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Supporting Information for
Elucidating the Intercalation Mechanism of Zinc Ions into α-MnO_2 for Rechargeable Zinc Batteries

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Methods, Figures S1-S4 and References

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Methods

Synthesis of α-MnO_2 nano-rod. The α-MnO_2 nano-rod was synthesized by a known literature method[1]. Briefly, $KMnO_4$ (0.1264 g) and NH_4Cl (0.0428 g) were homogeneously mixed with distilled water (40 mL) until they are completely dissolved. The solution was then poured into a Teflon-lined reactor and was subjected to hydrothermal condition at 140 ˚C for 24 h. Then, the resulting powder was filtered and washed with plenty of distilled water. Finally, the filtered powder was dried in a vacuum oven at 80 ˚C overnight.

Rechargeable Zn battery test. The cathode was prepared by uniformly mixing synthetic α-MnO_2 powder (70 mg) and carbon black (10 mg) with a spatula, where polyvinylidene fluoride (PVdF) binder (20 mg) was then added to make homogeneous mixture. Then, the whole mixture was ball-milled in N-methyl-2-pyrrolidone (NMP). The α-MnO_2 slurry was cast onto stainless steel foil (25 μm thickness) at a loading of approximately 5.0 mg cm^{-2}. The electrochemical performance was evaluated using type-2032 coin cells composed of the as-prepared cathode, a zinc foil anode (10 μm thickness), a glass wool separator, and a 1.0 M aqueous zinc sulfate ($ZnSO_4$) electrolyte. The cells were tested with a MACCOR cycler between 0.7 – 2.0 V at a C/20 rate for the initial 2 cycles, then at a C/5 rate for the remaining cycles (1 C = 210 mA g^{-1} of α-MnO_2).

GITT measurements and the calculation of the diffusion coefficients. For GITT measurement, rectangular current pulses were applied to the cell containing α-MnO_2 cathode repeatedly until it completes the first discharge-charge process. The current pulse lasted for 40 min at a rate of 0.1 C and then the cell was subject to relaxation for 1 h to allow the voltage profile to reach the equilibrium. The chemical diffusion coefficient of Zn^{2+} ions passing through the α-MnO_2 electrode can be calculated based on the equation (1) from the literatures.[2,3]

$$D_{Zn^{2+}} = \frac{4}{\pi}\left(\frac{mV_M}{MS}\right)^2\left(\frac{dE_s/d\delta}{dE_\tau/d\sqrt{\tau}}\right)^2 \approx \frac{4}{\pi\tau}\left(\frac{mV_M}{MS}\right)^2\left(\frac{\Delta E_s}{\Delta E_\tau}\right)^2 \quad (1)$$

,where m and M are the mass (g) and the molecular weight (g/mol) of the active material, respectively. V_M is the molar volume (cm^3/mol) of α-MnO_2, obtainable from the crystallographic information. S is the effective surface area (cm^2) between the active material and the electrolyte and can be considered to be Brunauer-Emmett-Teller surface area (S_{BET}). S_{BET} for α-MnO_2 nano-rod is 22 m^2/g. $dE_s/d\delta$ is the slope of the coulometric titration curve which can be obtained by plotting the equilibrium electrode voltage measured after each titration step δ. $dE_\tau/d\sqrt{\tau}$ denotes the slope of the linearized region of the potential E_τ during the current pulse of duration time τ (sec). This equation is valid when $\tau \ll L^2/D_{Zn^{2+}}$, where L (cm) is the thickness of the electrode and can be simplified as the right hand of the equation if $dE_\tau/d\sqrt{\tau}$ shows a linear behavior.

Characterization. The crystallographic structures were measured by powder X-ray diffraction (XRD) using Cu-K*α* radiation (*λ*=1.5405 Å, Rigaku D/MAX-2500/PC). The morphology of the α-MnO_2 electrodes was observed by high resolution transmission electron microscopy (HR-TEM, FEI Tecnai G2 operating at 200 KeV) and field-emission scanning electron microscopy (FE-SEM, Hitachi S-4000).

In-situ XRD measurements. The in-situ XRD patterns were collected using an X-ray diffracto metry system (Rigaku MicroMAX 007HF with R-AXIS IV++ image plate) with using Mo-Kα radi ation (λ=0.7107 Å). The electrochemical cell specially designed for in-situ XRD analysis was installed on the diffractometer and was connected to the potentiostat (WBCS3000, WonA tech). The cell was galvanostatically cycled at a scan rate of C/20 while XRD patterns were measured successively every eight minute. To compare the results with those reported in the literature, the 2θ values were converted to the ones that correspond to Cu-Kα radiation (λ=1.5405 Å).

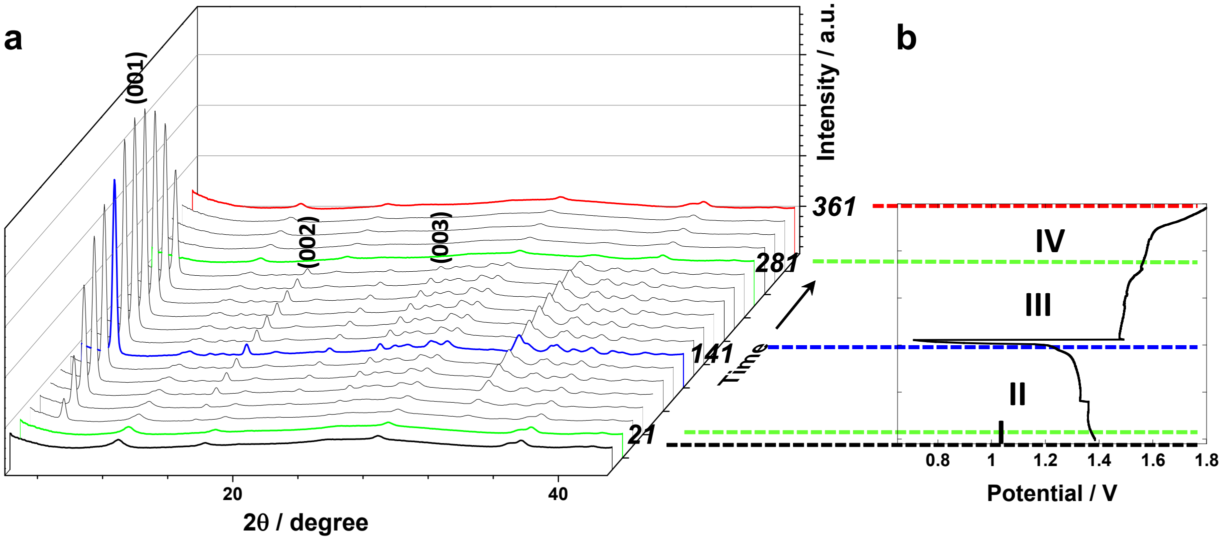


Figure S1. (a) In-situ X-ray diffraction (XRD) patterns of the zinc/α-MnO_2 rechargeable battery during the first cycle and (b) the corresponding potential profiles. The regions of interest are described as I, II, III, and IV in (b).

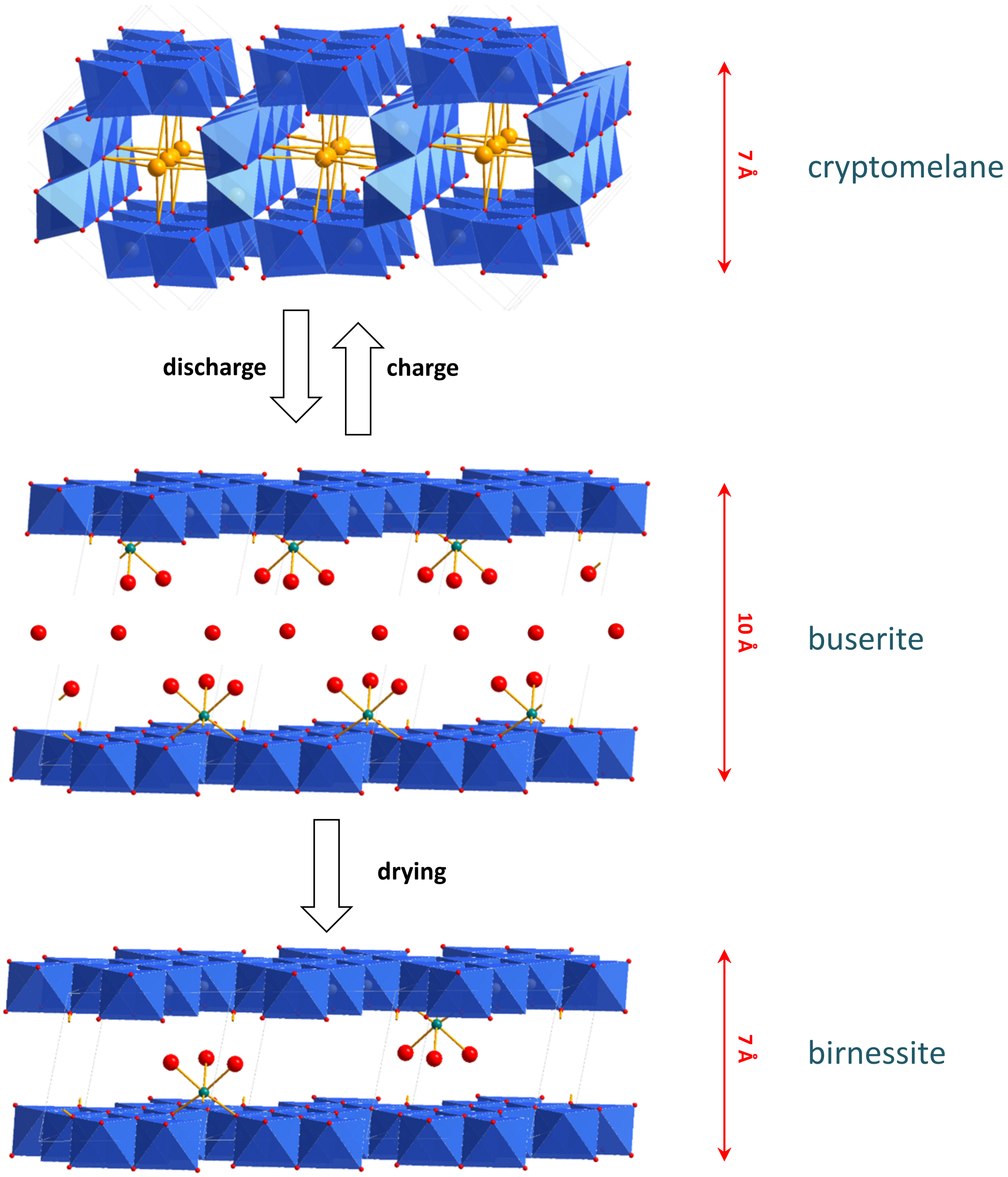


Figure S2. The structural development of α-MnO_2 after the insertion of zinc ions (buserite) and drying in the oven (birnessite).

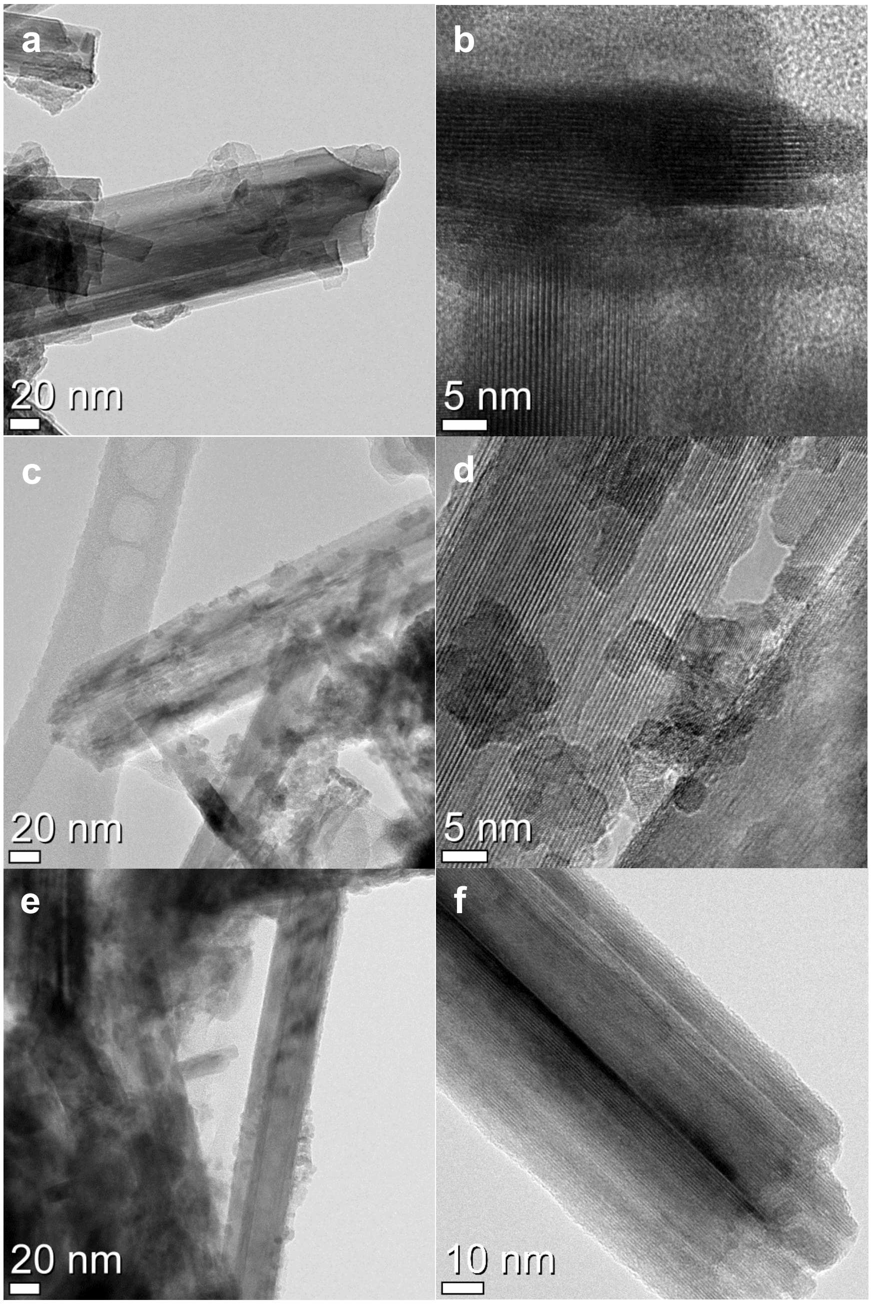
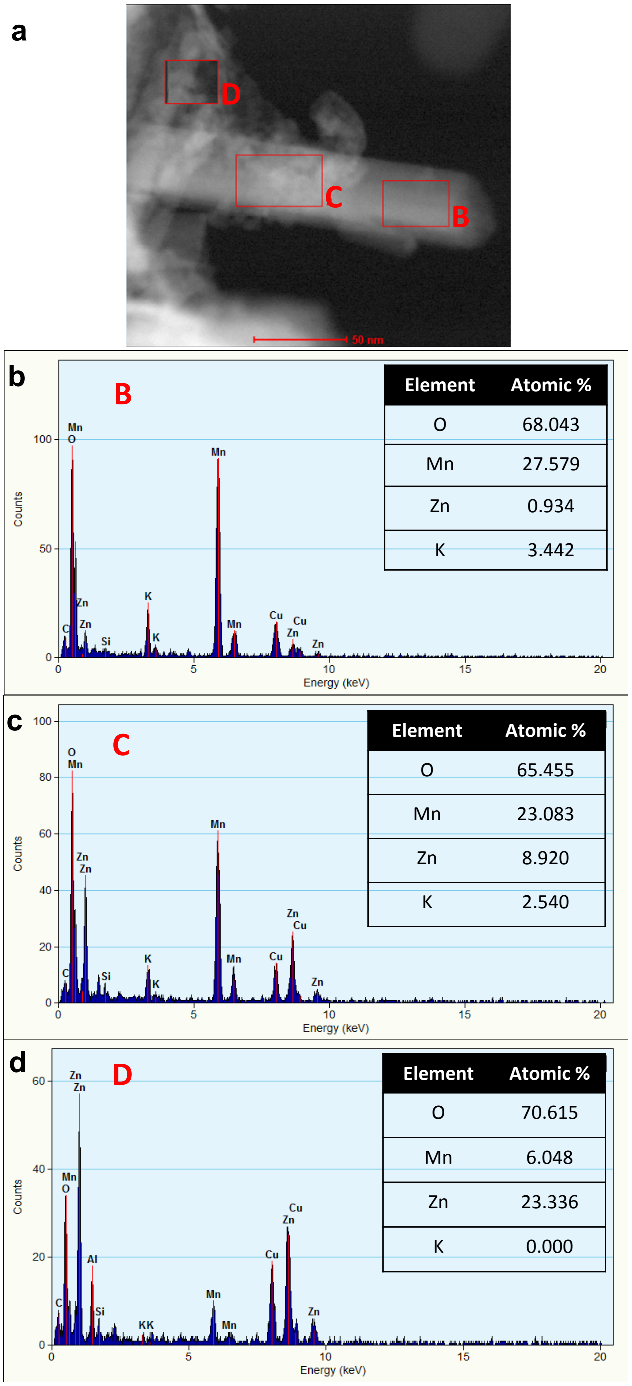


Figure S3. High-resolution transmission electron microscopy (HR-TEM) images of cathodes during the first discharge and charge processes. HR-TEM images for (a), (b) the original cathode containing an α-MnO_2 nanorod, (c), (d) the discharged cathode, and (e), (f) the discharged and then recharged cathode.



Element	Atomic %
O	68.043
Mn	27.579
Zn	0.934
K	3.442

Element	Atomic %
O	65.455
Mn	23.083
Zn	8.920
K	2.540

Element	Atomic %
O	70.615
Mn	6.048
Zn	23.336
K	0.000

Figure S4. (a) Transmission electron microscopy (TEM) image of the oven-dried discharged electrode containing regions **B**, **C**, **D** and (b), (c), (d) EDX compositional analysis for the marked area **B**, **C**, **D** in the discharged electrode, respectively. Note that the regions with scraps on the nano-rod, i.e., C and D, are rich in Zn, but the nano-rod contains very little zinc.

Reference

1. Gao, Y.; Wang, Z.; Wan, J., Zou, G.; Qian, Y. *J. Cryst. Growth* **2005**, 279, 415.

2. Li, Z.; Du, F.; Bie, X.; Zhang, D.; Cai, Y.; Cui, X.; Wang, C.; Chen, G.; Wei, Y. J. Phys. Chem. C. **2010**, 114, 22751.

3. Zhu, Y.; Wang, C. *J. Phys. Chem. C.* **2010**, 114, 2830.