Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

An organic-inorganic solid-electrolyte interface generated from dichloroisocyanurate electrolyte additive for a stable Zn metal anode in aqueous Zn batteries

Fangming Liu, Kuo Wang*, Qianrui Li, Guoli Zhang, Jiaqi Zhu, Xiao-Xia Liu and Xiaoqi Sun*

Department of Chemistry, Northeastern University, 3-11 Wenhua Road, Shenyang 110819, China

*Corresponding authors.

E-mail: 2110043@stu.neu.edu.cn; sunxiaoqi@mail.neu.edu.cn

1. Experimental Section

1.1 Synthesis of α-MnO_2. α-MnO_2 was obtained according to a literature procedure.[1] Typically, 0.3506 g $KMnO_4$ and 1.65 mL HCl (36%~38%) were mixed in 35 mL deionized water. The mixture was transferred to a 50 mL autoclave, which was heated at 140°C for 16 h. After cooling down to room temperature, the product was filtered, washed with deionized water and ethanol repeatedly, and dried at 60 °C for 24 h in a vacuum oven.

1.2 Characterizations. Ionic conductivities were measured on FiveEasy Plus FE38 (METTLER TOLEDO, Switzerland). X-ray photoelectron spectroscopy (XPS) was collected on Thermo Scientific K-Alpha, with the data analyzed using CasaXPS software and calibrated by referencing the C 1s peak to 284.8 eV. Fourier transform infrared (FT-IR) spectroscopy was measured on VERTEX70 (Germany). The Zn deposition microscopy images were recorded on CMM-90AE (China) metallurgical microscope. Scanning electron microscopy (SEM) images were obtained by HITACHI SU 8010 (Japan).

1.3 Electrochemical measurements. The cathodes were prepared by mixing α-MnO_2, Ketjen black (KB) carbon and polyvinylidene fluoride (PVDF) binder at the weight ratio of 7:2:1 in 1-methyl-2-pyrrolidinone (NMP). The slurry was drop casted on graphite paper substrate and dried at 90 °C in a vacuum oven. Zn||Zn, Zn||Cu and Zn||α-MnO_2 cells were assembled in CR2032 coin cells. The electrochemical impedance spectroscopy (EIS) was measured in Zn||Zn coin cells. Open circuit potential (OCP), Tafel and chronoamperometry (CA) measurements were performed in T-shaped Swagelok® three-electrode cells. OCP was measured with Zn foil as the working and counter electrodes, and saturated calomel electrode (SCE) as the reference electrode. Tafel plots were carried out with Zn foil, Cu foil and SCE as the working, counter and reference electrodes, respectively. CA measurements were performed with Zn foil as working, counter and reference electrodes. All electrochemical measurements were performed on LANHE CT2001A battery cycler or Bio-logic VMP3.

1.4 Theoretical calculations. The energy levels of lowest unoccupied molecular orbital (LUMO) were calculated using 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.

2. Supporting Figures

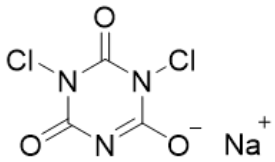

Fig. S1 The molecular structure of DCCNa.

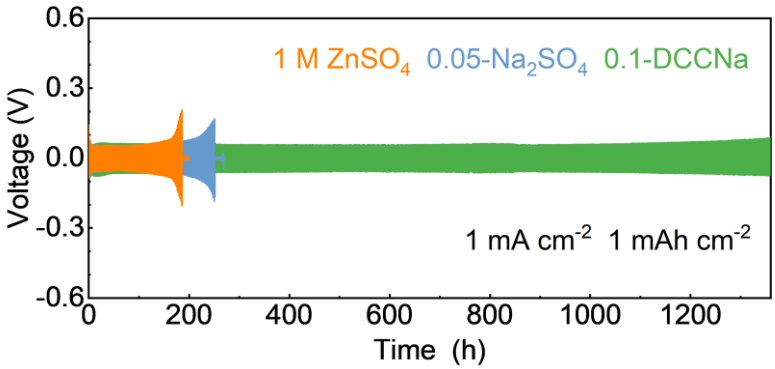

Fig. S2 Zn plating/stripping behaviors in symmetric Zn cells with different electrolytes at 1 mA cm^{-2} and 1 mAh cm^{-2}.

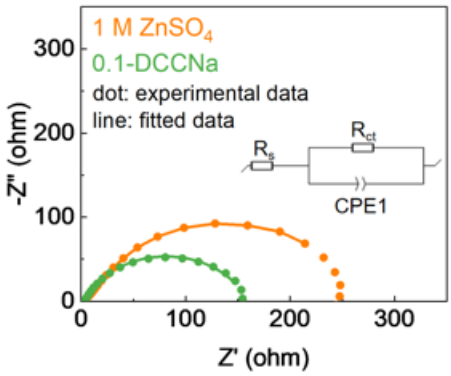

Fig. S3 Nyquist plots and fitted curves of Zn electrode in different electrolytes.

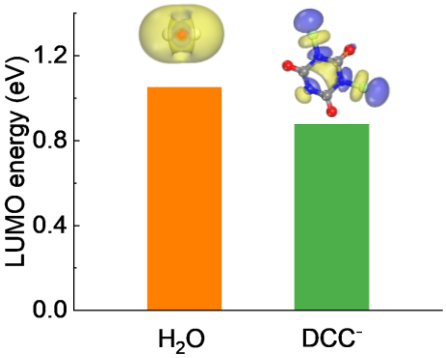

Fig. S4 The LUMO energy levels of H_2O and DCC^-.

3. Reference

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