# **Supporting Information**

# Revealing deposition/dissolution chemistry of MnO<sub>2</sub> for high-energy aqueous batteries

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### Experiment

#### 1. Chemicals

MnSO<sub>4</sub>·H<sub>2</sub>O (AR,  $\geq$ 99%), Na<sub>2</sub>SO<sub>4</sub> (AR,  $\geq$ 99%), FeSO<sub>4</sub>·7H<sub>2</sub>O (AR,  $\geq$ 99%), CuSO<sub>4</sub> (AR,  $\geq$ 99%), Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (AR,  $\geq$ 99%), KI (AR,  $\geq$ 99%), KBr (AR,  $\geq$ 99%) and TEMPO (2,2,6,6-tetramethylpiperidinyloxyl) were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. H<sub>2</sub>SO<sub>4</sub> (95%–98%) was purchased from Tianjin Jiangtian Chemical Technology Co., Ltd. All chemicals were used directly without further purification. Deionized water (18.2 M $\Omega$  cm<sup>-1</sup>) was used in all experiments.

#### 2. MnOOH synthesis

1 mmol KMnO<sub>4</sub> and 1.65 mmol CH<sub>3</sub>COONH<sub>4</sub> were dissolved in 30 mL deionized water, forming a uniform purplish red solution. The solution was magnetically stirred for 30 min, and then transferred to a stainless steel autoclave of 50 mL polytetrafluoroethylene for hydrothermal reaction at 180 °C for 24 h. After the reaction was cooled to room temperature, the black product was washed in centrifuge with deionized water and anhydrous ethanol for 3 times respectively, and then dried in vacuum oven at 60 °C for 12 h to obtain the black brown powder sample.<sup>1</sup> XRD patterns confirm that the MnOOH was successfully synthesized (Fig. S1).

#### 3. Material characterizations

Scanning electron microscopy (SEM) characterization was made using Regulus 8100 at 5 kV, and energy dispersive X-ray spectroscopy (EDX) mapping images were obtained at 15 kV. X-ray diffraction (XRD) patterns were collected on a Bruker D-8 diffractometer (Cu K $\alpha$  radiation,  $\lambda$ =0.154 nm) at room temperature. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo Fisher Scientific ESCALAB Xi<sup>+</sup> (Al K $\alpha$  radiation, hv = 1,486.6 eV). All of the binding

energies were referenced to the C 1s peak at 284.8 eV, referring to the XPS binding energy database of the US National Institute of Standard and Technology. Ultraviolet–visible (UV–vis) spectroscopy data were obtained using a UV–vis spectrometer (Evolution 220).

#### 4. EQCM measurements

Quartz crystal microbalance (QCM) operates based on the inverse piezoelectric effect of a quartz crystal and the change of the resonant frequency due to the change in the mass of the specimen. The validity of the rigid model of the QCM response is confirmed by the resonance resistance change ( $\Delta R$ ). The resistance value changes within the range from 472 to 486  $\Omega$ , which is much smaller than the frequency change (Fig. S2). Therefore, the mass change can be calculated from the resonator frequency change recorded by the QCM with the Sauerbrey equation<sup>2-5</sup> (Eq. S1):

$$\Delta f = -\left[\frac{2f_0}{A\left(\frac{\mu_q}{\rho_q}\right)^{\frac{1}{2}}}\right] \Delta m = -C_f \Delta m \qquad (Eq. S1)$$

where  $\Delta f$  is the frequency change (Hz),  $f_0$  is the fundamental resonance frequency of the crystal (Hz),  $\Delta m$  is the mass change (ng), and  $C_f$  (0.936 Hz ng<sup>-1</sup>) is the mass sensitivity of QCM. In this work, all deposited film layers are regarded as thin and rigid films.

EQCM measurements were carried out using a three-electrode system with an Au quartz crystal resonator as the working electrode, a carbon paper as the counter electrode and Ag/AgCl as the reference electrode. The geometric area of the Au quartz crystal resonator with a standard frequency of  $f_0 = 9.000$  M Hz. is 0.198 cm<sup>2</sup>. The electrode was cleaned in an aqueous solution containing H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub> (0.1 M) in the ratio of 1:3 followed by thorough rinsing with deionized water. After drying with nitrogen, the electrode was then immersed in the electrochemical cell. MnOOH electrodes: MnOOH powder, carbon nanotubes and polyvinylidene fluoride in mass

ratios of 7:2:1 were mixed in N-methyl-2-pyrrolidine using ultrasonic agitation to prepare a uniform slurry that was pasted onto an Au resonator and vacuum dried at 100 °C overnight. Pre-deposited MnO<sub>2</sub> electrodes: MnO<sub>2</sub> was deposited on an Au quartz crystal resonator through Linear sweep voltammetry (0~1.55 V vs. Ag/AgCl) in 5 mM MnSO<sub>4</sub>+0.1 M H<sub>2</sub>SO<sub>4</sub> electrolyte. Linear sweep voltammetry (LSV) and Cyclic voltammetry (CV) tests were performed on an electrochemical workstation CHI760E (CH Instruments) inputting to the quartz crystal analyzer QCM 922A (Princeton Applied Research, America).

For a redox reaction, the theoretical mass change is related to the quantity of charge transfer by Faraday's law (Eq. S2).

$$\frac{\Delta m}{\Delta Q} = \frac{M}{n F} \tag{Eq. S2}$$

where  $\Delta m$  is the mass change (g),  $\Delta Q$  is the charge exchanged (C), M is the molar mass of the sedimentary species (g mol<sup>-1</sup>), F is the Faraday constant (96485 C mol<sup>-1</sup>), and n is the number of electrons exchanged.

Therefore, the theoretical formula mass of  $Mn^{2+} \leftrightarrow MnOOH$  is:

$$\frac{\Delta m}{\Delta Q} = \frac{M}{nF} = \frac{87.94}{1 \times 96485} = 0.911 \, mg \, C^{-1}$$
 (Eq. S3)

The theoretical formula mass of MnOOH $\leftrightarrow$ MnO<sub>2</sub> is:

$$\frac{\Delta m}{\Delta Q} = \frac{\Delta M}{nF} = \frac{86.94 - 87.94}{1 \times 96485} = -0.010 \ mg \ C^{-1} \qquad (\text{Eq. S4})$$

The theoretical formula mass of  $Mn^{3+} \leftrightarrow MnO_2$  is:

$$\frac{\Delta m}{\Delta Q} = \frac{M}{nF} = \frac{86.94}{1 \times 96485} = 0.901 \ mg \ C^{-1}$$
(Eq. S5)

The theoretical formula mass of  $Mn^{2+} \leftrightarrow MnO_2$  is:

$$\frac{\Delta m}{\Delta Q} = \frac{M}{nF} = \frac{86.94}{2 \times 96485} = 0.450 \ mg \ C^{-1}$$
(Eq. S6)

The theoretical formula mass of  $Na^+ \leftrightarrow NaMnO_2$  is:

$$\frac{\Delta m}{\Delta Q} = \frac{M}{nF} = \frac{-23}{1 \times 96485} = -0.238 \, mg \, C^{-1}$$
(Eq. S7)

The theoretical formula mass of H<sub>3</sub>O<sup>+</sup> insertion/extraction is:

$$\frac{\Delta m}{\Delta Q} = \frac{M}{nF} = \frac{-19}{1 \times 96485} = -0.197 \ mg \ C^{-1}$$
(Eq. S8)

#### 5. Mn<sup>2+</sup>/MnO<sub>2</sub> deposition/dissolution reactions

1) The Mn<sup>2+</sup> deposition processes can be concluded as the following equations:<sup>6,7</sup>

$$Mn^{2^+} + 2H_2O \rightarrow MnOOH + 3H^+ + e^-$$
 (Eq. S9)

$$\mathrm{Mn}^{2^+} \to \mathrm{Mn}^{3^+} + \mathrm{e}^- \tag{Eq. S10}$$

$$Mn^{3+} + 2H_2O \rightarrow MnOOH + 3H^+$$
 (Eq. S11)

$$MnOOH \rightarrow MnO_2 + H^+ + e^-$$
 (Eq. S12)

$$Mn^{3+} + 2H_2O \rightarrow MnO_2 + 4H^+ + e^-$$
 (Eq. S13)

2) The reduction processes of  $MnO_2$  in different electrolytes can be concluded as the following equations:<sup>7-9</sup>

$$MnO_2 + H^+ + e^- \rightarrow MnOOH$$
 (Eq. S14)

a) In neutral and mildly acidic electrolytes (pH > 4),

$$MnO_2 + M^{x^+} + xe^- \rightarrow M_x MnO_2$$
 (Eq. S15)

where M<sup>n+</sup> represents metal ions.

b) In acidic electrolytes,

$$MnO_2 + 4H^+ + e^- \rightarrow Mn^{3+} + 2H_2O$$
 (Eq. S16)

MnOOH + 
$$3H^+$$
 +  $e^- \rightarrow Mn^{2+} + 2H_2O$  (Eq. S17)

c) The formation of "dead"  $MnO_2$  beyond cathodes in acidic electrolytes is via chemical reactions as the following equations:<sup>7-9</sup>

$$MnOOH + 3H^{+} \rightarrow Mn^{3+} + 2H_{2}O$$
 (Eq. S18)

$$2Mn^{3+} + 2H_2O \rightarrow MnO_2 + Mn^{2+} + 4H^+$$
 (Eq. S19)

### 6. Electrochemical measurements for Cu//MnO<sub>2</sub> batteries

Electrochemical performance of Cu//MnO<sub>2</sub> batteries was evaluated using a homemade cell (Fig. S14a) on a Neware battery test system (Shenzhen, China). The batteries were constructed using carbon cloth as the cathode current collector, air-laid paper as the separator and a Cu foil as the anode (Fig. S14b). The geometric area of the electrode is ~2 cm<sup>2</sup> (16 mm in diameter) for both the cathode and anode. The electrolytes are 1 mL solutions containing 0.4 M CuSO<sub>4</sub> + 0.4 M MnSO<sub>4</sub> + 0.5 M H<sub>2</sub>SO<sub>4</sub> with or without 0.005 M Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (0.01 M KBr or 0.01 M TEMPO). The cells were charged at 1.3 V (vs. Cu/Cu<sup>2+</sup>) to a specified areal capacity (2 mAh cm<sup>-2</sup>), with the chronoamperometry (constant-potential) technique applied to obtain an electrodeposited MnO<sub>2</sub> cathode. Galvanostatic currents 3 mA cm<sup>-2</sup> were employed in the process of discharge. CV tests were conducted in a three-electrode system using a carbon cloth as the working electrode, a Cu foil as the counter electrode and Ag/AgCl as the reference electrode on an electrochemical workstation CHI760E (CH Instruments). For CV tests of Mn<sup>2+</sup> and Fe<sup>3+</sup> on the carbon cloth, the electrolytes are 0.4 M MnSO<sub>4</sub> + 0.5 M H<sub>2</sub>SO<sub>4</sub> and 0.05 M Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> + 0.5 M H<sub>2</sub>SO<sub>4</sub>, respectively. The scanning rate is 5 mV s<sup>-1</sup>.

## **Supplementary Figures**



Figure S1. XRD patterns of MnOOH.



**Figure S2.** A plot of frequency (f) and resonance resistance (R) vs. potential V after deposition in 5mM  $MnSO_4+0.1 M Na_2SO_4$  at 5 mV s<sup>-1</sup>.



Figure S3. (a) LSV curves of carbon cloth electrodes in different electrolytes at 5 mV s<sup>-1</sup>. (b) XRD patterns of the electrodes after deposition in different electrolytes.
Note: To facilitate XRD characterization, MnO<sub>2</sub> was deposited on carbon cloth by the

LSV method. The LSV tests were conducted in a three-electrode system using the carbon cloth  $(1*1 \text{ cm}^2)$  as both the working electrode and the counter electrode and Ag/AgCl as the reference electrode on an electrochemical workstation CHI760E (CH Instruments). The carbon cloth electrode shows similar electrochemical process with the Au QCM electrode. XRD patterns indicate the successful generation of MnO<sub>2</sub> on the carbon cloth electrode after the anodic sweep.



Figure S4. Ultraviolet absorption spectra of different electrolytes after an anodic sweep.

**Note:** UV–vis tests were carried out by adding the  $Fe^{2+}$  indicator to various electrolytes after deposition. If the Mn<sup>3+</sup> is present in the solution,  $Fe^{2+}$  ions will be oxidized to  $Fe^{3+}$  ions that can be recognized using an UV–vis spectrophotometer.<sup>10,11</sup> Note that the absorption peak of  $Fe^{3+}$  was clearly observed merely in the electrolytes with a relatively high acid concentration (e.g., over 0.1 M H<sub>2</sub>SO<sub>4</sub>), demonstrating the existence of Mn<sup>3+</sup> in such acidic solution.



**Figure S5.** (a) The anodic sweep curve of the first-cycle (black) and the corresponding mass change profile (red) in 5 mM  $MnSO_4 + 0.09 M Na_2SO_4 + 0.01 M H_2SO_4$ . (b) The mass change-charge profile in 5 mM  $MnSO_4 + 0.09 M Na_2SO_4 + 0.01 M H_2SO_4$ .



Figure S6. Reduction process of MnO<sub>2</sub> in the neutral electrolyte (i.e., 0.1 M Na<sub>2</sub>SO<sub>4</sub>). (a) The LSV curve (black) and the corresponding mass change-potential profile (red). (b) Mass change-charge profiles. (c) The experimental and theoretical mass changecharge profiles. The black dotted line represents the theoretical profile of Na<sup>+</sup>. The upper boundary of the blue triangle represents the theoretical profile of H<sub>3</sub>O<sup>+</sup>, and the lower boundary represents the theoretical profile of H<sup>+</sup>. Solid lines represent the experimental results corresponding to  $\Delta m/\Delta q$ .



Figure S7. Schematic illustration for the reduction process of  $MnO_2$  in neutral electrolytes.



**Figure S8.** (a) XPS survey and (b) O 1s XPS spectra of the pre-deposited  $MnO_2$  electrode and the one reduced to 1.02 V vs. Ag/AgCl. The black and red curves correspond to the experimental and fitted results, respectively. The red, blue and orange spectra represent the fitted components of the Mn–O–Mn, Mn–O–H and H–O–H bonds, respectively.

**Note:** To verify the formation of MnOOH, XPS measurements were carried out for the pristine pre-deposited MnO<sub>2</sub> electrode and the one after applied a reduction potential of 1.02 V vs. Ag/AgCl. The two electrodes show pronounced Mn and O signals. In detail, the deconvoluted O 1s spectrum can be fitted with three components that are associated with the Mn–O–Mn bond (529.7 eV) for MnO<sub>2</sub>, the Mn–O–H bond (531.8 eV) for MnOOH and the H–O–H bond (532.6 eV) for residual water (Fig. S8b).<sup>12</sup> The electrode reduced to 1.02 V vs. Ag/AgCl shows a higher percentage of Mn–O–H bond than the pristine one. Furthermore, XPS depth-profiling shows that the excess Mn–O–H bond exists on the surface of the electrode reduced to 1.02 V vs. Ag/AgCl (Fig. 3d), which confirms that MnOOH is generated on the surface of MnO<sub>2</sub> during the initial stage of cathodic process.



B: A + initial electrolyte C: A + the electrolyte after reduced to 0.1 V

Figure S9. Optical photographs of the solutions of 0.1 M KI + 0.1 M H<sub>2</sub>SO<sub>4</sub> (A), 0.1 M KI + 0.1 M H<sub>2</sub>SO<sub>4</sub> + the initial 0.1 M H<sub>2</sub>SO<sub>4</sub> electrolyte before reduction (B) and 0.1 M KI + 0.1 M H<sub>2</sub>SO<sub>4</sub> + the 0.1 M H<sub>2</sub>SO<sub>4</sub> electrolyte after reduction to 0.1 V vs. Ag/AgCl (C).

**Note:** A solution of 0.1 M KI + 0.1 M  $H_2SO_4$  was prepared to verify the existence of  $Mn^{3+}$  in the acidic electrolytes based on the spontaneous redox reactions between  $Mn^{3+}$  and I<sup>-</sup>. If the  $Mn^{3+}$  is present in the solution, I<sup>-</sup> ions will be oxidized to I<sub>2</sub>, making the solution change from colorless to light yellow.<sup>10</sup> It is clearly observed that the solution after reduction to 0.1 V vs. Ag/AgCl changed to light yellow after adding KI, indicating the residue of  $Mn^{3+}$  ions in the electrolyte even after reduction to 0.1 V vs. Ag/AgCl.



Figure S10. Effect of acid concentrations on the dissolution of  $MnO_2$ . (a, c, e, g) LSV curves (black) and the corresponding mass change-potential profiles (red) in the electrolytes with (a) 0.05 M H<sub>2</sub>SO<sub>4</sub>, (c) 0.10 M H<sub>2</sub>SO<sub>4</sub>, (e) 0.50 M H<sub>2</sub>SO<sub>4</sub> and (g) 1.00 M H<sub>2</sub>SO<sub>4</sub>. (b, d, f, h) Mass retention in the electrolytes with (b) 0.05 M H<sub>2</sub>SO<sub>4</sub>, (d) 0.10 M H<sub>2</sub>SO<sub>4</sub>, (f) 0.50 M H<sub>2</sub>SO<sub>4</sub> and (h) 1.00 M H<sub>2</sub>SO<sub>4</sub>.



Figure S11. The mass-to-charge conversion efficiency of the pre-deposited  $MnO_2$  cathode with increasing the acid concentration from 0.05 M to 1.00 M.



**Figure S12.** (a) An optical photograph of the home-made battery. (b) Geometry model of the home-made battery device.



Figure S13. SEM image of the carbon cloth electrode reduced to 0.1 V vs. Ag/AgCl.



Figure S14. EDS mapping images of the residual  $MnO_2$  on the carbon cloth electrode.



Figure S15. Optical photograph of the sealing gasket in a cycled  $Cu//MnO_2$  battery using the Fe<sup>3+</sup>-free electrolyte.



Figure S16. EDS mapping images of "dead"  $MnO_2$  on the sealing gasket in a cycled  $Cu//MnO_2$  battery using the Fe<sup>3+</sup>-free electrolyte.



Figure S17. CV curves of the carbon cloth electrode in acidic electrolytes with  $Mn^{2+}$  or Fe<sup>3+</sup> additives.



**Figure S18.** Optical photograph of the solutions of pure  $0.1 \text{ M FeSO}_4+0.1 \text{ M H}_2\text{SO}_4$ and the one with pre-deposited MnO<sub>2</sub>.

**Note:** When the carbon cloth with  $MnO_2$  deposition was soaked in the solution of 0.1 M FeSO<sub>4</sub>+0.1 M H<sub>2</sub>SO<sub>4</sub>, it was found that the solution turned from colorless to reddishbrown after standing for 15 min at room temperature. This was because that Fe<sup>2+</sup> is oxidized by MnO<sub>2</sub> to generate colored Fe<sup>3+</sup>, indicating that the Fe<sup>2+</sup> is capable of reusing the "dead" and unreacted MnO<sub>2</sub>.



Figure S19. Optical photograph of the sealing gasket in a cycled  $Cu//MnO_2$  battery using the Fe<sup>3+</sup>-added electrolyte.



**Figure S20.** Electrochemical performance of Cu//MnO<sub>2</sub> batteries with addition of different redox mediators.

#### References

- Li, Z. *et al.* A facile route to growth of γ-MnOOH nanorods and electrochemical capacitance properties. *J. Colloid Interf. Sci.* 357, 286-291, (2011).
- 2 Buttry, D. A. Measurement of interfacial processes at electrode surfaces with the electrochemical quartz crystal microbalance. *Chem. Rev.* **92**, 6, (1992).
- Ji, Y. *et al.* From bulk to interface: electrochemical phenomena and mechanism studies in batteries via electrochemical quartz crystal microbalance. *Chem. Soc. Rev.* 50, 10743-10763, (2021).
- 4 Shpigel, N. *et al.* Can anions be inserted into mxene? *J. Am. Chem. Soc.* **143**, 12552-12559, (2021).
- Nimkar, A. *et al.* Influences of cations' solvation on charge storage performance in polyimide anodes for aqueous multivalent ion batteries. *ACS Energy Lett.* 6, 2638-2644, (2021).
- 6 Clarke, C. J. *et al.* An RDE and RRDE study into the electrodeposition of manganese dioxide. *Electrochim. Acta* **51**, 5773-5784, (2006).
- 7 Nijjer, S. *et al.* Oxidation of manganese(II) and reduction of manganese dioxide in sulphuric acid. *Electrochim. Acta* **46**, 395-399, (2000).
- 8 Lee, J. *et al.* The electrochemical reduction of manganese dioxide in acidic solutions. *J. Electroanal. Chem.* **79**, 79-104, (1977).
- 9 Maskell, W. C. The electrochemical reduction of manganese dioxide in acidic solutions. *J. Electroanal. Chem.* **198**, 127-137, (1985).
- Hamm, E. & Suwyn, A. Preparation and characterization of some aminopolycarboxylate complexes of manganese(III). *Inorg. Chem.* 6, 139-142, (1967).
- 11 Davies, G. *et al.* The kinetics and stoichiometry of the reaction between manganese(III) and hydrazoic acid in acid perchlorate solution. *Inorg. Chem.* 8, 663-669, (1969).
- 12 Chen, W. *et al.* A manganese–hydrogen battery with potential for grid-scale energy storage. *Nat. Energy* **3**, 428-435, (2018).