Electronic Supplementary Information

A low concentration electrolyte additive for constructing solid-electrolyte interphase on a Zn metal anode for aqueous batteries

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1. Experimental Section

1.1. Electrolyte preparation. Zinc sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$, Aladdin, 98%), manganese sulfate monohydrate ($MnSO_4 \cdot H_2O$, Aladdin, 99%), and 1,4-dioxane (DX, Innochem, 99.8%) were used as received. The benchmark electrolyte was 2 M $ZnSO_4$. The electrolytes with DX additive were prepared by dissolving $ZnSO_4$ in DX-water mixed solvents.

1.2. Electrode Preparation. The α-MnO_2 cathode material was prepared according to a previous report.[1] Typically, 0.35 g $KMnO_4$ and 1.65 mL HCl (36 ~ 38 %) were dissolved in 35 mL deionized water. The solution was transferred into a 50 mL autoclave and heated at 140 °C for 16 h. The product was filtered, washed with water and dried at 60 °C. For the cathode preparation, the α-MnO_2 active material, Super P carbon, and poly(vinylidene difluoride) (PVDF) binder were mixed with a mass ratio of 7:2:1 in N-methylpyrrolidone (NMP). The obtained slurry was drop casted on carbon paper substrate and dried at 80 °C.

1.3. Material Characterizations. X-ray diffraction (XRD) was measured on a PANalytical Empyrean diffractometer with Cu Kα radiation. The morphology was obtained by a SU8010 scanning electron microscope (HITACHI, Japan). For the characterizations of solid-electrolyte interphase (SEI), Zn powder electrodes were cycled at 2 mA cm^{-2} and 2 mAh cm^{-2} for 20 times in the 1% DX electrolyte. Subsequently, high-resolution transmission electron microscopy (HRTEM) images were recorded on JEM-ARM200F and Fourier transform infrared (FT-IR) spectroscopy was conducted with a Vertex-70 spectrometer (BRUKER, Germany). In-situ zinc deposition microscope images were recorded on metallurgical microscope CMM-90AE (Shanghai optical instrument factory, China). Contact angles were measured on JY-82. They were tested after the stabilization of the contact, which took approximately 30 seconds to 1 min. They did not change over time afterwards.

1.4. Electrochemical Measurements. Zn//Zn, Zn//Cu, and Zn-MnO_2 cells were assembled in coin cells with filter paper as separators. Linear sweep voltammetry (LSV) was used to evaluate the HER behaviors in three-electrode cells with Cu, carbon paper, and saturated calomel electrode (SCE) as the working, counter, and reference electrodes, respectively. Cyclic voltammetry (CV) measurements were performed with the replacement of carbon paper and SCE by Zn as counter and reference electrodes. Chronoamperometry (CA) tests were performed with Zn as the working, counter and reference electrodes. All electrochemical measurements were carried out on LANHE CT2001A battery cycler or Bio-logic VMP3.

1.5 Theoretical calculations. The adsorption energy and binding energy calculations were performed using the DMol3 package. The Perdew-Burke-Ernzerhof (PBE) functional based on the generalized gradient approximation (GGA) with D2 dispersion correction was used. The energy convergence criterion was set to 10^{-6} Hartree. A 15 Å vacuum was applied in the z-direction. A 5×5 supercell with four Zn (002) layers was used to study the adsorbed surface, with the bottom two layers kept fixed to maintain bulk properties. The energy levels calculations were performed using the Gaussian16 software.
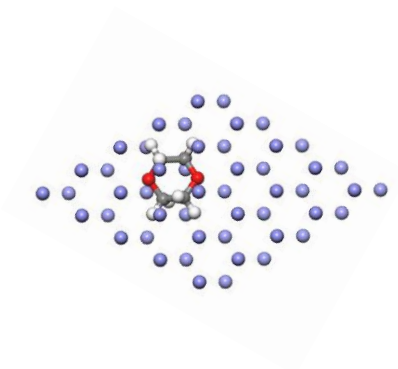
2. Supplementary Figures

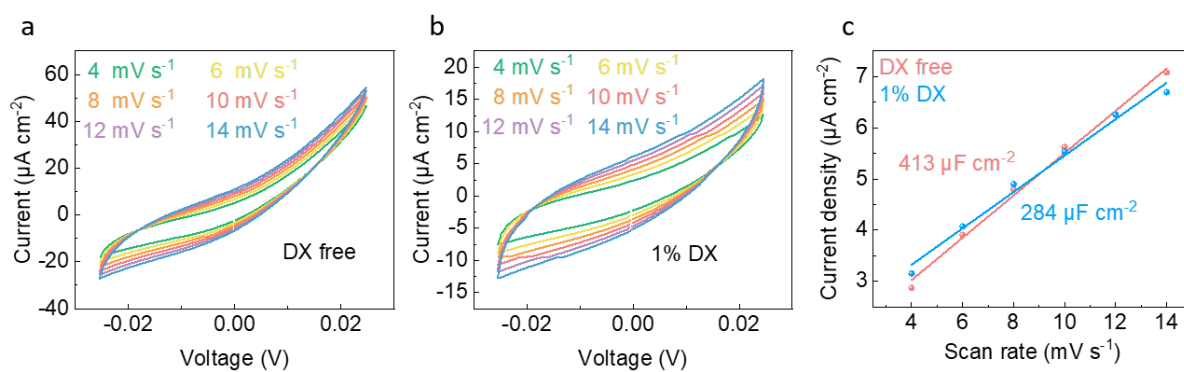Fig. S1 Top view of DX adsorption on the surface of Zn.

Fig. S2 CV curves of Zn electrode in (a) DX free, (b) 1% DX electrolytes in the non-Faraday region at various scan rates, and (c) the linear fits to calculate EDLC.
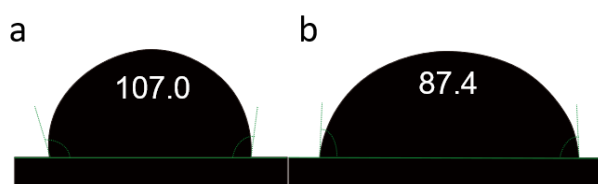

Fig. S3 Contact angle measurements of (a) DX free and (b) 1% DX solutions on Zn foil.
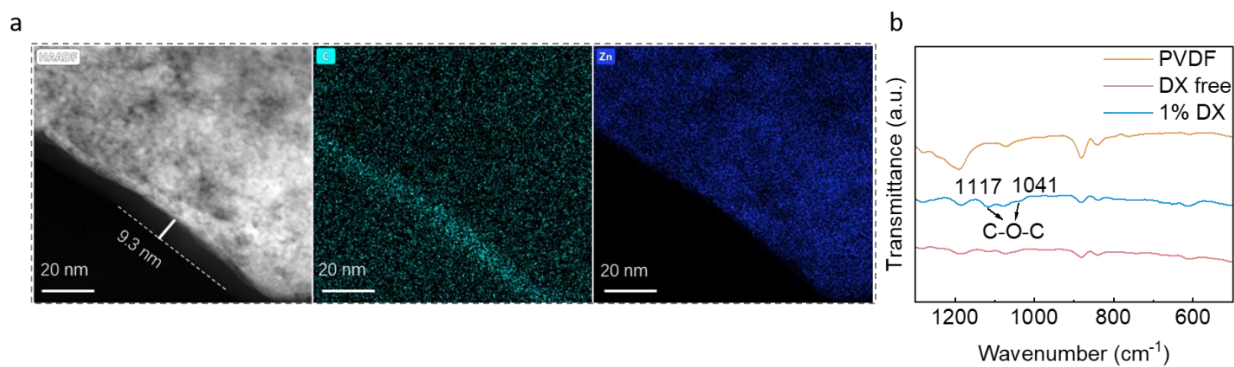
Fig. S4 (a) EDS mapping of Zn powder electrode cycled in the 1% DX electrolyte. (b) FT-IR spectra of Zn powder electrode cycled in the two electrolytes and PVDF binder.
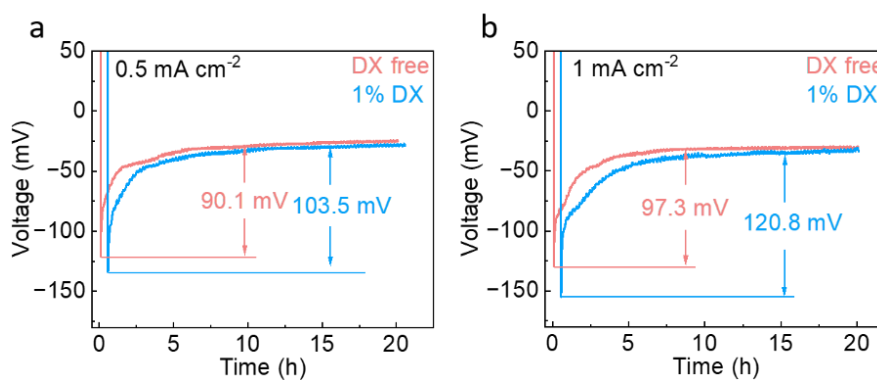

Fig. S5 The galvanostatic deposition at a) 0.5 mA cm^{-2} and b) 1.0 mA cm^{-2}.
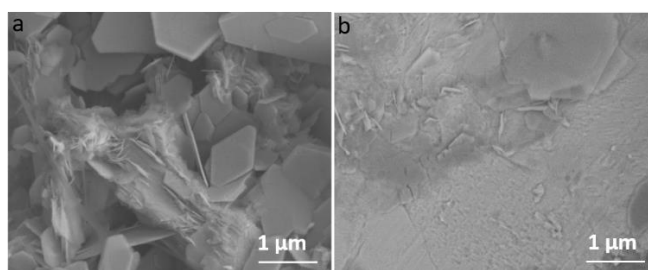

Fig. S6 SEM images of Zn electrodes subjected to 20 cycles with the ZnSO$_4$ electrolytes (a) without and (b) with 1% DX.
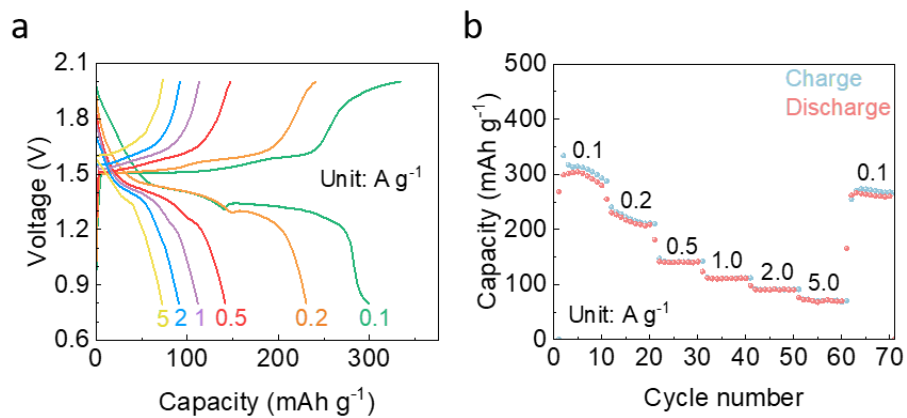
Fig. S7 (a) Charge-discharge curves and (b) capacities at different current densities of the MnO$_2$ cathode in the ZnSO$_4$ electrolyte.

3. Reference

1. W. Chen, R. B. Rakhi, H. N. Alshareef, J. *Mater. Chem. A*, 2013, **1**, 3315-3324.