

## Supporting Information

### First-Cycle Evolution of Local Structure in Electrochemically Activated $\text{Li}_2\text{MnO}_3$

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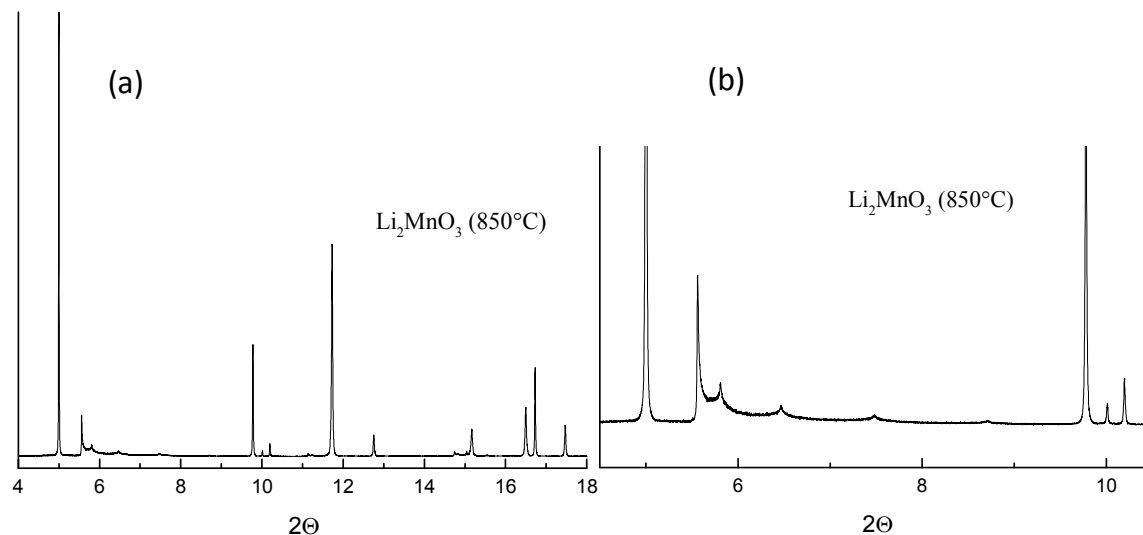


Figure SI-1. (a) High-resolution ( $\Delta Q/Q \approx 2 \times 10^{-4}$ ) synchrotron X-ray powder diffraction data (HR-XRD) of  $\text{Li}_2\text{MnO}_3$  annealed at  $850^\circ\text{C}$  for 24 hours. (b) Magnified region of the  $\sim 5$ - $10$   $2\theta$  range. Data were collected at 11-BM at the Advanced Photon Source (APS), Argonne National Laboratory. Scans were collected in transmission mode on spinning Kapton capillaries using a fixed wavelength of  $0.413710 \text{ \AA}$  at a temperature of  $295 \text{ K}$ .

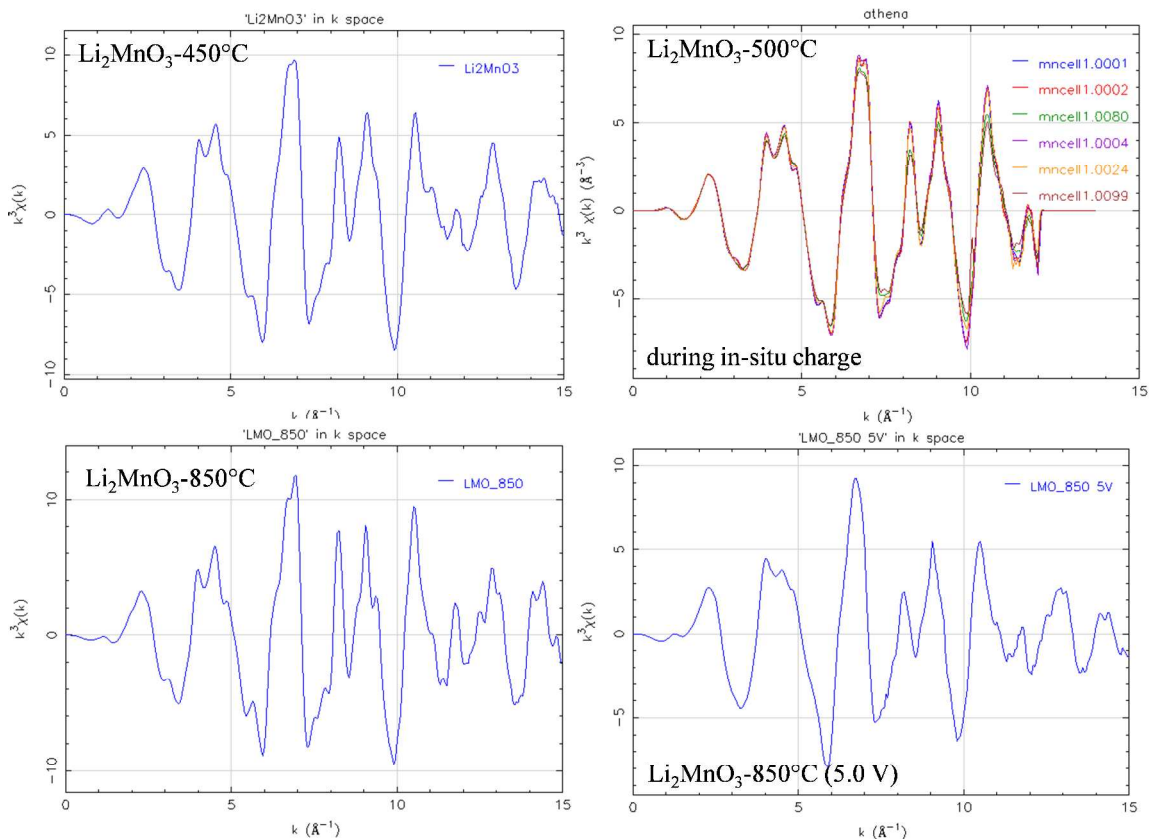


Figure SI-2. Raw, extracted,  $k^3$ -weighted EXAFS data of  $\text{Li}_2\text{MnO}_3$ .

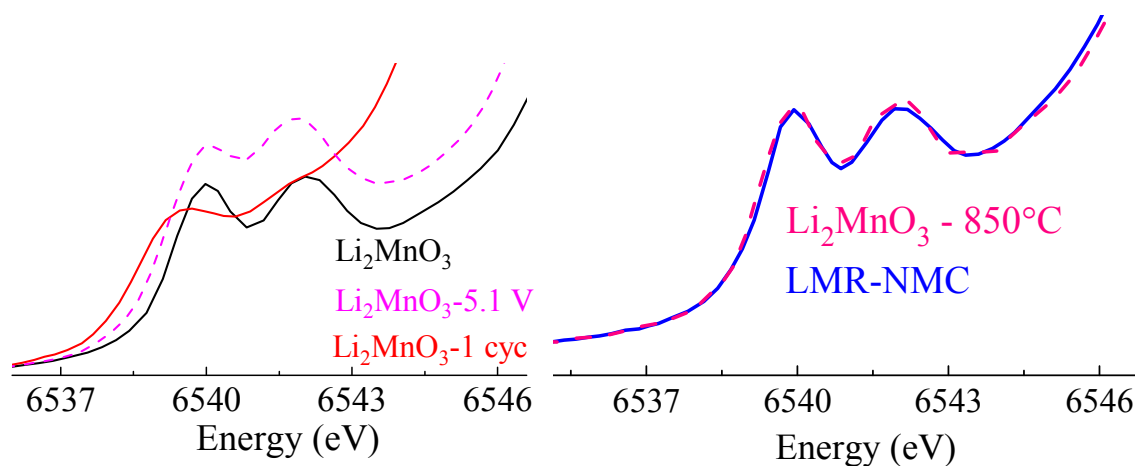


Figure SI-3. Comparison of Mn K, pre-edge data for fresh and cycled  $\text{Li}_2\text{MnO}_3$  (left) and high temperature ( $850^\circ\text{C}$ )  $\text{Li}_2\text{MnO}_3$  and LMR-NMC (right).

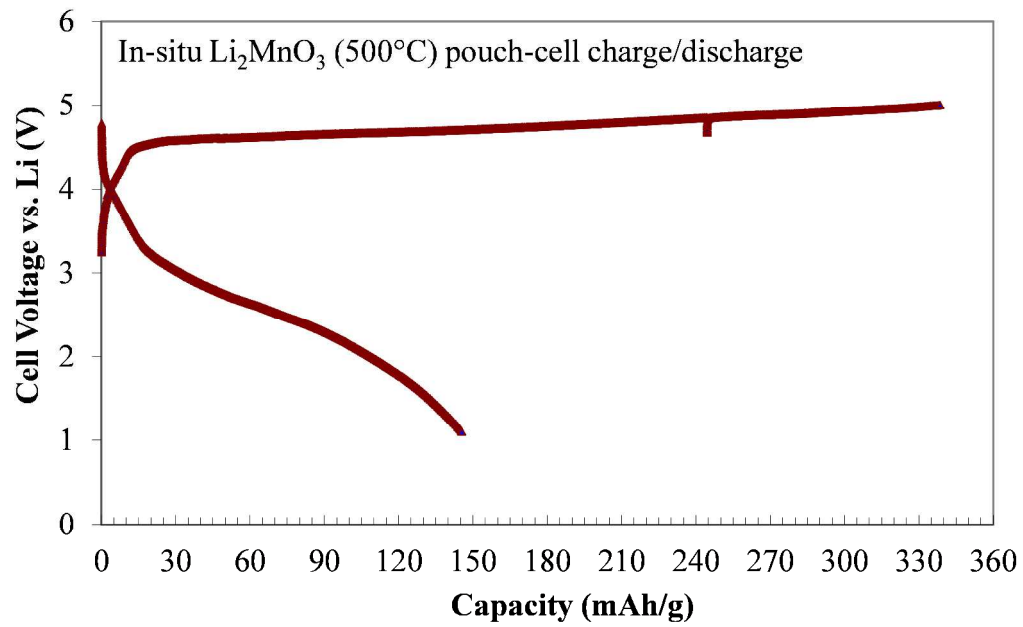


Figure SI-4. First-cycle charge and discharge curves for the in-situ  $\text{Li}_2\text{MnO}_3$  (500°C) pouch cell.

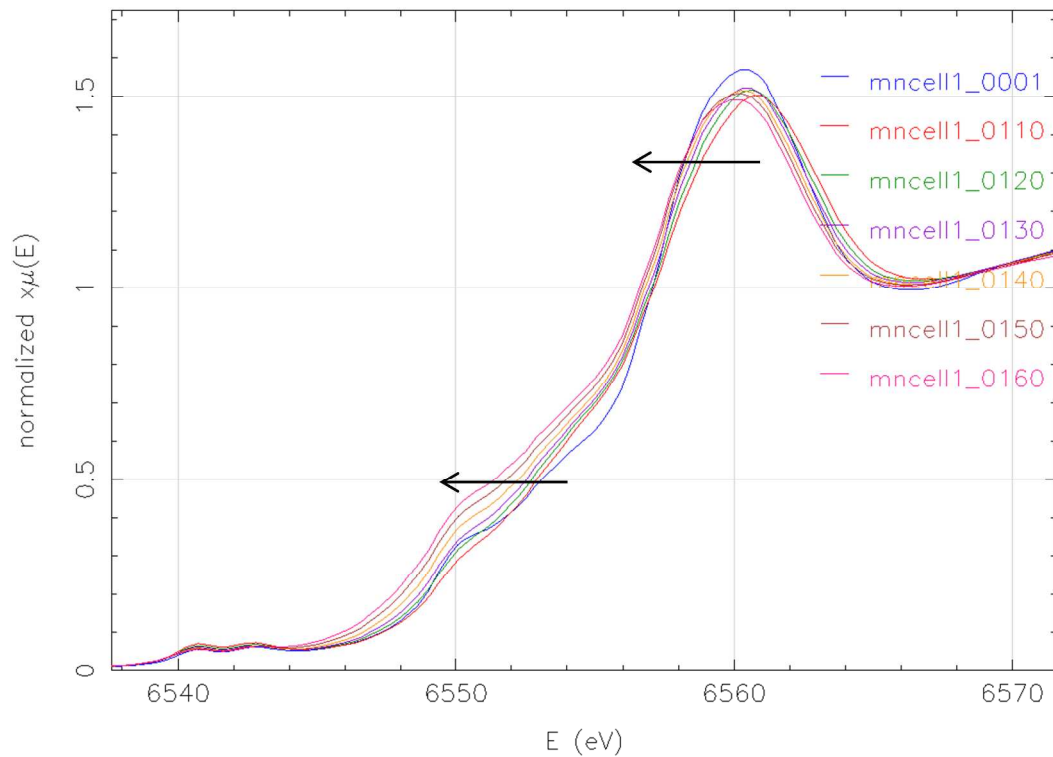


Figure SI-5. XANES data of the first-cycle discharge between 5.0-1.0 V for the in-situ  $\text{Li}_2\text{MnO}_3$  (500°C) pouch cell. Arrows show a systematic shift to lower energy as the discharge progresses from 5.0 V (mncell1\_110, red) to 1.0 V (mncell1\_0160, magenta). The fresh cell is labeled as mncell1\_001 (blue).