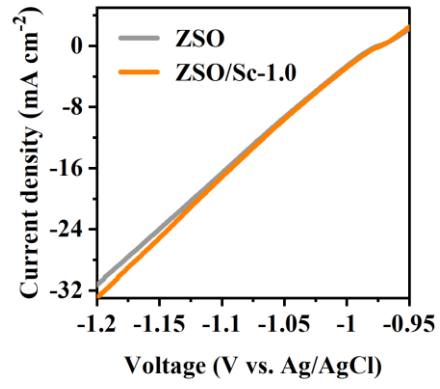


Fig. S7 The LSV curve of ZnSO₄ electrolytes with/without Sc³⁺ additive at a scan rate of 1.0 mV s⁻¹.

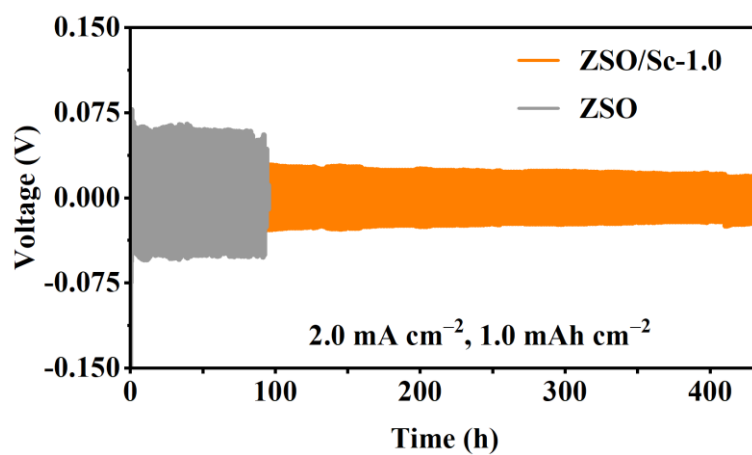


Fig. S8 The charging and discharging curves of Zn||Zn cells with and without Sc³⁺-electrolyte additive at a current density of 2.0 mA cm⁻² and an areal capacity of 1.0 mA h cm⁻².

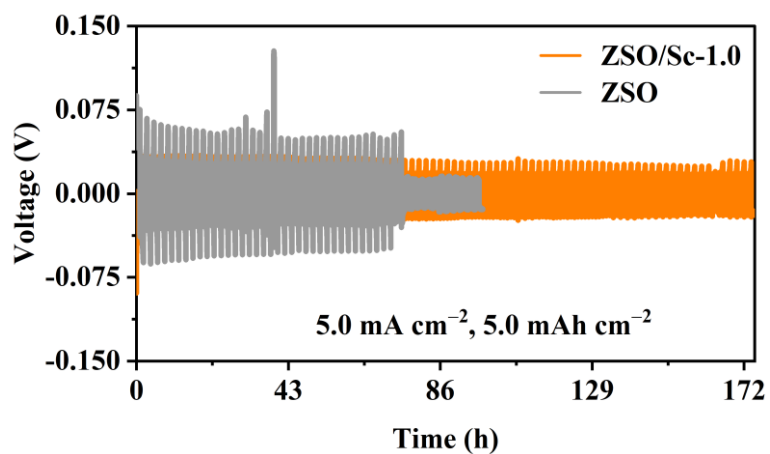


Fig. S9 The charging and discharging curve of Zn||Zn cells with and without Sc³⁺ at a current density of 5.0 mA cm⁻² and an areal capacity of 5.0 mA h cm⁻²

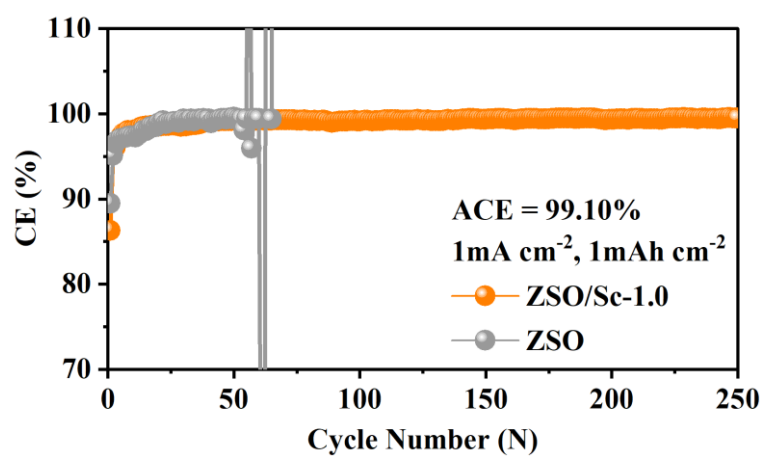


Fig. S10 The CE of Zn||Cu cell with and without Sc³⁺ at a current density of 1.0 mA cm⁻² and an areal capacity of 1.0 mA h cm⁻².

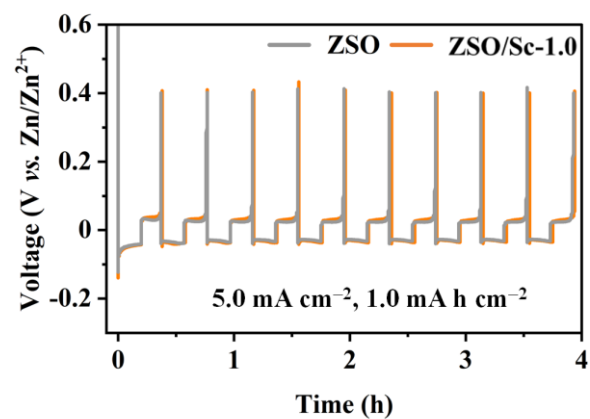


Fig. S11 The voltage profile of Zn||Cu asymmetrical battery tested at a current density of 5.0 mA cm^{-2} and a areal capacity of 1.0 mA h cm^{-2} .

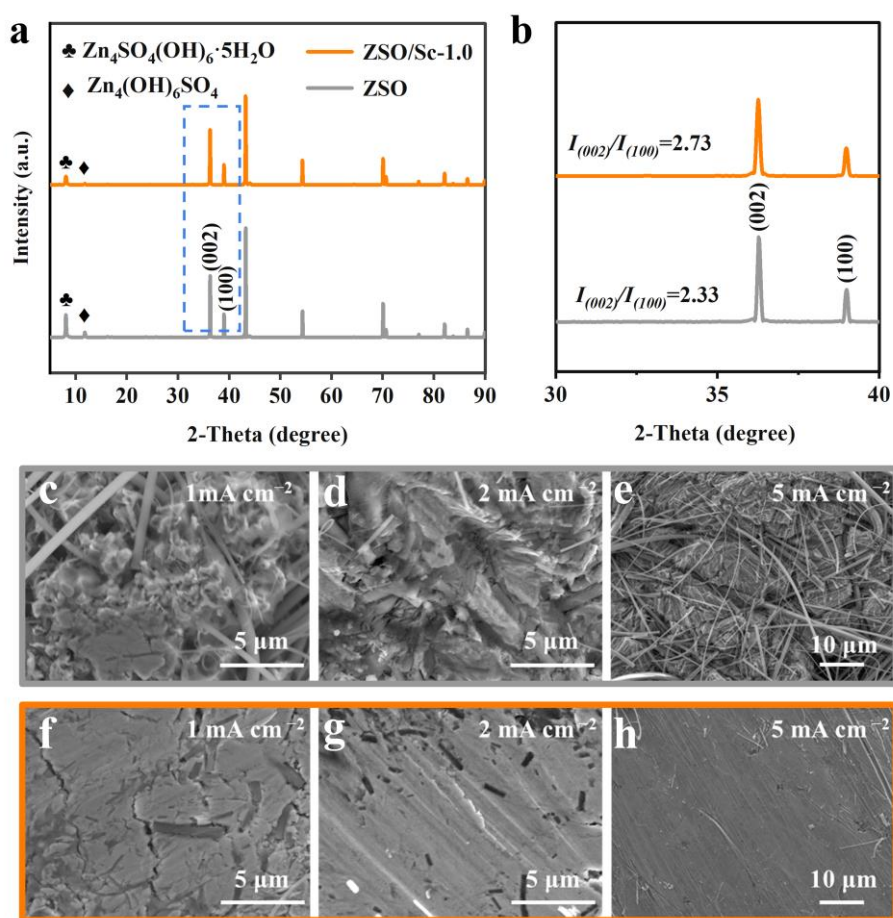


Fig. S12 The structural analysis of plated Zn. (a, b) The XRD patterns of ZMAs disassembled from the Zn||Zn cells with ZSO and ZSO/Sc-1.0 electrolytes after 30 cycles at 1.0 mA cm^{-2} under 1.0 mA h cm^{-2} . The SEM images of Zn foils after plating Zn of 2.0 mA h cm^{-2} in the Zn||Zn cells with (c-e) ZSO and (f-h) ZSO/Sc-1.0 electrolyte at 1.0 , 2.0 , and 5.0 mA cm^{-2} .

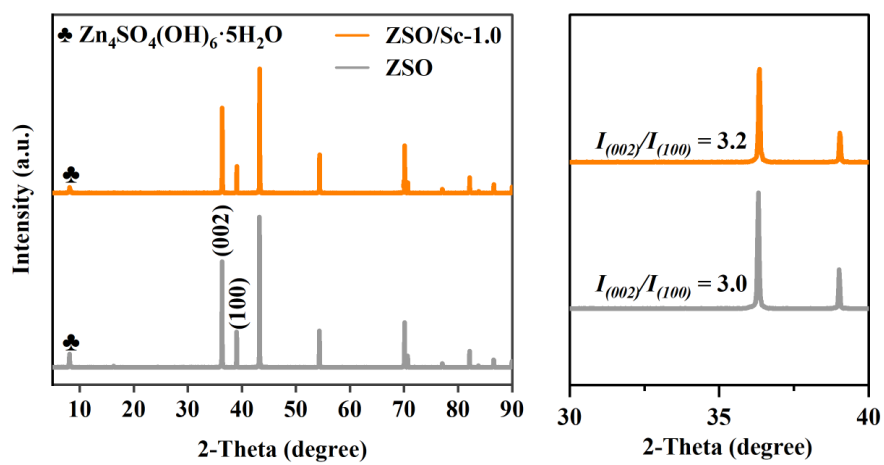


Fig. S13 The XRD pattern of Zn metal anodes disassembled from the Zn||Zn cells with ZSO and ZSO/Sc-1.0 electrolytes after 50 cycles at a current density of 5.0 mA cm^{-2} with an areal capacity of 1.0 mA h cm^{-2} .

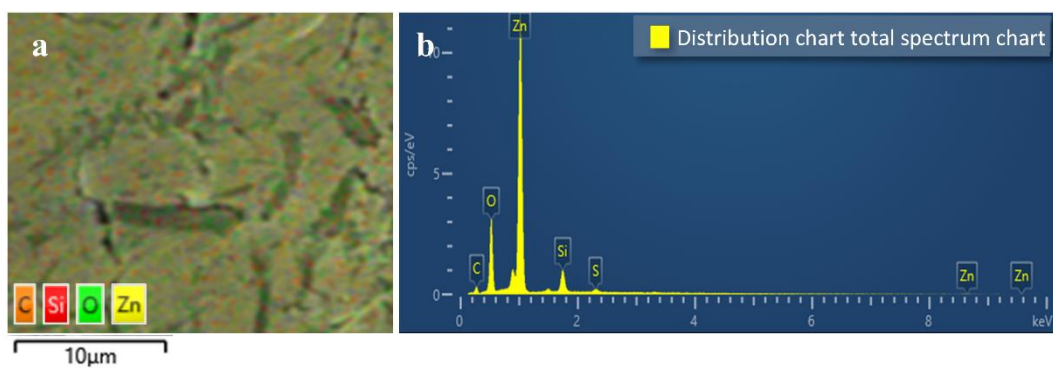


Fig. S14 (a) EDX mapping image of the Zn disassembled from the Zn||Zn symmetrical cell assembled by ZSO/Sc-1.0 electrolyte and (b) the corresponding spectrum.

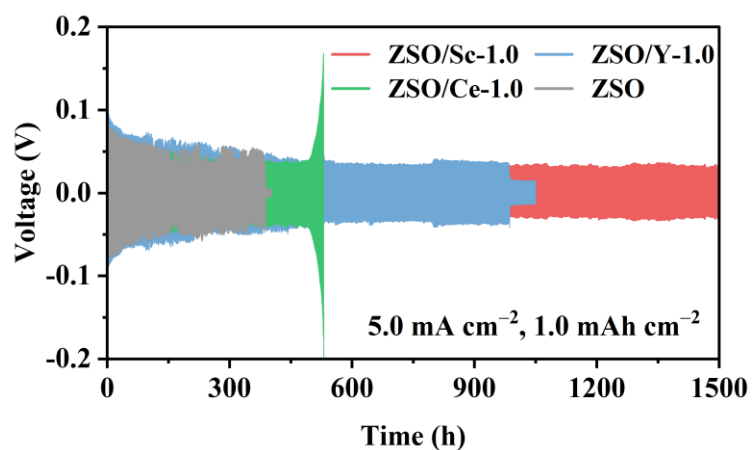


Fig. S15 The long-term galvanostatic Zn stripping/plating of the Zn||Zn symmetric cells using ZSO electrolyte with different rare earth ions (1 mol%) at 5.0 mA cm^{-2} under 1.0 mA h cm^{-2} .

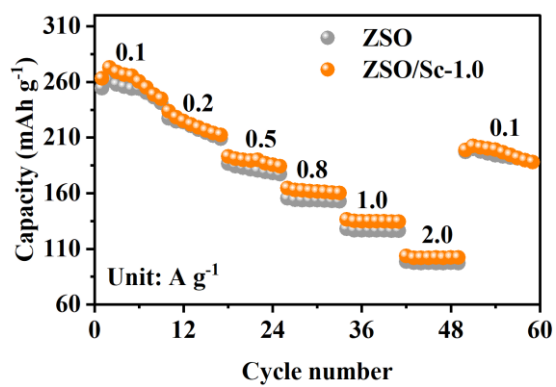


Fig. S16 Rate performance of Zn||V₂O₅ full cells with ZSO and ZSO/Sc-1.0 electrolytes.

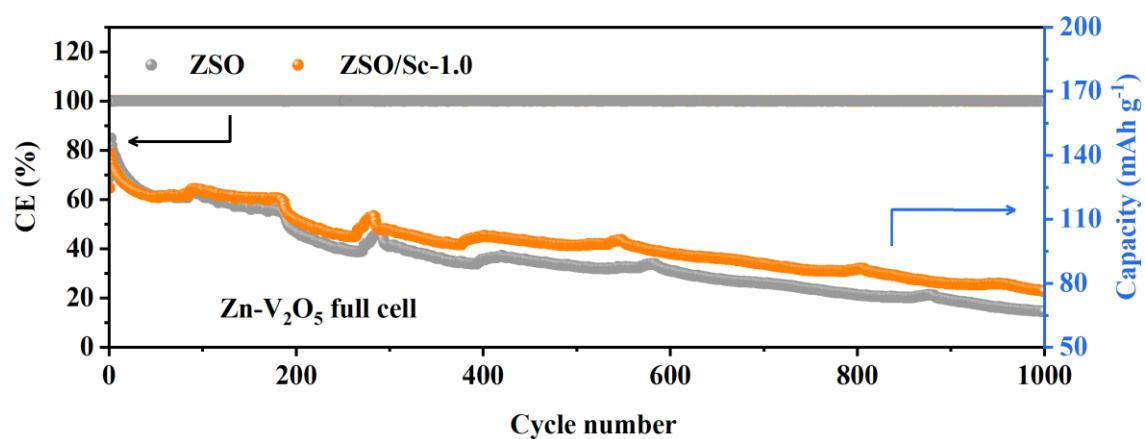


Fig. S17 The cycle stability of Zn||V₂O₅ full cells with ZSO and ZSO/Sc-1.0 electrolytes.

3. Reference

- 1 B. D. Adams, J. Zheng, X. Ren, W. Xu and J.-G. Zhang, *Adv. Energy Mater.*, 2018, **8**, 1702097.