Supporting Information

Reversible Cl/Cl⁻ Redox in a Spinel Mn_3O_4 Electrode

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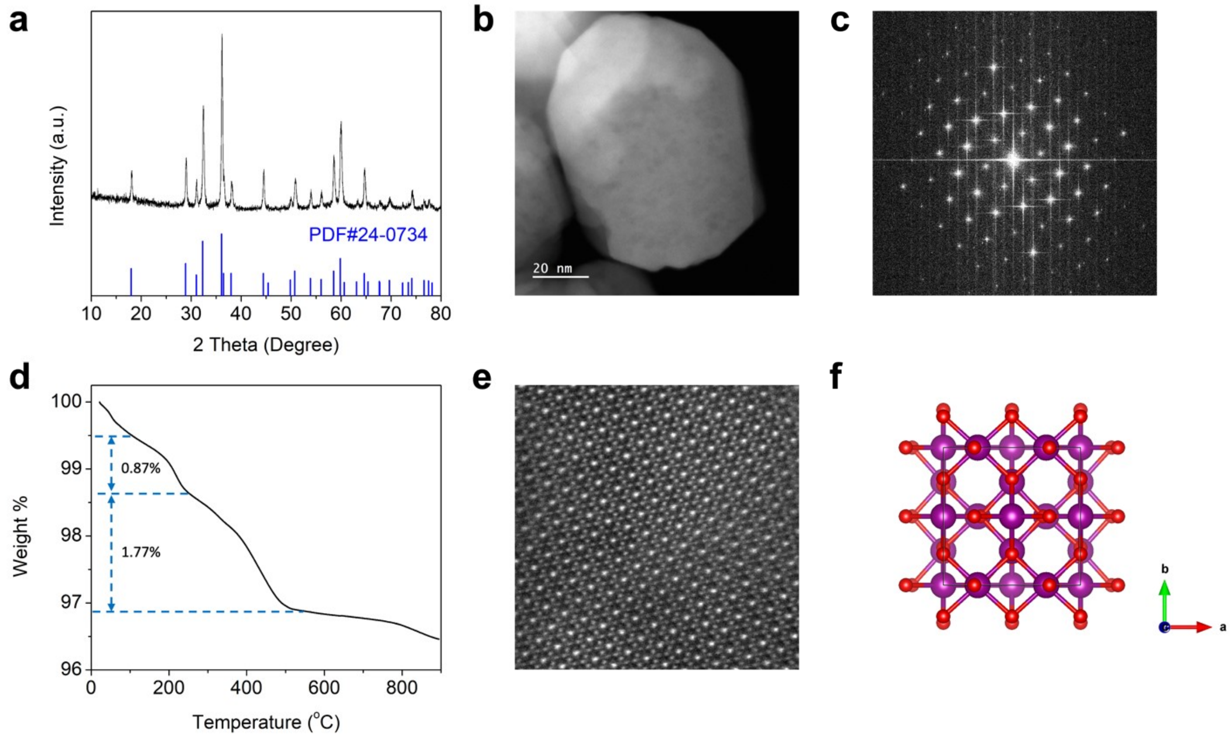

Figure S1. Material characterization of the as synthesized Mn_3O_4. (a) XRD pattern of the Mn_3O_4 powder. (b) STEM image of a representative Mn_3O_4 particle and (c) the associated electron diffraction pattern. (d) TGA curve of the Mn_3O_4 powder obtained under argon atmosphere at a ramp rate of 10 °C/min. (e) STEM image and (f) an ideal spinel crystal structure of the as synthesized Mn_3O_4 powder.

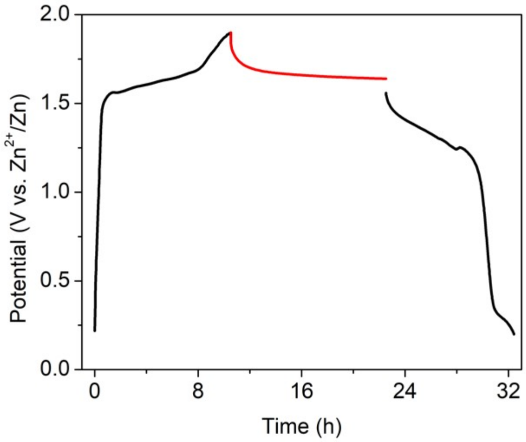

Figure S2. Self-discharge performance of the Zn^{2+}-trapped Mn_3O_4 electrode after being charged in the 20 *m* $ZnCl_2$ + 5 *m* NH_4Cl WiSE. The red portion of the curve shows the self-discharge behavior while resting the cell for 12 hours. Cycling was done using a Mn_3O_4 free-standing film electrode at 100 mA/g. The Coulombic efficiency after idling the cell was 94.3%.

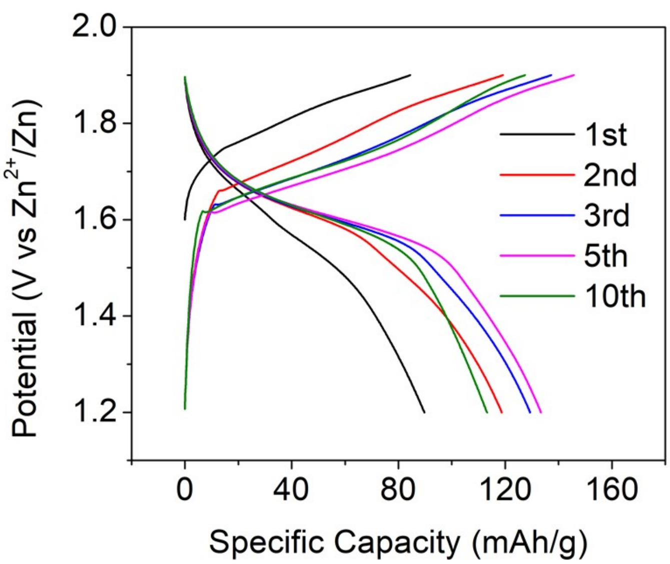

Figure S3. GCD profiles of the first, second, third, fifth, and tenth cycles of the Mn_3O_4 electrode without initially trapping Zn^{2+} ions (charging first and increasing the lower cutoff potential to 1.2 V) at a current rate of 50 mA/g.

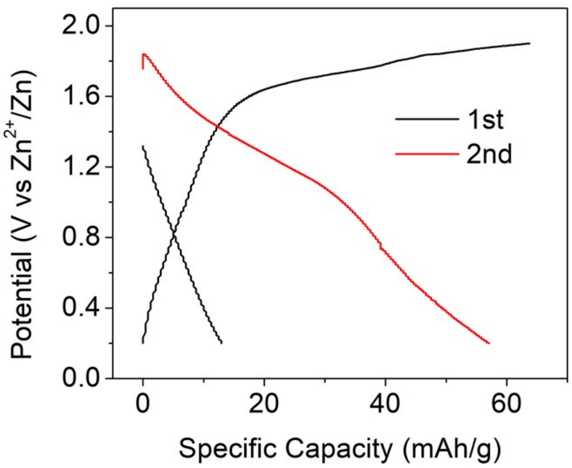

Figure S4. GCD profiles of the Mn_3O_4 electrode obtained at 50 mA/g using 15 *m* TEACl as the aqueous electrolyte. Activated carbon was used as the counter electrode and Ag/AgCl was used as the reference electrode. Reference potentials were converted to being vs Zn^{2+}/Zn for comparison.

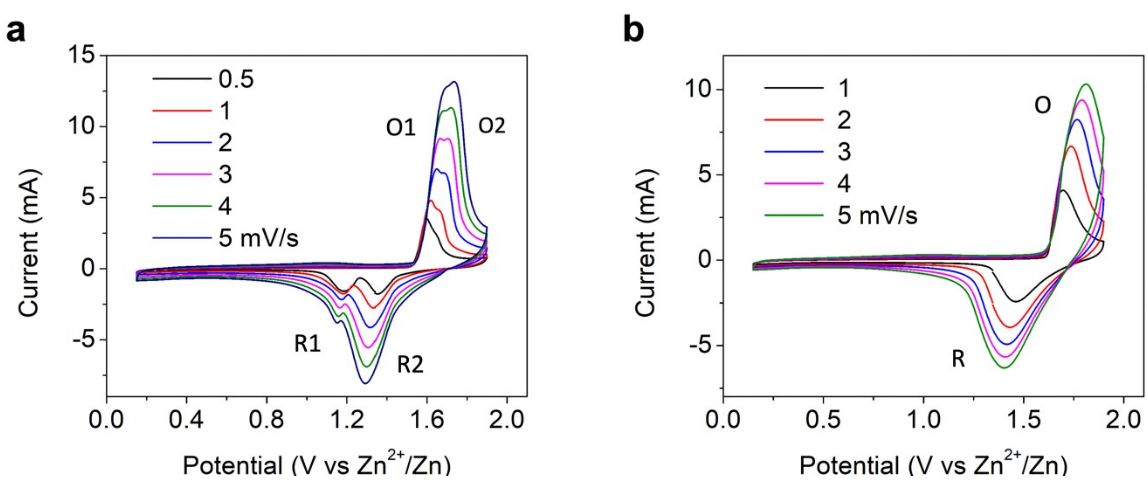

Figure S5. CV curves of the Mn_3O_4 electrode in (a) 2 M $ZnSO_4$ and (b) 20 *m* $ZnCl_2$ + 5 *m* NH_4Cl electrolytes at a scan rate of 1 mV/s.

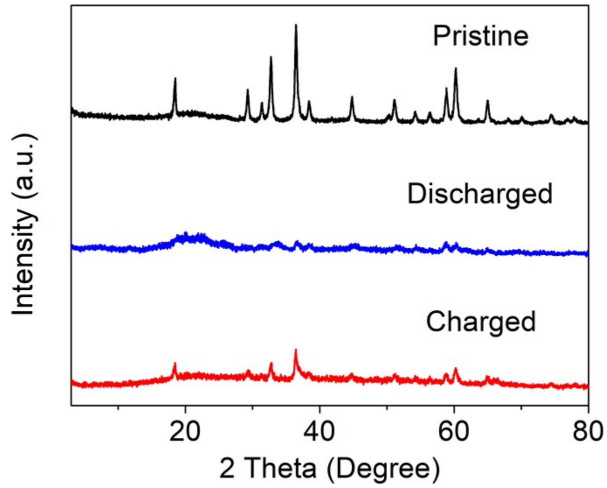

Figure S6. XRD patterns of the pristine, discharged, and charged Mn_3O_4 electrodes in the WiSE.

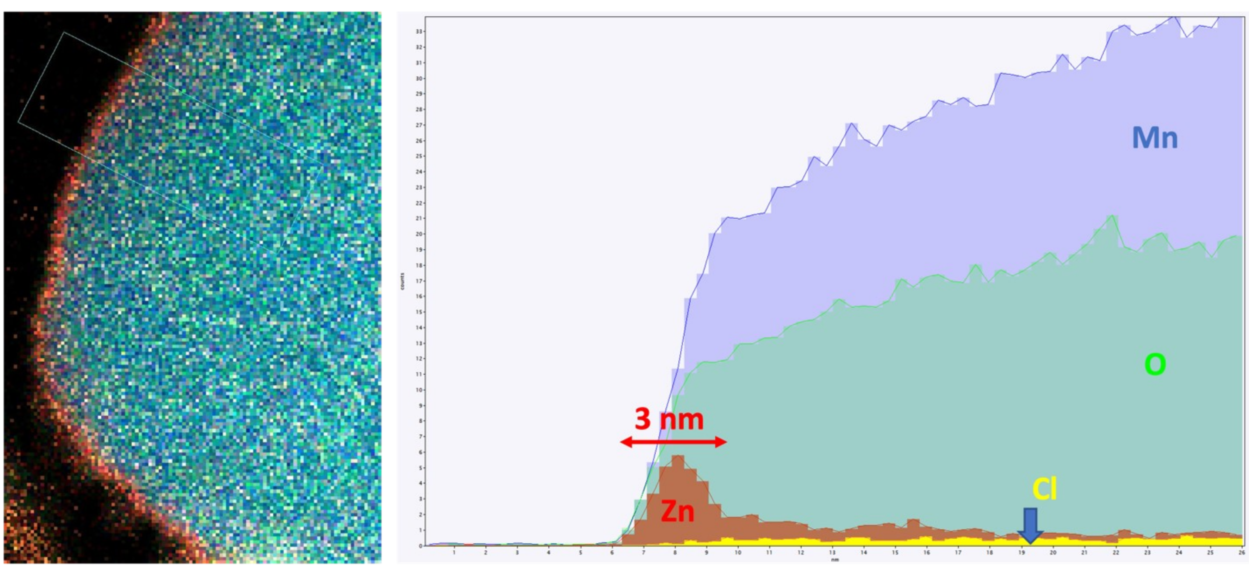

Figure S7. EDS line scanning profile of the Mn_3O_4 electrode after the first charge. The Mn, O, and Cl contents are distributed fairly uniform throughout the particle, whereas the Zn content is concentrated toward the outer 3 nm of the particle.

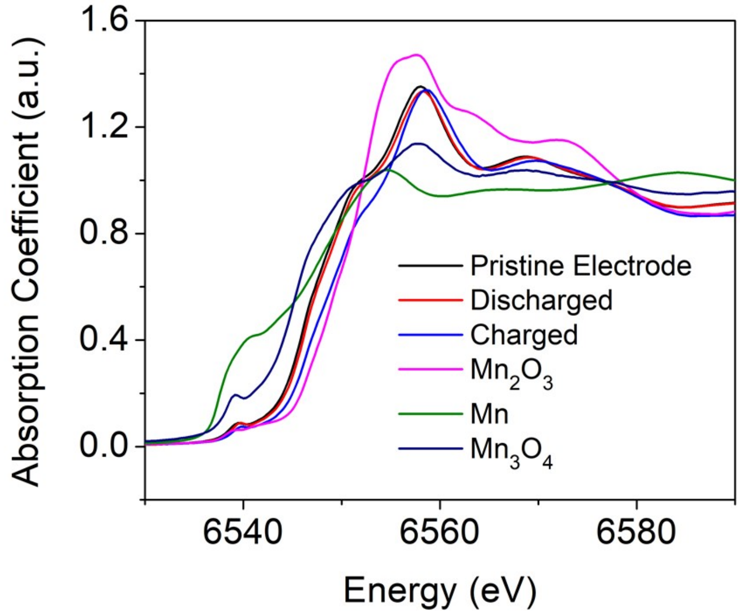

Figure S8. Normalized XANES of the Mn K-edge spectra of the pristine Mn_3O_4 electrode, the Mn_3O_4 electrode after the first discharge and the first charge in the 20 *m* $ZnCl_2$ + 5 *m* NH_4Cl WiSE, and the Mn_2O_3, Mn_3O_4, and Mn metal standards. The similar edge positions between the pristine, discharged, and charged samples highlight the lack of significant Mn redox after cycling the electrode.

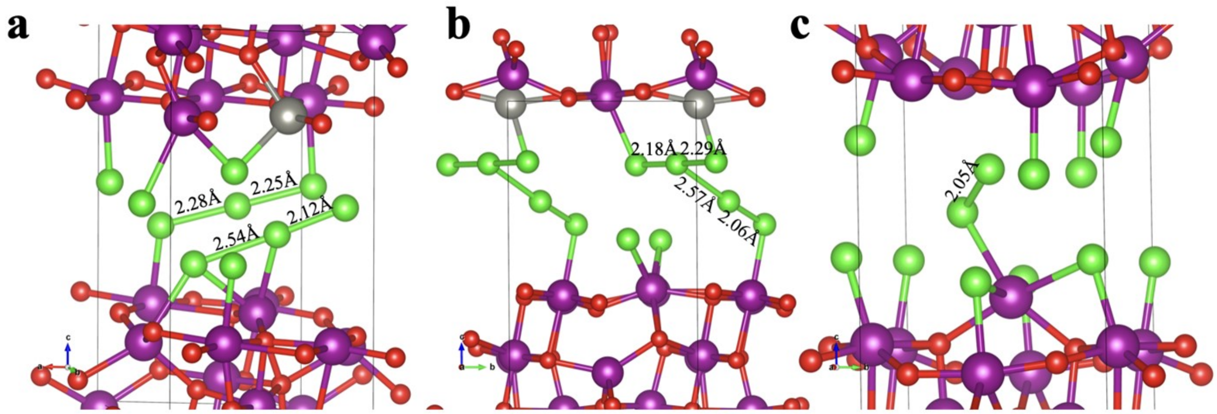

Figure S9. Zoomed-in images of Cl inserted in Mn_3O_4 structure with Zn-trapped in (a) octahedral site, (b) tetrahedral site, and (c) pristine Mn_3O_4 structure without Zn-trapped. The formation of trichloride $[Cl_3]^-$ in ZnOh, T-shaped pentachloride $[Cl_5]^-$ in ZnTd, and dichloride in Mn_3O_4 with corresponding bond distances between Cl atoms are shown in the figure.

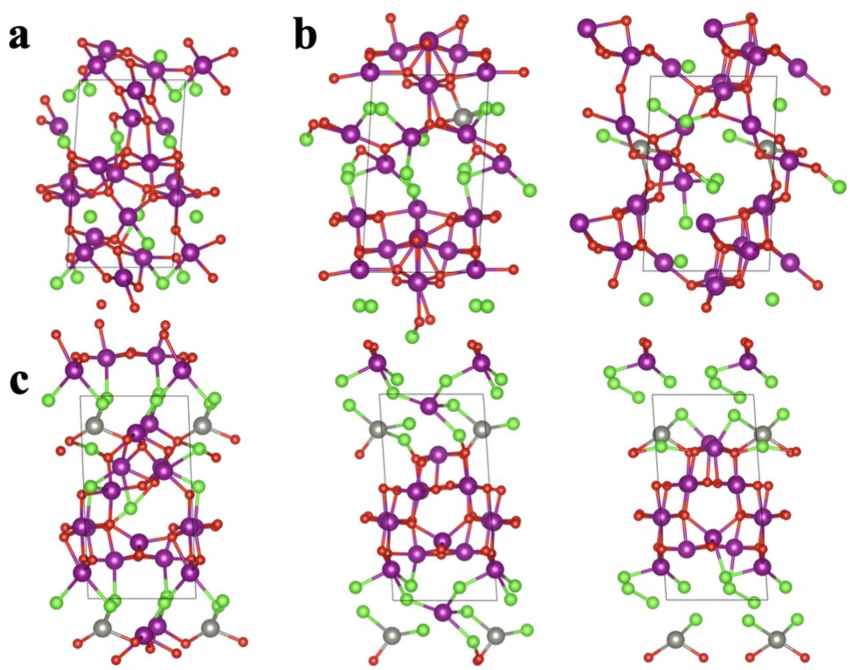

Figure S10. Possible optimized structures of Cl intercalation in (a) pristine Mn_3O_4, (b) ZnOh, and (c) ZnTd.

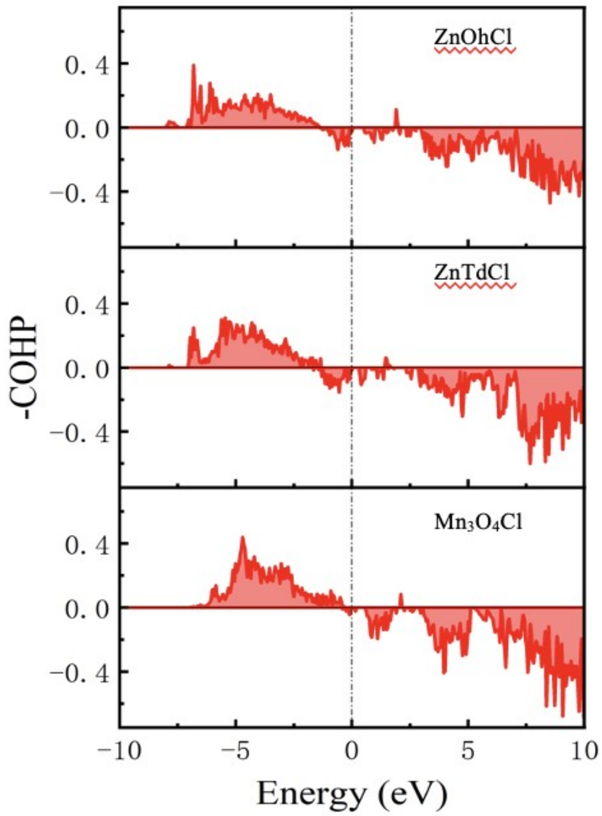

Figure S11. COHP analysis of Mn-Cl bond after Cl insertion in (a) ZnOh, (b) ZnTd, and (c) Mn_3O_4 models.

Table S1. Calculated Zn insertion energies of ZnOh, and ZnTd.

	ZnOh	**ZnTd**
Zn insertion energy (eV)	-0.86	-0.98

Table S2. Bader charge analysis of Mn, O, Zn, and Cl before and after Cl/Cl^- insertion in the pristine Mn_3O_4, the octahedral site Zn-trapped Mn_3O_4, and the tetrahedral site Zn-trapped Mn_3O_4.

Average Bader charge	Mn	O	Zn	Cl
Mn_3O_4	1.57	-1.17	-	-
ZnOh	1.52	-1.21	1.16	-
ZnTd	1.51	-1.21	1.17	-
Mn_3O_4 (after Cl insertion)	1.62	-1.06	-	-0.34
ZnOh (after Cl insertion)	1.56	-1.13	1.18	-0.27
ZnTd (after Cl insertion)	1.57	-1.14	1.18	-0.26