Supplementary Information

Dynamic surface protection of a Zn anode by *N*,*N*-dimethylamide-based molecules for use in aqueous batteries

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Experimental section

Preparation of electrolytes

The 3 mol kg^{-1} $ZnSO_4$ electrolyte was prepared by dissolving $ZnSO_4 \cdot 7H_2O$ in deionized water. Different *N*,*N*-dimethylamide additives with 0.1 vol% were further added. Due to the low amount of DMB additive, it presented minor effect on the physical properties of the electrolyte (Fig. S10).

Preparation of cathode material

The $V_6O_{13} \cdot H_2O$ material was obtained with a previously reported method.[1] In a typical synthesis, 2.73 g V_2O_5 and 4.52 g $H_2C_2O_4$ were added into 40 mL deionized water. The mixture was stirred at 90 ◦C for 1 h and transferred into a Teflon-lined autoclave. Subsequently, 10 mL H_2O_2 and 30 mL ethanol were added. The autoclave was heated at 180 ◦C for 3 h. After cooling down to room temperature, the product was filtered, washed with deionized water and ethanol, and dried at 60 ˚C under vacuum overnight.

Material characterizations

The morphologies were obtained on a SU8010 scanning electron microscope (HITACHI). The in situ Zn deposition microscopy images were recorded on the metallurgical microscope (CMM-90AE, China). X-ray diffraction (XRD) was performed on a PANalytical Empyrean diffractometer with Cu Kα radiation. Contact angles were measured on JY-82. Viscosities were measured on DV-II+ Pro (AMETEK Brookfield). Conductivies were measured on FE38 (METTLER TOLEDO). pH was measured on PHS-3E.

Electrochemical measurements

The electrochemical performance of Zn//Zn, Zn//Cu, and Zn//$V_6O_{13} \cdot H_2O$ cells was tested in 2032 coin-type cells. The separators consisted of two layers of filter paper with an average thickness of 0.1 mm, and 70 µL electrolyte was added. The $V_6O_{13} \cdot H_2O$ cathode was prepared by mixing the active material, Super P carbon and polyvinylidene fluoride (PVDF) binder at a mass ratio of 6:3:1 in *N*-methyl pyrrolidone (NMP), drop cast on graphite foil substrate and vacuum dried at 60 ºC overnight. The electrochemical double layer capacitance (EDLC) was calculated by the linear fits of i–v plots. Linear polarization was carried out in three-electrode cells with Zn foil, Cu foil, and saturated calomel electrode (SCE) as the working, counter, and reference electrodes, respectively. All electrochemical measurements were performed on Bio-logic VMP3 or LANHE CT2001A battery test systems at 27 ºC.

Theoretical calculations

The adsorption energies of different molecules on Zn were calculated by the DMol3 program package in Materials Studio. The exchange and correlation terms were determined using the Generalized Gradient Approximation (GGA) in the form proposed by Perdew, Burke, and Ernzerhof (PBE). The energy convergence criterion was set to 10^{-6} Hartree. All calculations including geometry optimization, single-point energy and electronic density were carried out under a periodic boundary condition. In the Z direction, there was about 15 Å vacuum for erasing the effect of periodic condition for slab model. The 6 × 6 supercells with four layers of Zn (002) or Zn (100) face were used to represent the adsorbed surface. All simulations were carried out with the standard periodic boundary condition and the simulation time was long enough to ensure the equilibrium states of electrolyte systems.

Supplementary figures

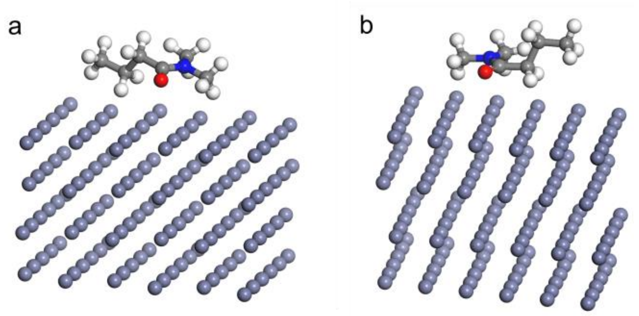

Fig. S1. The adsorptions of DMB on the surface of (a) Zn (100) and (b) Zn (002) planes.

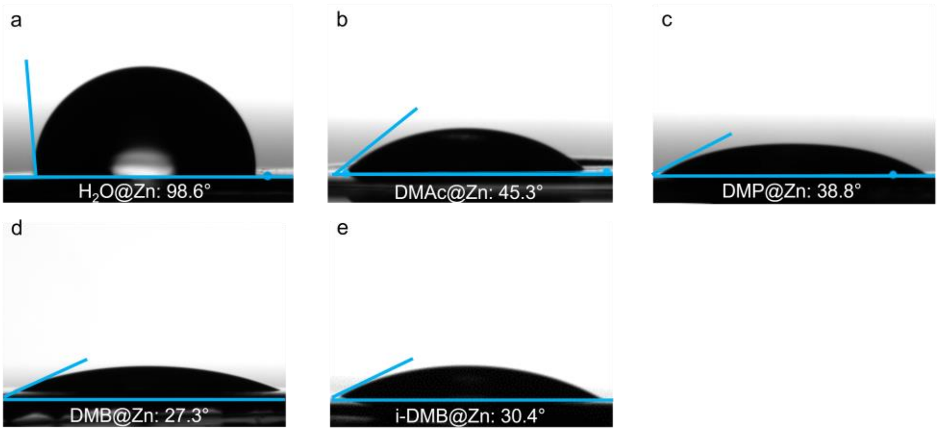

Fig. S2. Contact angle measurements of (a) water, (b) DMAc, (c) DMP, (d) DMB, and (e) i-DMB solvents on Zn foil.

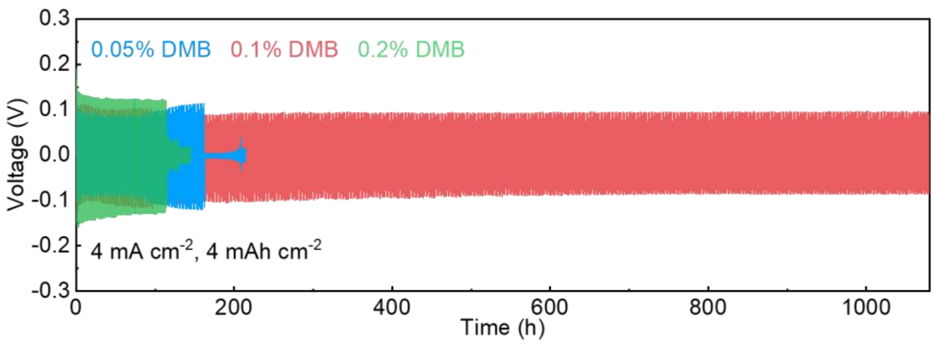

Fig. S3. The cycle performance of Zn symmetric cells in the $ZnSO_4$ electrolytes with different percentages of DMB additive.

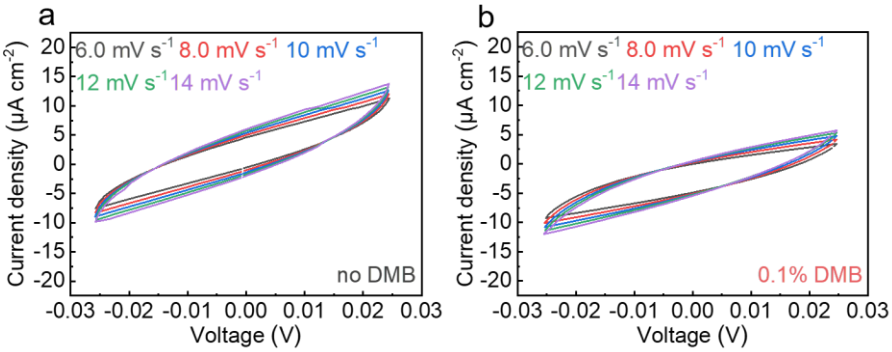

Fig. S4. CV curves of Zn symmertic cells in the non-Faradic range in the $ZnSO_4$ eletrolytes (a) without and (b) with the DMB additive.

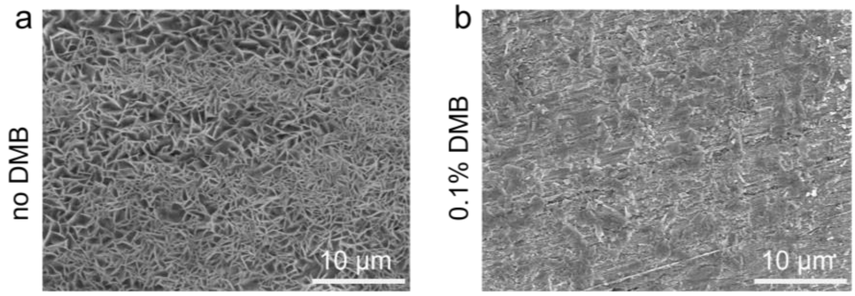

Fig. S5. SEM images of Zn foils soaked in the $ZnSO_4$ electrolytes (a) without and (b) with the DMB additive for 12 h.

Fig. S6. Optical images of Zn plating/stripping in beaker cells at the 50th cycle in the $ZnSO_4$ eletrolytes (a) without and (b) with the DMB additive.

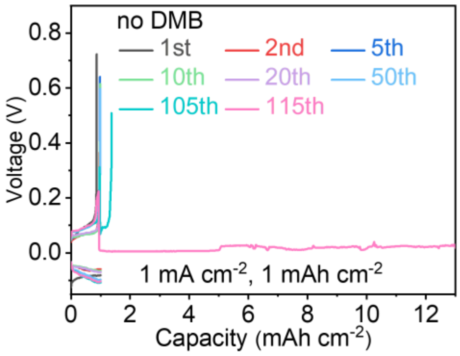

Fig. S7. Voltage curves of Zn plating/stripping on Cu substrate in the $ZnSO_4$ electrolyte.

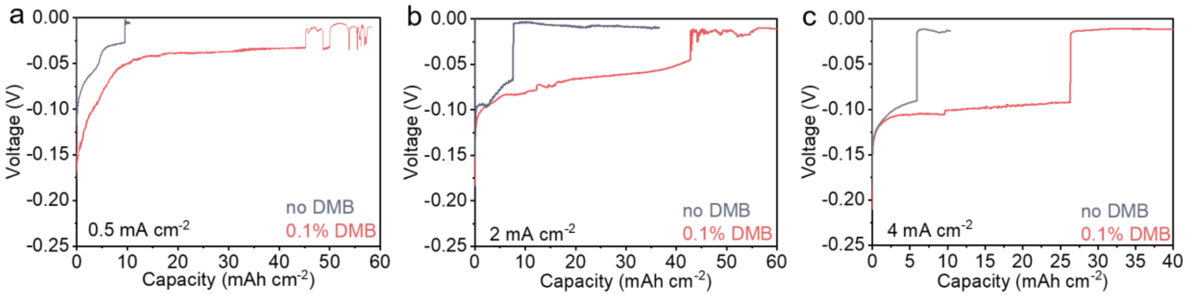

Fig. S8. Voltage-capacity curves of single continuous Zn deposition at different current densities in the two electrolytes.

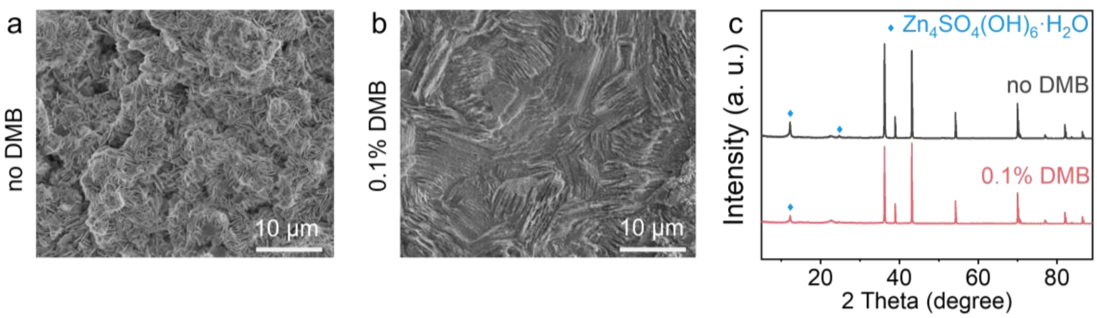

Fig. S9. (a,b) SEM images (c) XRD patterns and of Zn anodes after 50 cycles from full batteries with the two electrolytes at 5 A g^{-1}.

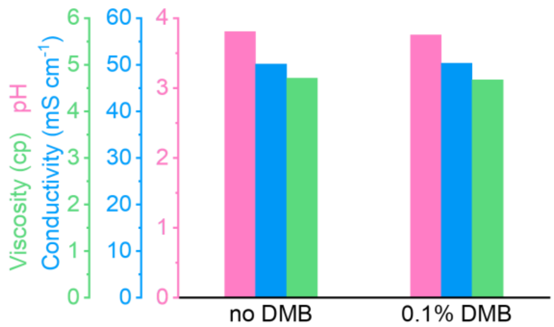

Fig. S10. The physical properties of the two electrolytes.

Reference

[1] J. Lai, H. Zhu, X. Zhu, H. Koritala and Y. Wang, ACS Appl. Energy Mater., 2019, **2**, 1988−1996.