Supporting Information

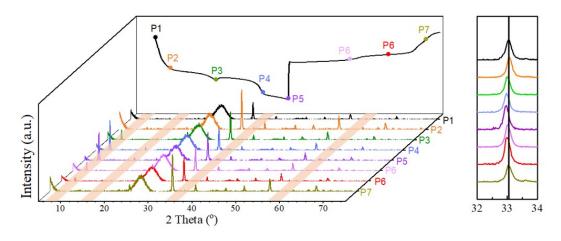


Fig. S1 Ex-situ XRD patterns of Mn₂O₃ electrode at various charge/discharge states.

In order to reveal the structural transformation of Mn_2O_3 electrode, ex-situ XRD was carried in various discharging/charging states, as shown in Fig. S1. When discharging to 1 V, the obvious peaks at 8.2°, 16.3°, 35.5° and 58.6° that are covered

in pink area appeared and they can be indexed to typical $Zn_4SO_4(OH)_6 \cdot 5H_2O$

(JCPDS: 39-0688). The result is consistent with many previous works about manganese oxide materials [1-4]. The zinc hydroxide sulfate hydrate is formed by integrating the OH⁻, H₂O and ZnSO₄ in aqueous electrolyte, indicating H⁺ is inserted into the Mn₂O₃ electrode [2]. When the electrode was charged to 1.9 V, the peaks of zinc hydroxide sulfate hydrate gradually disappeared, showing well reversibility of the electrode reaction. In addition, the peak at 33° shifted slightly during the charge and discharge period. According to Bragg's law, the diffraction angles will decrease when lattice spacing increases. So when discharging, the peak of 33° shifted slightly to lower angles can be assigned to the insertion of Zn²⁺ in lattice spacing [3,5]. Also, the peak of 33° shifted slightly to higher angles during charging process can be explained by the extraction of Zn²⁺. Based on the above analysis, two energy storage mechanisms can be proposed for the Mn₂O₃ electrode, involving H⁺ and Zn²⁺ insertion/extraction, respectively.

Reference

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