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Rechargeable and Highly Stable Mn Metal Batteries Based on Organic Electrolyte

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Experimental Section

Materials. Chemicals for electrolyte preparation: N, N-Dimethylformamide (99.9%, Aladdin), ethylenediamine (AR. Guangzhou), Thiourea (99%, Aladdin), and Manganese bis(trifluoromethanesulfonate) (98%, BIDE) were directly used as received. Materials for anode and cathode preparation: Mn plates (99.8%, Tuopu metal materials of China) were polished to remove the surface passivation layer before using; 3，4，9，10-Perylenetetracarboxylic diimide (PTCDI, 95%, Macklin), nmethyl-2-pyrrolidone (NMP , 99%, Aladdin), poly(vinylidene fluoride) (PVDF, average Mw ~400000,

Aladdin), and Carbon coated aluminum foil (Canrd) were directly used. Glass fiber film (GF/D 1823-047, Whatman) was used as separator after being tailored into discs.

Electrolyte preparation. 0.5M $Mn(OTF)_2$ was dissolved in electrolyte with DMF:EDA=3:1, which was used as the experimental electrolyte. Meanwhile, 0.5M $Mn(OTF)_2$ was dissolved in DMF, DMF: thiourea= 3:1 and water as electrolytes of control group.

Electrode preparation. Mn plate was polished with sandpaper to remove the external passivation layer. PTCDI was mixed with Super C, and PVDF at the ratio of 7:2:1 using NMP as dispersing agent to produce a homogeneous slurry, which was pasted on carbon coated aluminum foil and then dried at 120℃ for about 12h to obtain the PTCDI cathode. The loading mass of PTCDI cathode is ca. 1 mg cm^{-2}.

Battery assembly. In Mn||Mn symmetric cells, Mn metal plates were used as the electrodes with glass fiber film as separator in various electrolytes for measurements. In preparation of Mn||PTCDI full cells, PTCDI cathodes were paired with Mn metal anodes and two pieces of glass fiber film as separator in electrolytes.

Electrochemistry measurements. The galvanostatic charge-discharge was performed with a battery tester (LAND) at room temperature, and the cyclic voltammetry (CV) was measured on an electrochemical workstation (CHI 660E). All electrochemical tests are performed under

environmental conditions.

Characterization. Morphology and microstructure observation for samples were measured by scanning electron microscopy (SEM, Hitachi Regulus 8100). The surface element analysis of the composite materials was conducted by X-ray photoelectron spectroscopy (XPS, K-Alpha 1063).

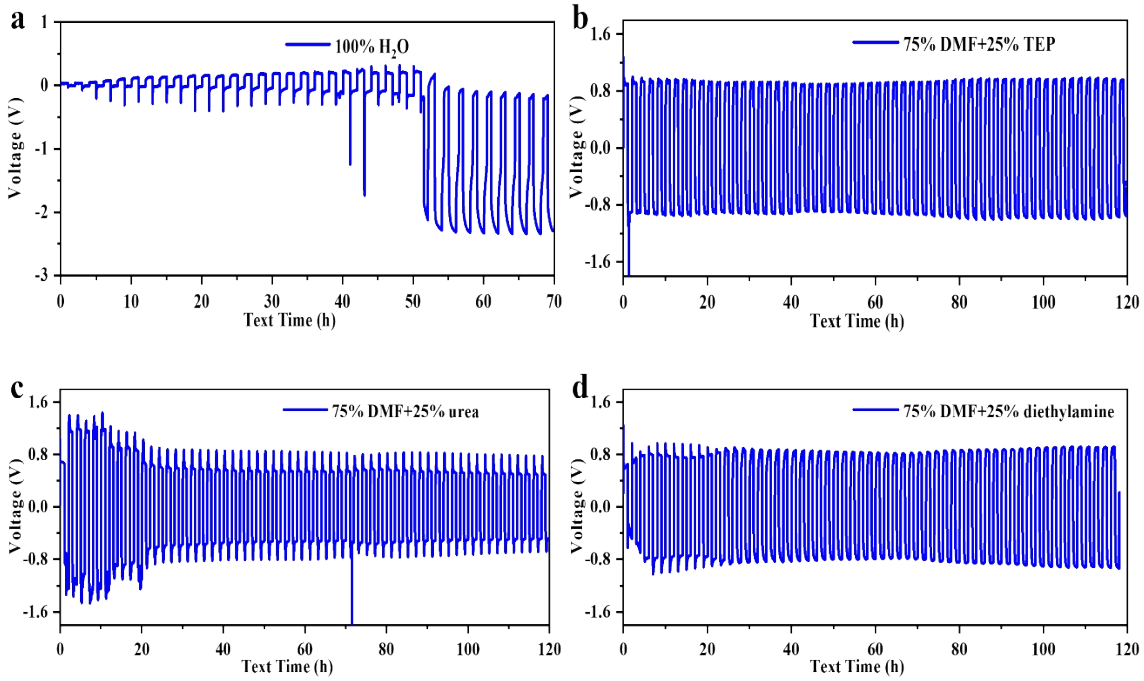

Figure S1. Long-term galvanostatic cycling of Mn||Mn symmetrical cells in various electrolyte with 0.5 M $Mn(OTF)_2$ at current density of 0.2 mA cm^{-2} and the area capacity for Mn anode is 0.2 mAh cm^{-2}. a) the electrolyte of 100% H_2O. b) the electrolyte of 75% DMF and 25% triethyl phosphate (TEP). c) the electrolyte of 75% DMF and 25% urea. d) the electrolyte of 75% DMF and 25% diethylamine.

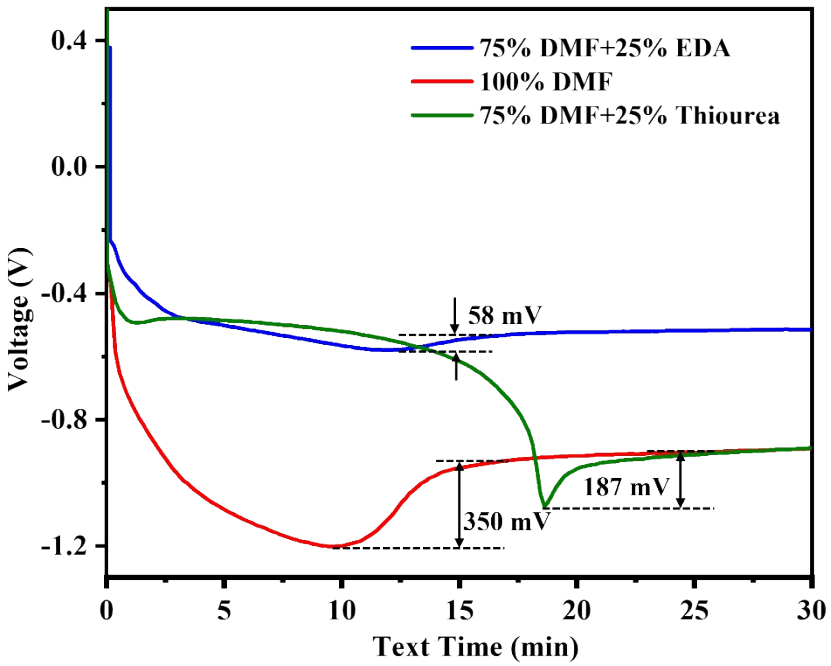

Figure S2. Nucleation overpotential of Mn||Mn symmetric cells in various electrolytes with 0.5 M $Mn(OTF)_2$ at current density of 0.2 mA cm^{-2} and the area capacity for Mn anode is 0.2 mAh cm^{-2}.

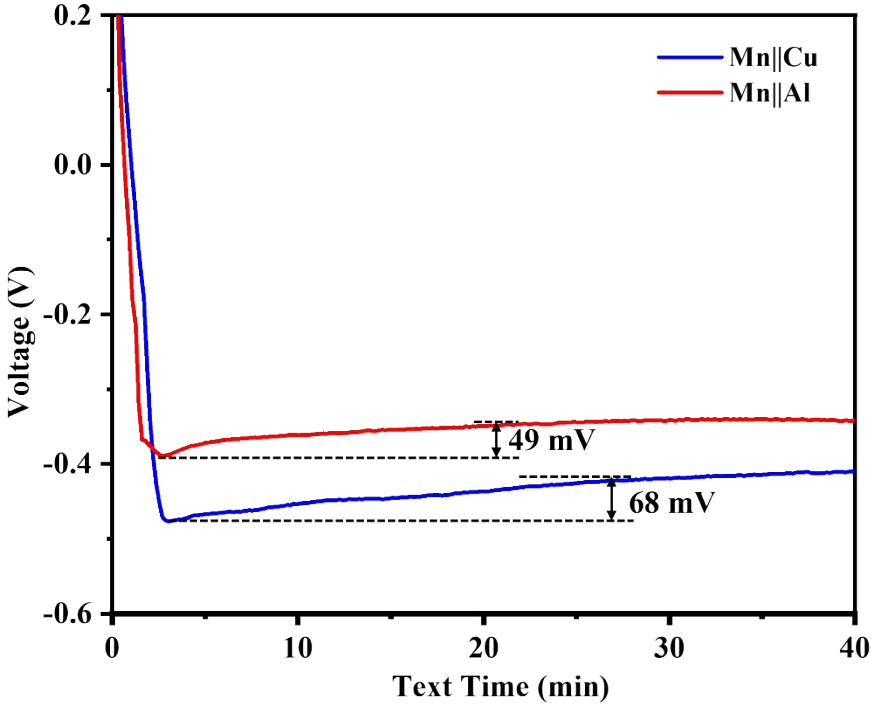

Figure S3. Nucleation overpotential of Mn||Cu and Mn||Al cells in DMF: EDA (3:1) electrolyte with 0.5 M $Mn(OTF)_2$ at current density of 0.2 mA cm^{-2}.

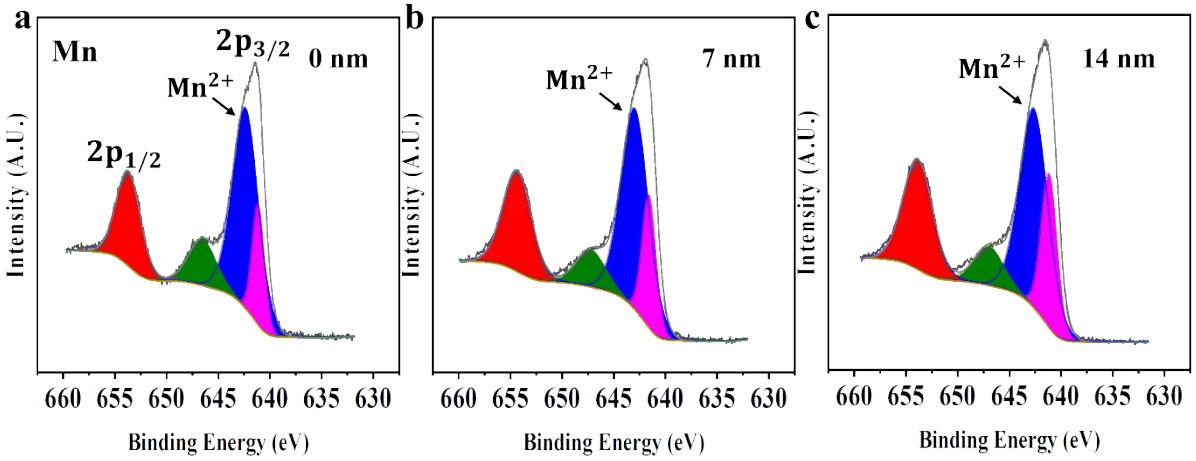

Figure S4. XPS spectra of Mn2p for Mn metal anode after 50 cycles in Mn||PTCDI full cells at C-rate of 0.5 C. a-c, In-depth XPS spectra of Mn2p after Ar^+ etching for 0 nm (a), 7 nm (b) and 14 nm (c).