Supplementary Information

Multifunctional Electrolyte Additive of Zinc Gluconate towards Dendrite-Free and Long-Life Zinc Ion Batteries

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Experimental Section

Fabrication of functional electrolytes.

For the preparation of pure 2 M $ZnSO_4$ (ZSO) electrolyte, the accurately weighed amount of zinc sulfate heptahydrate (57. 512 g) was dissolved in deionized water of 60 mL and then transferred to a volumetric flask (100 mL). Next, the solution was fully mixed at room temperature. Meanwhile, as-prepared ZSO electrolyte was adopted as the precursor solution and modified electrolyte containing ZG additive could be obtained by adding specific amounts of ZG additive (0.0228 g, 0.0456 g, 0.0911 g, 0.2278 g and 0.4557 g) into the solution (10 mL), which were determined at the concentration of 5, 10, 20, 50, 100 mM respectively.

Material Characterization.

The scanning electron microscope (Gemini SEM500) was used to obtain the morphology observation of samples. And all XRD tests were conducted by Siemens D

500 to determine the structure information. Real-time observation of zinc deposition was explored by a home-made device. Dataphysics OCA20 has been applied for measuring the contact angles.

Electrochemical measurements.

All electrochemical behaviors of zinc plating/stripping were estimated by CR2032 coin cells using glass fiber (GF/D) as the separator and specific electrolytes, which were assembled in the air atmosphere. Symmetric/asymmetric cells were correspondingly assembled by clean zinc foil (40 μm) and copper foil (20 μm). Specially, the usage amount of electrolyte was controlled at 100 μL for per cell. The preparation of $NH_4V_4O_{10}$ cathode was synthesized by a reported hydrothermal method.[1] Afterwards, weighed $NH_4V_4O_{10}$ powder was mixed with conductive carbon (Super P) and polyvinylidene fluoride binder in a mass ratio of 7:2:1, and then dispersed in N-Methyl-2-pyrrolidone (NMP) for the subsequent casting on stainless foil. These foils were dried in a vacuum oven for 10 h. The stability measurement was investigated on a Neware battery testing under different current densities and areal capacities. The CA curves could be measured in the symmetric cells by an intact electrochemical workstation (CHI760E) produced by Shanghai Chenhua Instrument. Tafel curves of zinc foils in different electrolytes were examined by a three-electrode system with an Ag/AgCl reference electrode.

Related calculations method.

The ionic conductivity of electrolytes can be measured in a SS|SS symmetric cell by an intact electrochemical workstation (CHI 760E) produced by Shanghai Chenhua Instrument. The measurement was performed in the 10^5 Hz to 10^{-2} Hz frequency range by applying an amplitude of 5 mV. The electrolyte resistance was obtained from the intercept of Nyquist plot on the real (impedance, Z) axis, then ionic conductivity was calculated according to the following equation:

$$\sigma_{Zn^{2+}} = \frac{L}{R_b \cdot A}$$

where σ (S cm^{-1}) is the conductivity, R_b is the resistance of different electrolytes, L (cm) is the distance between the two SS electrodes, and A is the area of electrode (cm^{-2}).

The calculation of activation energy can utilize the Arrhenius equation:

$$\frac{1}{Rct} = Ae^{-\frac{E_a}{RT}}$$

where Rct, A, R, and T denote the charge transfer impedance, frequency factor, gas constant, and absolute temperature respectively.

The transfer number of Zn^{2+} ($t_{Zn}{}^{2+}$) was calculated based on the following equation:

$$t_{Zn^{2+}} = \frac{I_s(\Delta V - I_0 R_0)}{I_0(\Delta V - I_s R_s)}$$

$t_{Zn^{2+}}$ =where I_0 and I_s denote the initial current (μA) and steady current (μA) from the *i-t* curve, respectively, while R_0 and R_s represent the impedance (Ω) before and after the *i-t* test, respectively. The constant potential (ΔV) was set at 20 mV. All symmetric cells were standing for 2 h before measurements.

Theoretical calculation.

All calculations were performed by the first-principle method through the Cambridge serial total energy package (CASTEP) module in Materials Studio.

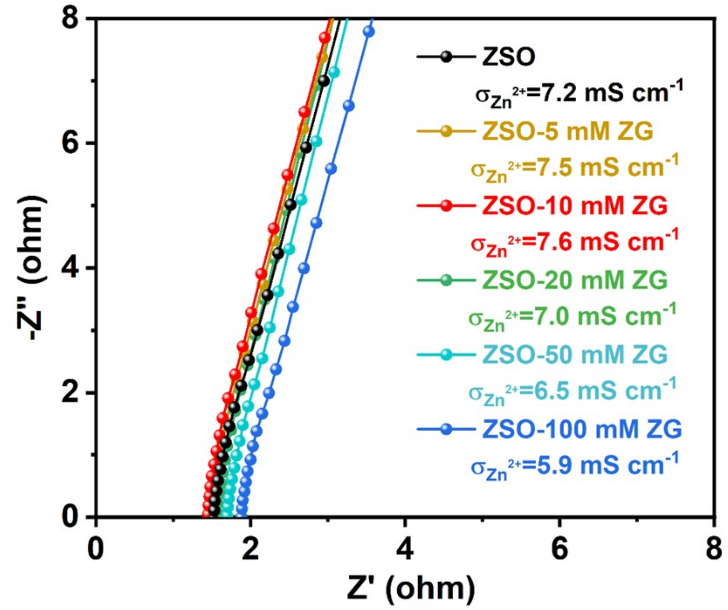

Fig. S1 The ionic conductivities of ZSO and ZSO-ZG with various ZG concentrations.

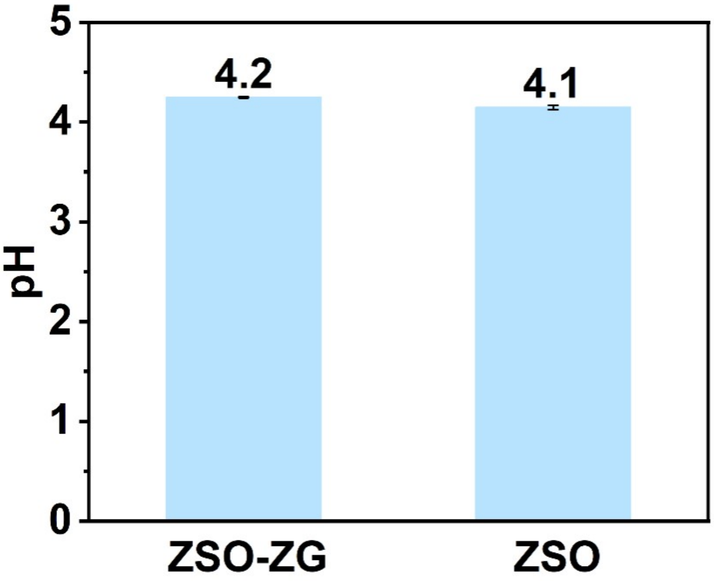

Fig. S2 The pH results of different electrolytes.

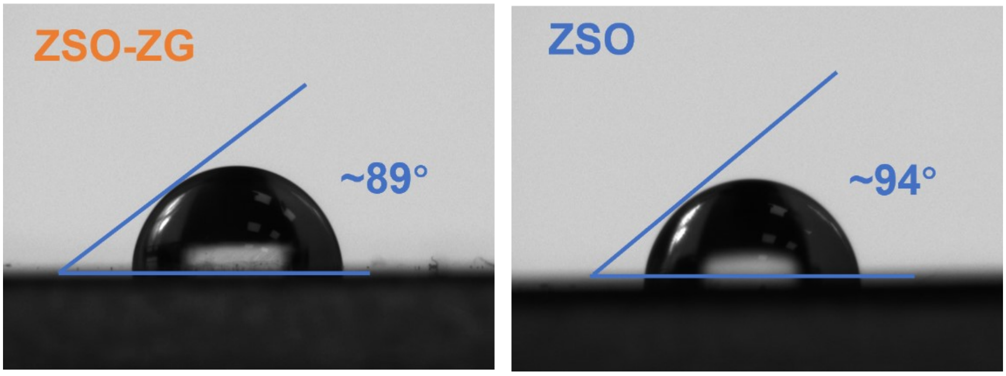

Fig. S3 Contact angle tests of ZSO-ZG and pure ZSO electrolytes on Zn foil.

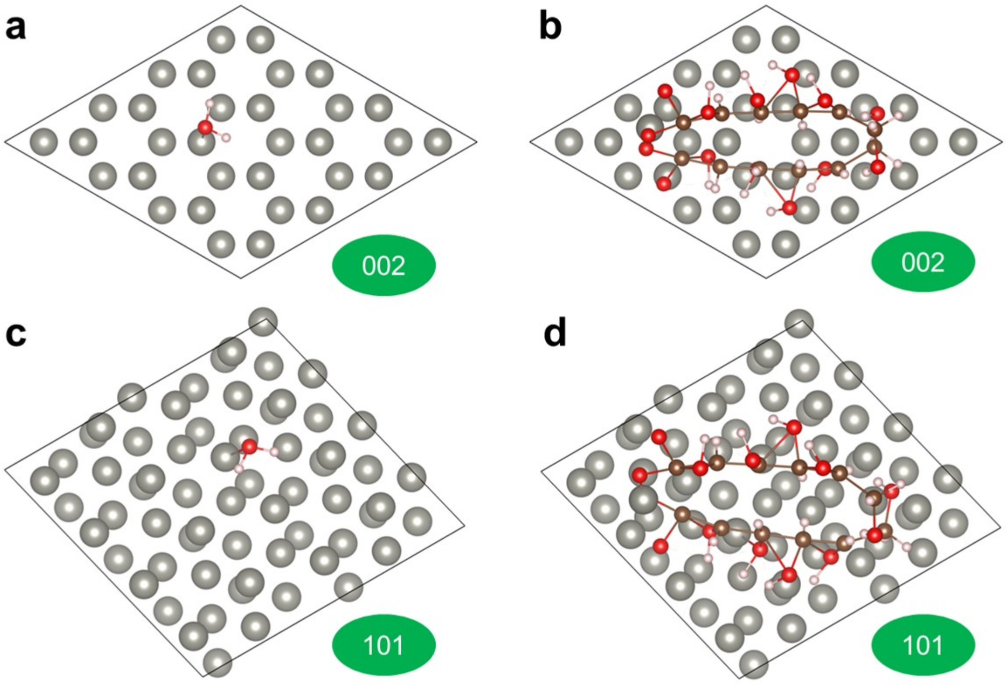

Fig. S4 The corresponding molecular models for adsorption.

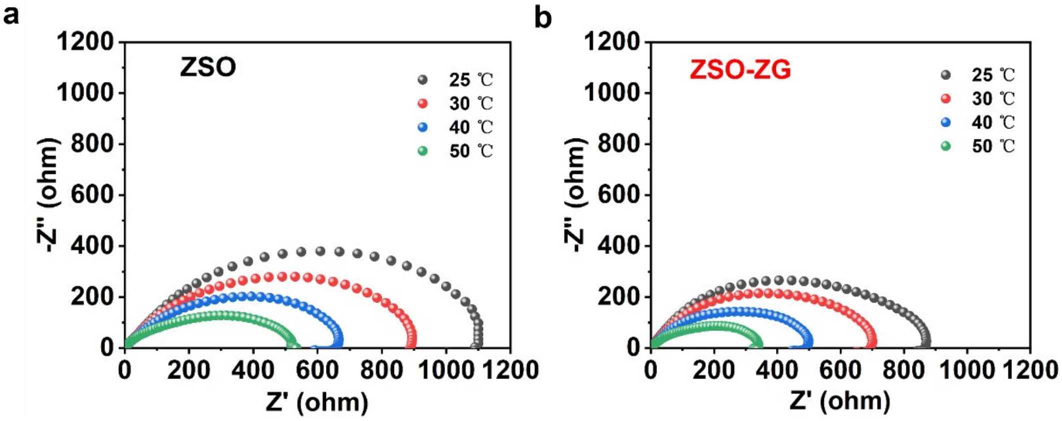

Fig. S5 The temperature-dependent EIS plots of the different electrolyte (a) ZSO and (b) ZSO-ZG.

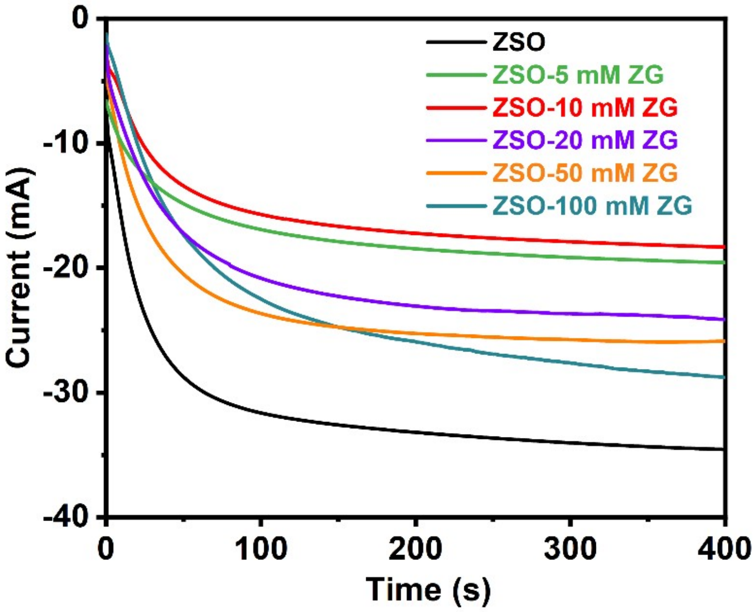

Fig. S6 The CA results of various electrolytes.

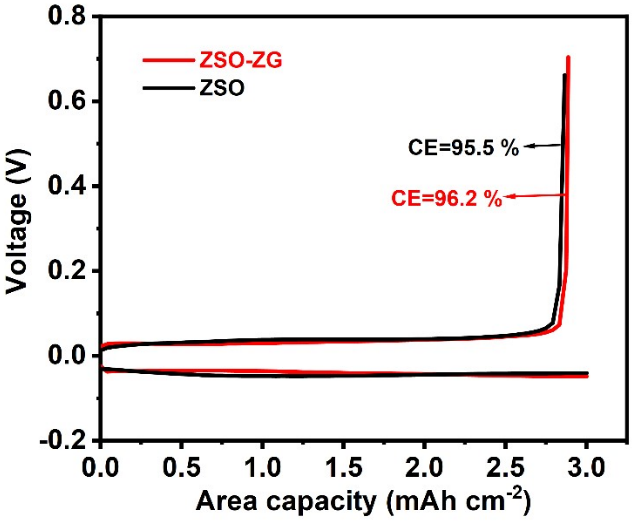

Fig. S7 The Coulombic efficiency comparison of asymmetric cells at 1st cycle.

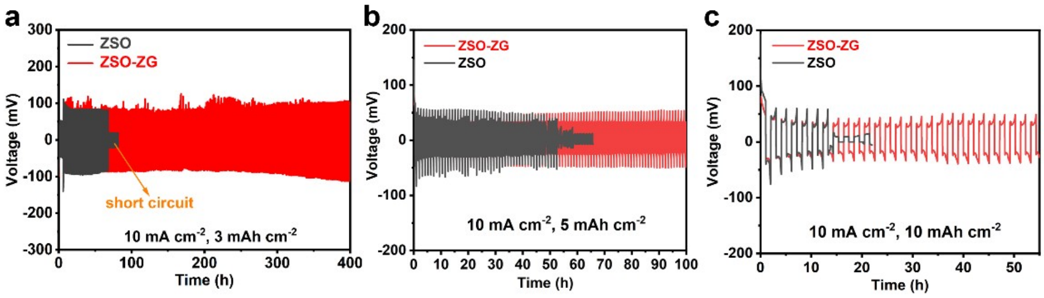

Fig. S8 The cycling performance of Zn|Zn symmetric cells with different electrolytes at (a) 10 mA cm^{-2}, 3 mAh cm^{-2} (DOD: 10%), (b) 10 mA cm^{-2}, 5 mAh cm^{-2} (DOD: 17%) and (c) 10 mA cm^{-2}, 10 mAh cm^{-2} (DOD: 33%).

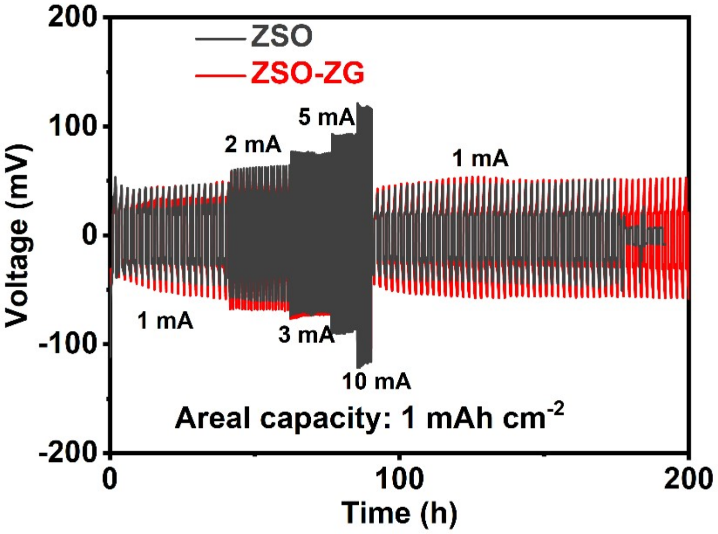

Fig. S9 The rate performance of Zn|Zn symmetric cells with different electrolytes.

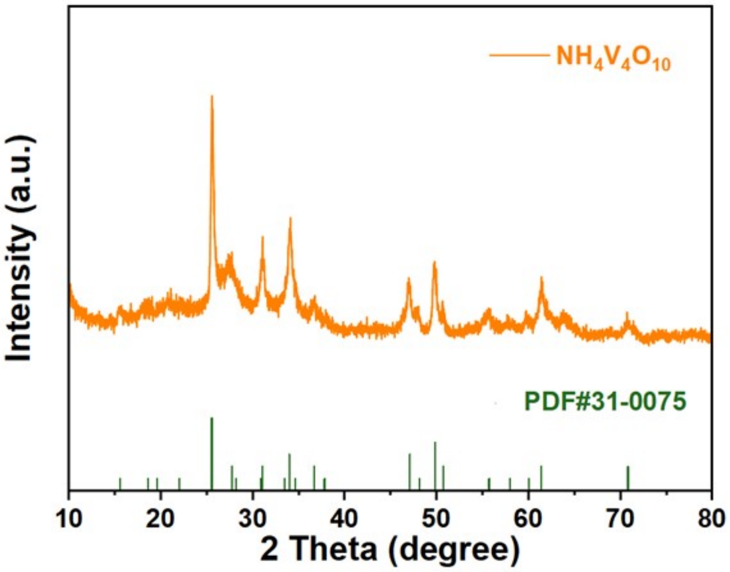

Fig. S10 The XRD pattern of NVO material and related standard pattern (PDF#31-0075).

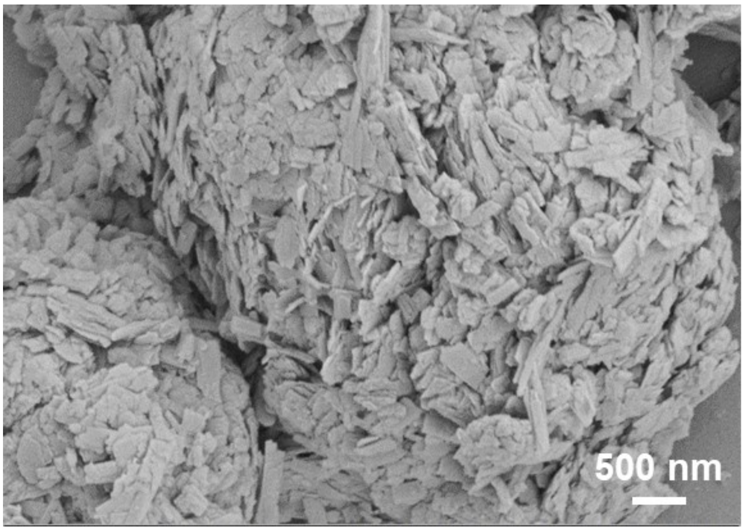

Fig. S11 The SEM image of prepared NVO sample.

Reference

1 B. Y. Tang, et al, Engineering the Interplanar Spacing of Ammonium Vanadates as a High-performance Aqueous Zinc-ion Battery Cathode, *J. Mater. Chem. A*, 2019, **7**(3), 940-945.