Supplementary Information (SI) for Journal of Materials Chemistry A.

Rational design of an organic-anionic electrolyte additive for zinc-ion battery

Shan Wang,† Shuo Li,† Junsheng Zhu*

School of Chemical Engineering and Technology, China University of Mining and Technology, Xuzhou, 221116, China.

* Corresponding author: Junsheng Zhu (J. Zhu), Dr.

E–mail address: zhujschina@163.com, zhujunsheng@cumt.edu.cn (J. Zhu)

† These authors contributed equally to this work.

1. Experiments and Characterization

1.1. Synthesis of $K_{0.5}Mn_2O_4{\cdot}1.5H_2O$

First, 0.5 g of $KMnO_4$ was sufficiently ground and transferred into a tube furnace. The powder was heated to 500 ^{o}C for 4 h in an Ar atmosphere. After cooling to room temperature, the product was washed with deionized water and filtered for seven times. Finally, the resultant powder was dried at 65 ^{o}C for 9 h, yielding the target product $K_{0.5}Mn_2O_4{\cdot}1.5H_2O$ (KMO).

1.2 Characterization and electrochemical tests of the materials

The crystal structures of the zinc anodes were investigated by using XRD (X-ray diffraction, Bruker D8 Advance), the microstructure and structure of the zinc anodes and KMO were analyzed by using FESEM (Field emission scanning electron microscope, TESCAN MAIA3LMH). The elemental composition of zinc anodes had been confirmed by using XPS (X-ray photoelectron spectroscopy, ESCALAB 250Xi).

The active material, acetylene black and PTFE were mixed evenly with deionized H_2O as the solvent in a ratio of 7:2:1 by mass, and coated onto a stainless-steel mesh (14 mm in diameter). The amount of the active material on each positive electrode was ~1 mg. Subsequently, the battery was constructed into a CR2032 cell battery using a piece of zinc foil (the thickness is 0.1 mm and the diameter is 14 mm) as the anode and glass fiber filter as the septum (16 mm in diameter) for testing the electrochemical performance. The cyclic voltammetry (CV) tests were conducted on an electrochemical workstation model CHI604E. Additionally, electrochemical impedance spectroscopy

(EIS) measurements were performed within a frequency range spanning from 100000 Hz to 0.01 Hz. The galvanostatic charge-discharge (GCD) experiments were carried out on the Neware battery tester by applying voltage limits between 0.8 V and 1.8 V.

$$Z^{'} = R_{s} + R_{SEI} + R_{ct} + \sigma\omega^{-0.5} \tag{S1}$$

$$D = \frac{R^2T^2}{2A^2n^4F^4C^2\sigma^2} \tag{S2}$$

Where R is the constant, F is 96485 C mol^{-1}, T represents the absolute temperature, A represents the electrode area, C is the concentration of zinc ion, σ is the Warburg factor, n is the number of electrons per molecule in the oxidation

1.3 DFT calculation

The density functional theory (DFT) calculations were performed using the CASTEP module in Materials Studio. The calculations employed the PBE functional under the generalized gradient approximation (GGA) to describe the exchange-correlation interaction. The plane wave cutoff energy was set at 450 eV. For the adsorption system, the geometries of the individual substrate model and the adsorbed molecule were fully optimized until the forces on the atoms were less than 0.05 eV/Å and the energy change of the system was less than 1.0×10^{-5} eV/atom. Subsequently, the adsorbate was placed on the substrate surface, the adsorption configuration was constructed, and it was subjected to the same structural relaxation to obtain the most stable adsorption geometry. The total energy of the system was calculated on the optimized structure. The adsorption energy (E_{ads}) was calculated using the formula $E_{\text{ads}} = E_{\text{total}} - (E_{\text{slab}} + E_{\text{molecule}})$, where E_{total} is the total energy of the adsorption system, E_{slab} is the energy of the substrate, and E_{molecule} is the energy of the isolated adsorbed molecule.

1.4 Molecular dynamics (MD) simulations

The radial distribution functions (RDF) and coordination numbers of Zn^{2+} and water molecules were calculated for the pure $ZnSO_4$ solution (containing 2700 water molecules and 35 $ZnSO_4$) and the $ZnSO_4$ solution with added AM and SABS (containing 2700 water molecules, 35 $ZnSO_4$, 21 AM and 7 SABS) systems, respectively. The simulation was completed using Materials Studio. The water molecules were described using the Amorphous Cell model, and the remaining molecules were described using the COMPASS III force field.

The simulation was carried out under periodic boundary conditions (PBC), and the initial size of the simulation box was set at 4.5 nm × 4.5 nm × 4.5 nm. The NPT ensemble was adopted. The temperature control was carried out using the Langevin integrator (with an integration step size of 2 fs and a friction coefficient of 1 ps^{-1}), and the pressure control was implemented using the Monte Carlo pressure coupling method. The trajectory is output once every 0.1 ns (i.e., 50,000 steps), and the total simulation duration is 4 ns. Then the production run was subsequently performed at $T = 298$ K over 5 ns in the NVT ensemble.

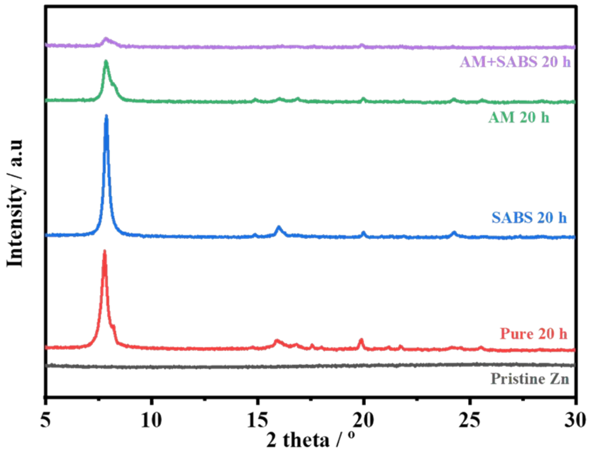

Fig. S1 The XRD patterns of zinc anodes after cycling for 20 h in Pure, AM, SABS and AM+SABS.

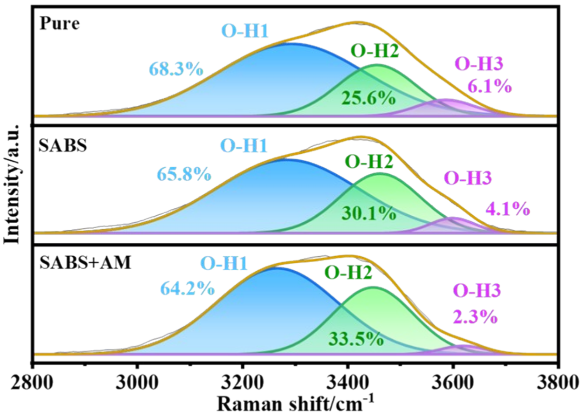

Fig. S2 The Raman spectra of the Pure, SABS and SABS+AM electrolyte.

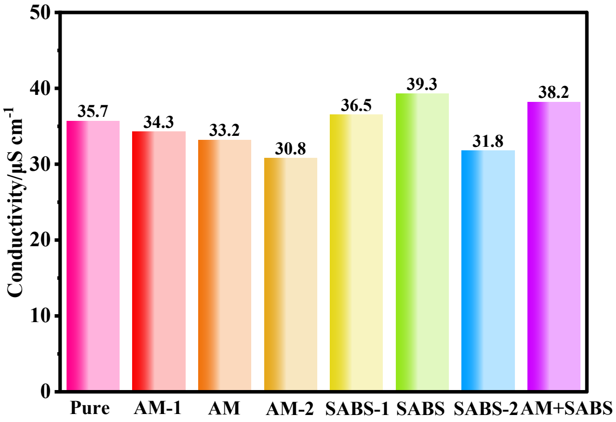

Fig. S3 The ionic conductivity of different electrolyte.

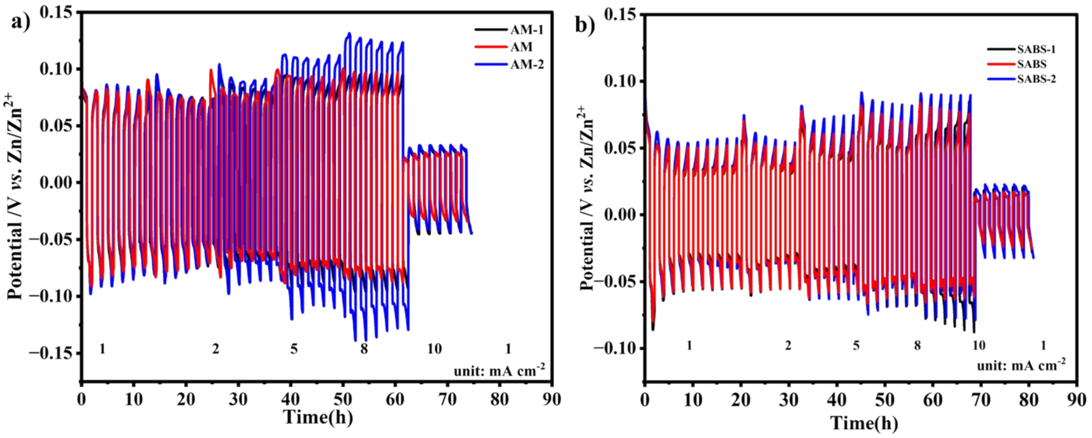

Fig. S4 (a) The rate performance of AM-1, AM and AM-2 from 1 to 10 mA cm^{-2} with 1 to 10 mAh cm^{-2}; (b) The rate performance of SABS-1, SABS and SABS-2 from 1 to 10 mA cm^{-2} with 1 to 10 mAh cm^{-2}.

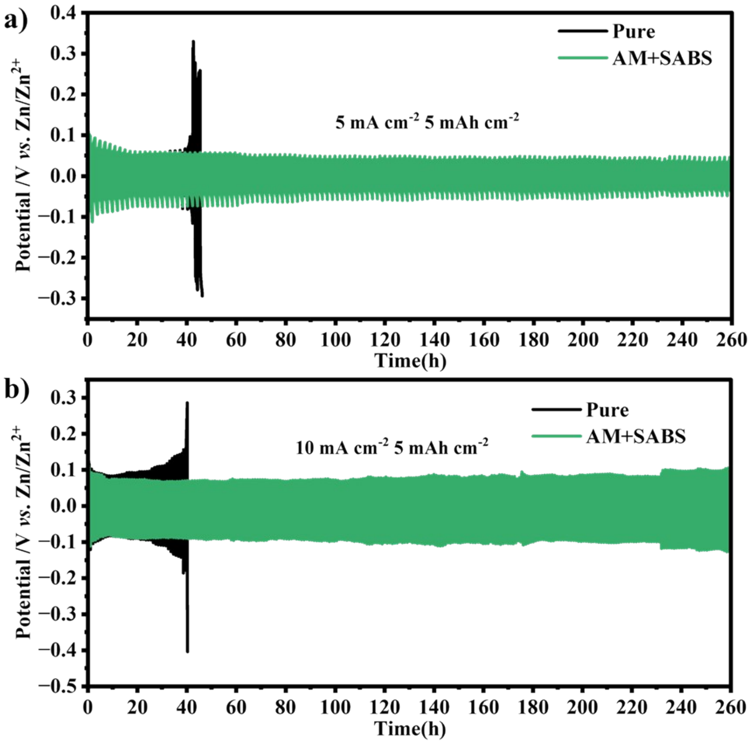

Fig. S5 The cycling performance of the Zn||Zn symmetric cells at (a) 5 mA cm^{-2} and (b) 10 mA cm^{-2}.

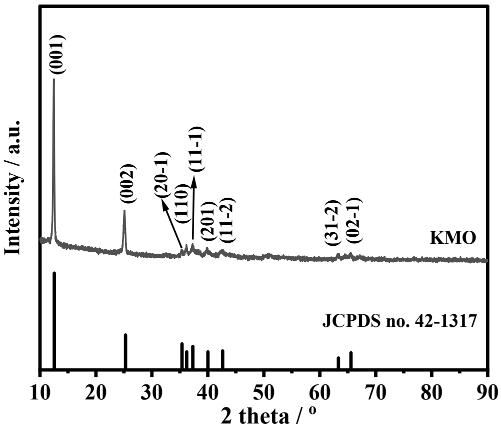

Fig. S6 The XRD pattern of KMO.

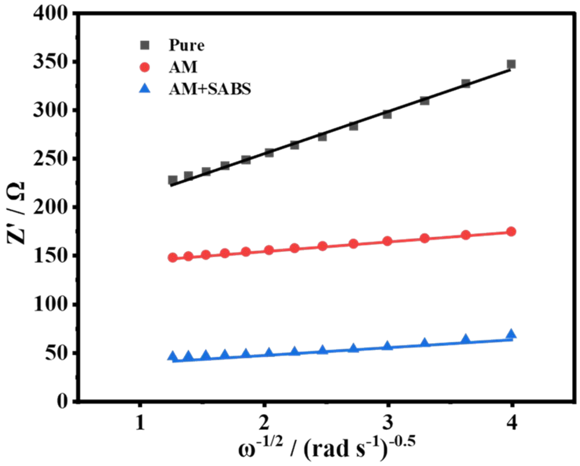

Fig. S7 The Z' *vs.* $\omega^{-0.5}$ plots of Zn||KMO with Pure, AM, and AM+SABS.

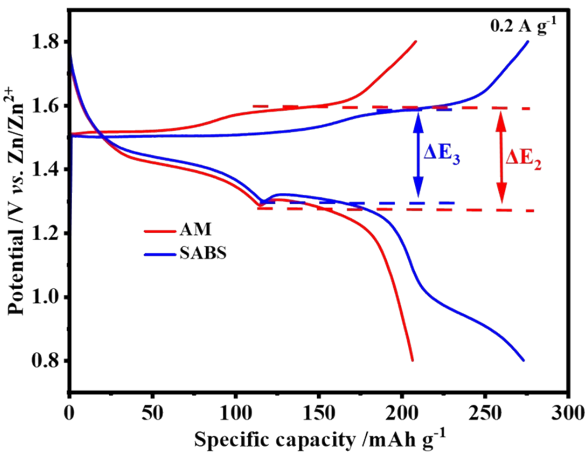

Fig. S8 The GCD curves of Zn||KMO with AM, and SABS.

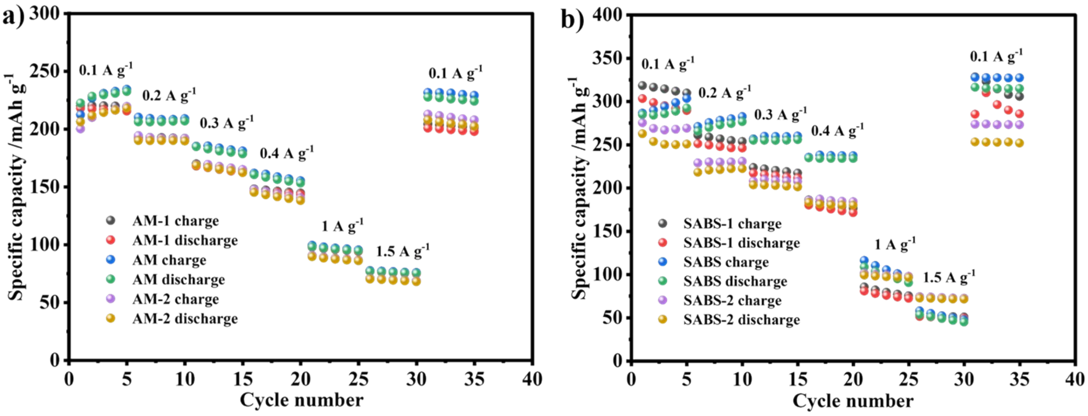

Fig. S9 (a) The rate performance of Zn||KMO using the AM-1, AM and AM-2 electrolyte; (b) The rate performance of Zn||KMO using the SABS-1, SABS and SABS-2 electrolyte.

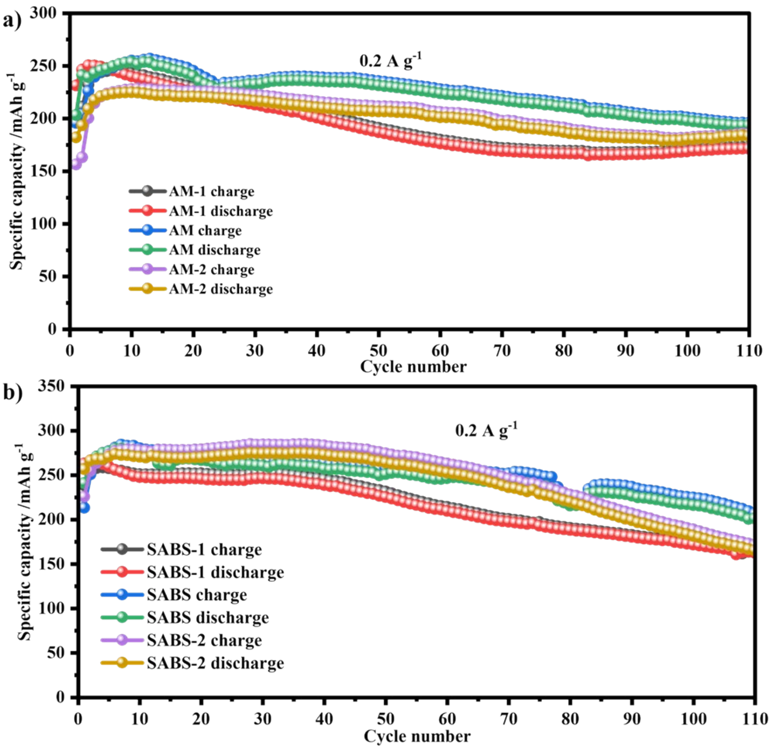

Fig. S10 (a) The cycling performance of Zn||KMO using the AM-1, AM, and AM-2 electrolyte at 0.2 A g^{-1}; (b) The cycling performance of Zn||KMO using the SABS-1, SABS, and SABS-2 electrolyte at 0.2 A g^{-1}.