Supporting Information

Oxidation State of Cross-over Manganese Species on the Graphite Electrode of Lithium-ion Cells

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Experimental details

Materials

A12 graphite powder was purchased from Conoco Phillips; the $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) and $Li_2MnO_3.LiMn_{0.31}Co_{0.25}Ni_{0.44}O_2$ (LMR-NMC 'HE5050') samples were obtained from Toda Kogyo Corporation. $Li_{1+x}Mn_{2-x-y}Al_yO_4$ (LMAO) was supplied by Tronox. The Mesoporous Microbead (MCMB) graphite powder was obtained from Osaka Gas Chemicals, and the carbon black (C45), Super P carbon black, and SFG-6 graphite additive samples from Timcal. Battery grade lithium perchlorate was purchased from Sigma Aldrich. 99.995% Manganese perchlorate hexahydrate (Fisher Scientific) was used in electrolyte preparation after drying at 70° C in a vacuum oven for 24 hrs. Coin cell (CR2032) parts and the coin cell crimping machine were obtained from Hoshen. An electrolyte solution (E1) composed of 1M lithium perchlorate solution was dissolved in a solvent mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) in a 1:1 weight ratio. The second electrolyte solution (E2) containing ~200 ppm Mn^{2+} ions was prepared by dissolving a known amount of dried $Mn(ClO_4)_2$ salt into the E1 electrolyte[1]. A 1M solution of lithium hexafluorophosphate in 3:7 (v:v) EC and ethylmethyl carbonate (EMC) was used as the electrolyte solution (E3) for the LMR-NMC cathode study.

Electrochemical methods

The graphite electrodes with an active material loading of 5.44 mg/cm² (G1) and 16 mg/cm² (G2) consisted of A12 graphite (94%), polyvinylidene difluoride (PVDF) binder (4%) and and a C45 carbon additive (2%) coated on 10μm Cu foil whereas MCMB electrodes (active loading 6.53 mg/cm²) contained active material (92%) and PVDF (8%) coated on the same Cu foil. NCA electrodes consisted of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ active material (86%), PVDF binder (8%), C45 additive (2%) and SFG-6 additive (4%) coated on Al foil; LMR-NMC electrodes contained

$Li_2MnO_3.LiMn_{0.31}Co_{0.25}Ni_{0.44}O_2$ (active material) (86%), PVDF (4%), C45 additive (2%) on Al foil; and SFG-6 additive (4%), and LMAO electrodes contained $Li_{1+x}Mn_{2-x-y}Al_yO_4$ active material (84%), PVDF (8%) and Super P Li carbon additive (8%) on Al foil. The active material loadings for the NCA, LMR-NMC and LMO electrodes were, 15.94 , 10.23 , 6.53 mg/cm^2 respectively. Coin cells were assembled in an Ar-filled glove box with O_2 and moisture levels less than 0.1 and 1.5 ppm, respectively. The electrochemical tests were conducted on cells assembled with NCA, LMR-NMC or LMAO positive electrodes with graphite negative electrodes using E1, E2 or E3 electrolyte solutions soaked in a Celgard 2325 separator. Using EC:DMC based electrolytes was challenging because they did not easily wet the Celgard 2325 separator. This problem was alleviated by i) allowing the cell to stand for 24 h before initiating the electrochemical tests, or ii) using a surface-coated Celgard 3500 separator. Cells C1 and C2 contained the G2 negative electrode, whereas cells C3 to C6 contained the G1 negative electrode.

Characterization

X-ray absorption

X-ray absorption near edge structure (XANES) data were collected in fluorescence mode at the Sector 20 BM beamline of Argonne's Advanced Photon Source. Mn K-edge data of the graphite electrodes were acquired in the fluorescence geometry using an energy discriminating, multi-element, Ge detector. The incident beam was monochromatized using a Si(111) fixed-exit, double-crystal monochromator. In all cases, a Mn foil was simultaneously measured, and energy calibrated with the threshold energy (E0) defined according to Kraft et al.[2] Harmonic rejection was facilitated by the use of a Rh-coated mirror as well as a 20% detuning of the beam intensity at ~400 eV above the edge of interest. The normalized XANES data were generated using established methods with the ATHENA/IFEFFIT software package[3]. To estimate of the amount of Mn in the zero valent state we have scaled the peak height of the first derivative of the spectra of our samples to that of a pure Mn metal standard. Based on the scaling factor, we estimate the percentage of Mn in the zero valent state in our cycled graphite electrodes. The graphite electrodes were extracted from the cells in the charged form. The cells were decrimped using an MTI decrimper and the graphite electrode subsequently sealed between aluminized mylar and kapton tape inside an Ar-filled glove box with water and O_2 levels below 1 and 0.5 ppm respectively. The sealed electrode was placed into a box with inlet and outlets for helium flow during the XAS measurement. The sample box was quickly connected to a helium flow which was maintained throughout the XAS measurement to eliminate the effect of atmospheric contaminants on the Mn species in the graphite anode.

Inductively Coupled Plasma – Mass Spectrometry (ICP-MS)

Graphite electrode samples extracted from NCA/Gr cells that contained ~200 ppm Mn^{2+} in the electrolyte were analyzed by ICP-MS by the Analytical Chemistry Laboratory at Argonne National Laboratory.

Transmission Electron Microscopy

Transmission electron microscopy (TEM) images and energy dispersive X-ray (EDX) spectra of electrode samples were obtained with a JEOL JEM-2100F microscope operating at a voltage of 200 kV. For TEM characterization, samples were prepared by scraping off some of the cycled electrode onto the TEM grid using a clean tweezer.

Figures
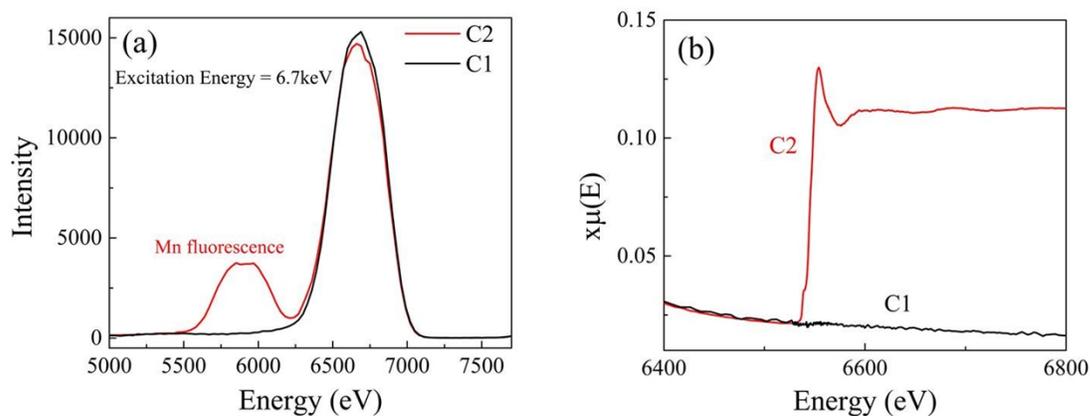
Fig. S1 (a) Energy dispersive spectra with an excitation X-ray energy of 6.7 keV (b) unnormalized raw X-ray absorption spectra for graphite electrodes extracted from cells C1 (Gr/E1/NCA – no Mn^{2+} in electrolyte) and C2 (Gr/E2/NCA – ~200 ppm Mn^{2+} in electrolyte). Absence of the Mn fluorescence peak (a) at ~5900 eV and the absorption edge (b) for the graphite electrode from cell C1, thereby confirming the absence of any background signal of trace Mn from the laminate, the electrolyte, or other parasitic contributions.
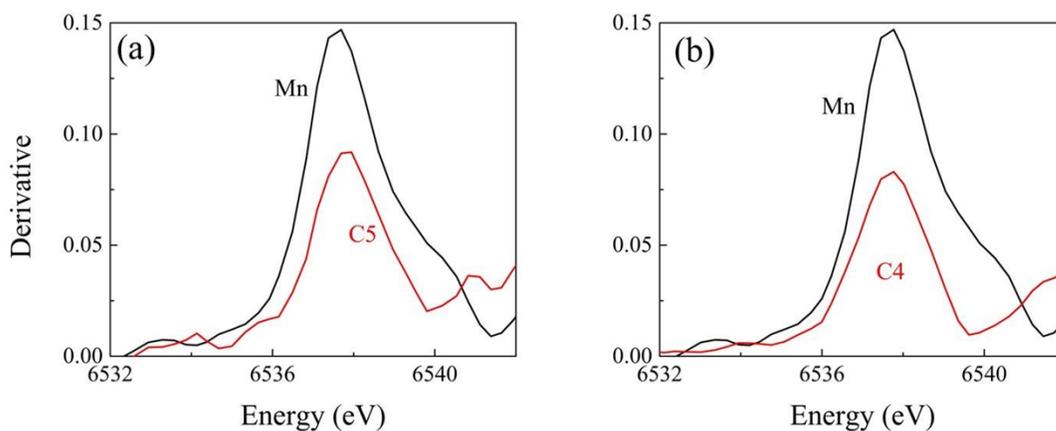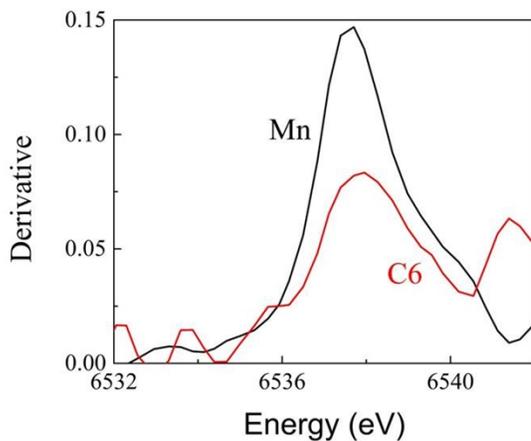

Fig. S2 First derivative of XANES of graphite electrode extracted from (a) charged Gr/E2/NCA cell (C5) with Mn^{2+} enriched electrolyte and (b) charged Gr/E3/LMR-NMC cell (C4) after 27 galvanostatic cycles, compared with XANES of Mn metal reference. The first derivative maxima

for graphite electrodes from cells C5 and C4 are at ~ 6537.7 eV confirming the presence of zero-valent manganese.
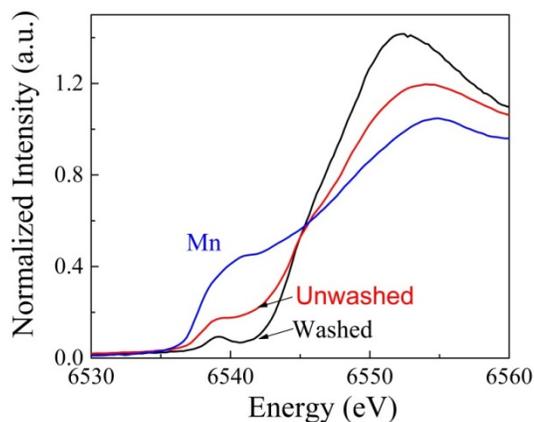
Fig. S3 XANES of two graphite electrodes extracted from Gr/E2/NCA cells with ~200 ppm Mn^{2+} in 1M $LiClO_4$ in EC:DMC (1:1) electrolyte, with and without washing after cell decrimping at the charged state relative to a Mn metal reference.

Fig. S4 First derivative of XANES of graphite electrode extracted from cycled MCMB-Gr/E3/LMAO cell (C6) compared with that of Mn foil reference. The MCMB-Gr/E3/LMAO cell was cycled twice, at 10 mA/g, between 3.6 and 4.4 V at room temperature. The cell was then raised to 55 °C, charged to 4.4 V at 10 mA/g and held at 4.4 V for 60 hours. Thereafter, the cell was disassembled in the charged state. Lithium metal was pressed onto the uncoated side of the copper foil and the entire electrode sealed within an electrolyte containing aluminized mylar pouch to minimize oxidation of the electrode between sample preparation and beam exposure.
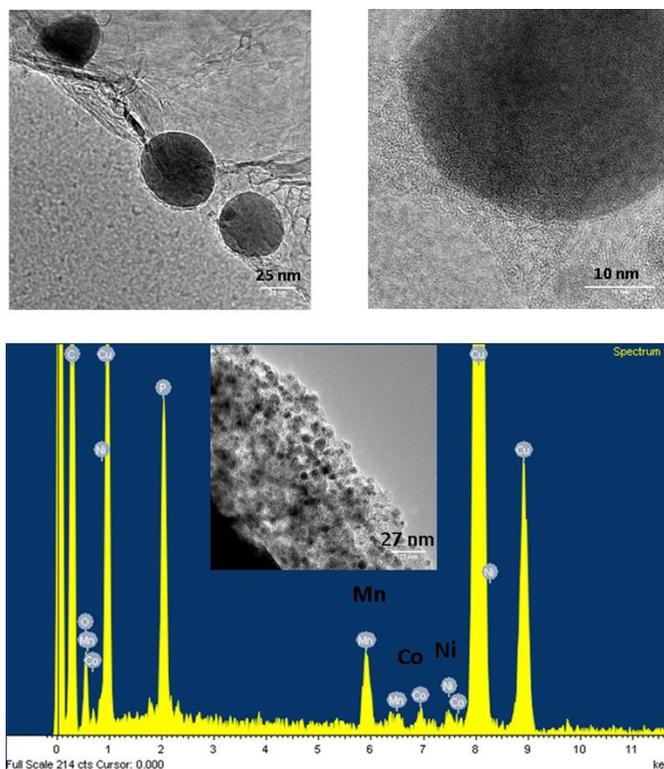
Fig. S5 TEM images and EDX data of graphite particles extracted from a Gr/E3/LMR-NMC full cell after 51 cycles. TEM images show the presence of nanoparticles of size 10-40 nm at the cycled graphite electrode. EDX spectrum (from inset TEM image) indicates the presence of Ni, Co and Mn due to transition metal dissolution from the LMR-NMC positive electrode, as well as various residual electrolyte species on the graphite.

References

1.   Y. J. Kang, J. H. Kim and Y. K. Sun, *J. Power Sources*, 2005, **146**, 237-240.
2.   S. Kraft, J. Stümpel, P. Becker and U. Kuetgens, *Review of Scientific Instruments*, 1996, **67**, 681-687.
3.   B. Ravel and M. Newville, *Journal of Synchrotron Radiation*, 2005, **12**, 537-541.