

## Unraveling Manganese Dissolution/Deposition Mechanisms on the Negative Electrode in Lithium Ion Batteries

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$\text{Li}_{1.05}\text{Mn}_2\text{O}_4$  spinel as the positive electrode and natural graphite as the negative electrode were used in this study with capacity ratio of 1:1.15. Both positive (Timco) and negative electrode (Sigma Aldrich) formulations contained 80 wt% active materials, 10 wt% carbon black (Alfa-Aesar), and 10 wt % polyvinylidene (PVDF, Alfa-Aesar). Coin cells (2032 hardware) were assembled inside an Ar-filled glovebox. Microporous tri-layered polypropylene (PP) and polyethylene (PE) polymer membrane (Celgard 2325, USA) and 1 M  $\text{LiPF}_6$  in a mixed solution of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 volume ratio, Novolyte, USA) were used as the separator and electrolyte, respectively. The cell was held at 55°C for 100 h before testing. Electrochemical measurements were performed with a constant current density of 10 mA  $\text{g}^{-1}$  based on the mass of the positive electrode and cycled within the voltage window of 3 - 4.8 V at 55 °C operating temperature for 100 cycles.

Figure S1a shows the electrochemical performance of  $\text{Li}_{1.05}\text{Mn}_2\text{O}_4/\text{graphite}$  in a full cell after being held at 55°C for 100 hours. As expected, the first cycle efficiency is only about 40% due to the harsh testing conditions, which leads to poor capacity retention. Most of the capacity was lost after 30 cycles. As reflected in the  $dQ/dV$  curves shown in Figure S1b, several pronounced peaks around 3.5 V are evident in the first charge cycle. They correspond to the Mn reduction and SEI formation on graphite. Typically, the first cycle efficiency for graphite based electrodes is approximately 80% to 90% due to SEI formation under normal testing conditions at room temperature and without calendar life. We expect that pre-dissolved Mn ions from the cathode is occurring as a result of our accelerated aging process and were reduced as metallic particles (reduction potential  $\sim 1.8$  V vs  $\text{Li}^+/\text{Li}$ ) on the graphite surface prior to the SEI formation.

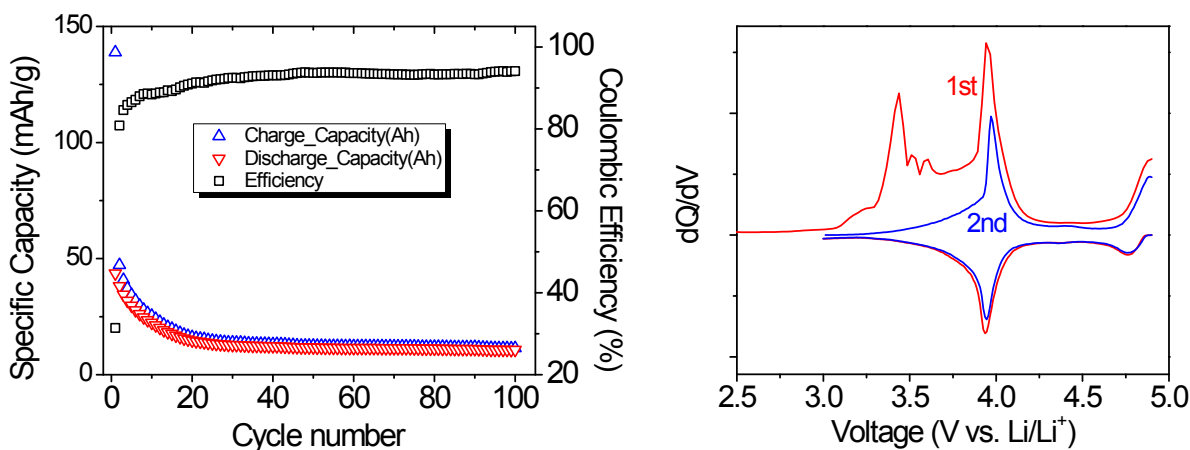


Figure S1 Electrochemical properties of  $\text{Li}_{1.05}\text{Mn}_2\text{O}_4$ . (a) cycling stability under the extreme condition up to 4.8 V and 55°C operating temperature, (b) dQ/dV curves of the full cells during the 1<sup>st</sup> (red) and 2<sup>nd</sup> (blue) cycles.

A specimen for HRTEM characterization was prepared using a standard FIB *in situ* lift-out method from an individual graphite flake. A thin layer of tungsten was ion beam deposited on the surface of graphite in order to protect the surface of the SEI layer from Ga ion beam damage incurred from the 40 keV FIB milling process. A low energy 5 keV cleanup procedure was used for final specimen thinning to electron transparency and to reduce the amount of Ga implantation. Directly from FIB instrument, the specimen was transferred to a Hitachi HF3300 S/TEM for high-resolution TEM characterization using a vacuum transfer holder.

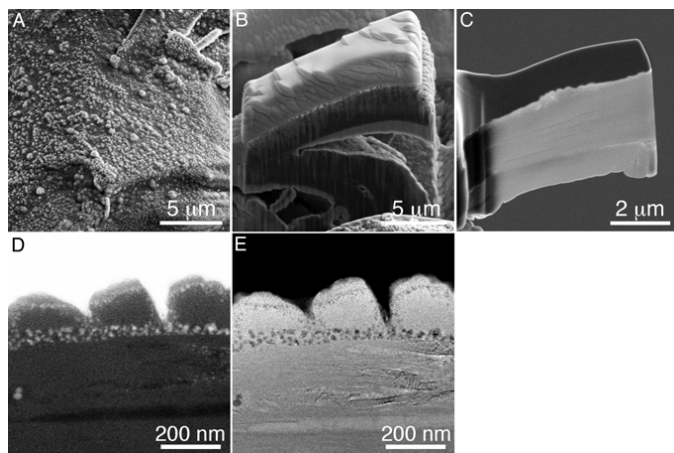


Figure S2. A) SEM image of cycled natural graphite electrode showing SEI on the surface of an individual graphite flake, B-C) SEM images of the FIB-prepared TEM cross sections, D) high angle annular dark-field STEM and E) bright-field STEM image of the TEM cross section showing Mn nanoparticles dispersed in the SEI.