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Supporting Information

LT-$LiMn_{0.5}Ni_{0.5}O_2$: A Unique Co-Free Cathode for High Energy Li-Ion Cells

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Materials Synthesis

A $Mn_{0.5}Ni_{0.5}(OH)_2$ precursor was synthesized by a co-precipitation method in a continuously-stirred-tank-reactor (CSTR) following a previous report.[1] A stoichiometric amount of $Mn_{0.5}Ni_{0.5}(OH)_2$ was thoroughly mixed with lithium carbonate (Li_2CO_3>99%, Sigma-Aldrich) using a mortar and pestle. The mixture was pressed into a pellet and calcined at a 'low-temperature' (LT) of 400 °C for 72 h in air. The heating rate was 2 °C/min while cooling was uncontrolled. The calcined pellet was ground to obtain a homogeneous fine powder.

Materials Characterization

The quality and structure of the LT-$LiMn_{0.5}Ni_{0.5}O_2$ product was first characterized by X-ray diffraction (XRD) using a laboratory Rigaku MiniFlex 600 diffractometer with Cu Kα radiation (1.5406 Å). High resolution synchrotron XRD data were subsequently obtained using the synchrotron 11-ID-C beamline (calibrated wavelength: 0.1173 Å) at the Advanced Photon Source (APS), Argonne National Laboratory. The data were collected in transmission mode using a spinning Kapton capillary tube. Rietveld refinement analyses of the LT-$LiMn_{0.5}Ni_{0.5}O_2$ sample were conducted with the TOPAS software package.

The particle morphology was studied using scanning electron microscopy (SEM) (JCM-6000 PLUS Neoscope microscope). Specimens for high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) characterization were prepared with a routine focused-ion-beam (FIB) lifting-out procedure using a Thermo Scientific Helios DualBeam microscope working at 2-30 keV. HAADF STEM imaging was performed on an aberration-corrected JEOL GrandARM-300F microscope with an operation voltage of 300 kV. The convergence semi-angle was 22.4 mrad; signals with semi-angles spanning from 60 to 409 mrad were collected for HAADF STEM imaging.

Mn K-edge and Ni K-edge XAS data were collected at the 12-BM beamline of the APS. The standard samples for Mn^{n+} ($n = 4$) and Ni^{n+} ($n = 2$ and 3) were prepared as 7mm diameter pellets with boron nitride as a dispersing agent. In addition, a $Ni^{3.7+}$ standard sample was produced electrochemically by charging a Li/$LiNiO_2$ cell to 4.4 V to the cathode composition $Li_{0.3}NiO_2$. All spectra were collected in transmission mode; the data were reduced using ATHENA in the Demeter software package.[2] The standard Mn K-edge (6539 eV) and Ni K-edge (8333 eV) energy was calibrated and aligned using the first inflection point of the edge region of a metallic Mn and Ni foil collected simultaneously with each measurement. For each spectrum, the built-in AUTOBK algorithm was used to normalize the absorption coefficient, μ(k), and separate the χ(k) functions from the isolated atom absorption background. The extracted EXAFS signal, χ(k), was weighted by k^2; fourier transform (FT) was then applied in k-ranges of 3.0–9.749 $Å^{-1}$ for Mn and 2.7-11.8 $Å^{-1}$ for Ni, respectively, using the Hanning window function to obtain the magnitude plots of the EXAFS spectra in R-space (Å). The FT peaks were not phase-corrected, and thus the actual bond lengths are approximately 0.2–0.4 Å longer.

Electrochemical Testing and Ex Situ Electrodes Analysis

LT-$LiMn_{0.5}Ni_{0.5}O_2$ cathode laminates were prepared by coating a cathode slurry on aluminum foil. The composition of the slurry was 84 wt% active material: 8 wt% super P carbon: 8 wt % polyvinylidene difluoride (Solvay) binder homogeneously dispersed in an N-methyl-2-pyrrolidone (NMP) solvent. The typical electrode loading was 4.4 mg/cm^2. Electrochemical tests were conducted using 2032-type coin cells that were assembled in an Ar-filled glovebox. A lithium metal chip was used as the anode. The electrolyte was made of 1.2 M lithium hexafluorophosphate ($LiPF_6$) dissolved in a 3:7 mixture solvent of ethylene carbonate (EC) and ethyl methyl carbonate (EMC). The coin cells were placed in a climate chamber, which was maintained at 30 ^oC, and tested using a MACCOR battery cycler. For *ex situ* XRD and XAS tests, the charged/discharged electrode samples were collected from the disassembled coin cells in an Ar-filled glove box. The harvested electrodes were sealed with Kapton film to prevent air exposure. The *ex situ* XRD and XAS data were obtained from different electrode discs each of which was cut from the same laminate.

Supporting Information References

(1) Feng, Z.; Barai, P.; Gim, J.; Yuan, K.; Wu, Y. A.; Xie, Y.; Liu, Y.; Srinivasan, V. In Situ Monitoring of the Growth of Nickel, Manganese, and Cobalt Hydroxide Precursors during Co-Precipitation Synthesis of Li-Ion Cathode Materials. *J. Electrochem. Soc.* **2018,** *165*, A3077-A3083.

(2) Ravel, B; Newville, M. ATHENA, ARTEMIS, HEPHAESTUS: Data Analysis for X-ray Absorption Spectroscopy using IFEFFIT, *J. Synchrotron Radiat.* **2005**, *12*, 537–541.

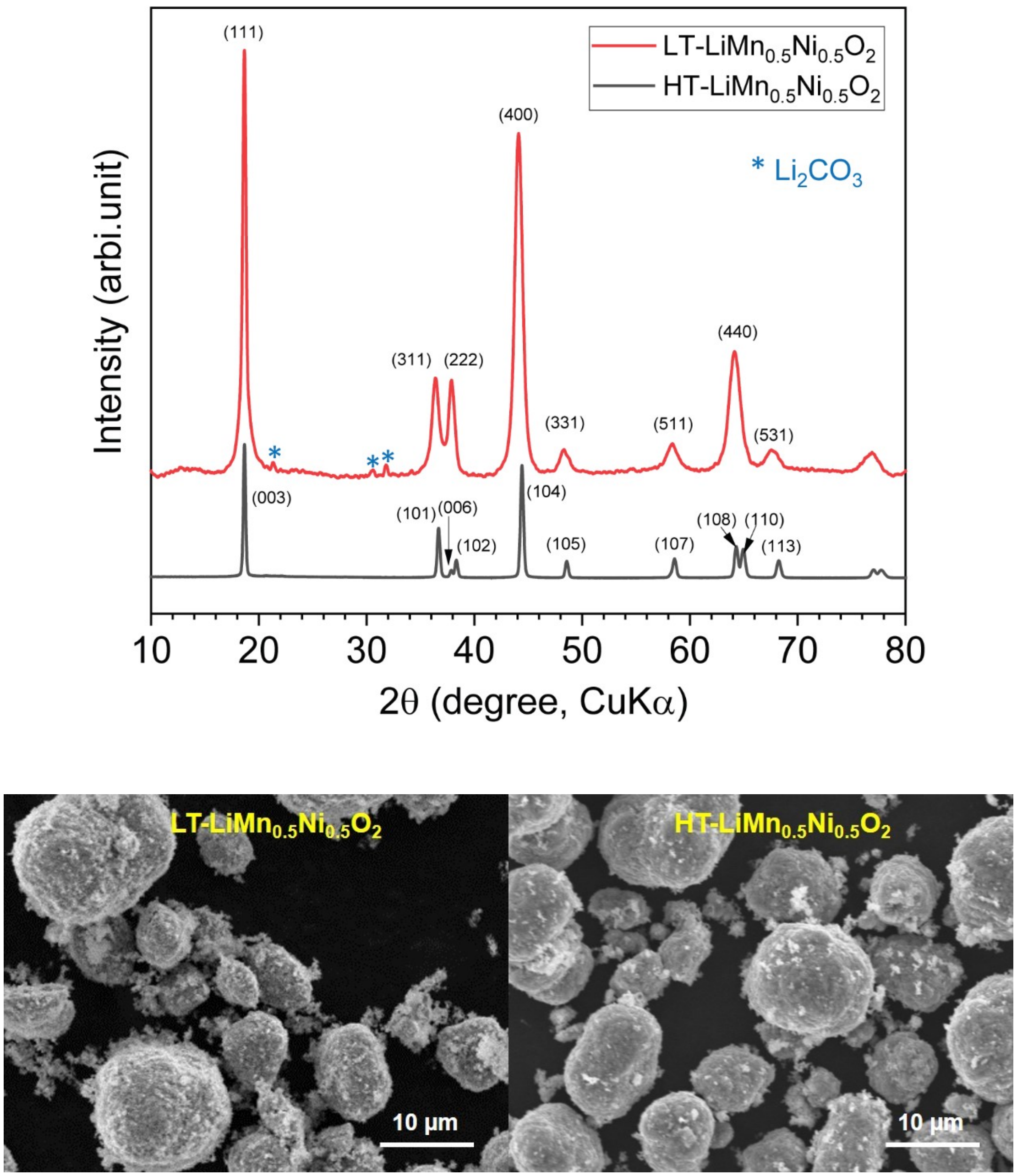


Fig. S1 Comparison of XRD patterns and SEM images for LT-LiMn$_{0.5}$Ni$_{0.5}$O$_2$ and HT-LiMn$_{0.5}$Ni$_{0.5}$O$_2$ samples. The HT-sample, which has a layered structure, was synthesized in air at 850 °C for 15h.

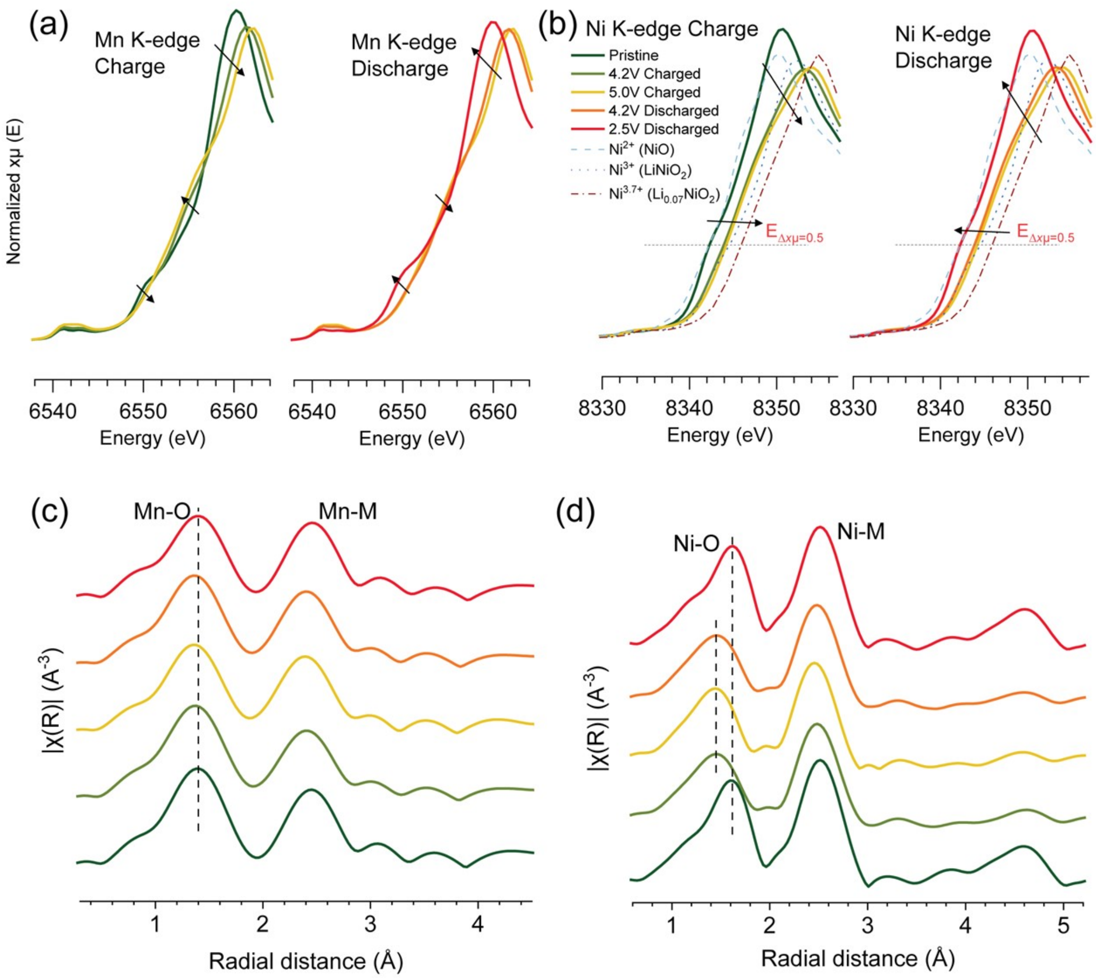


Fig. S2 *Ex situ* Mn K-edge and Ni K-edge XAS analysis of LT-$LiMn_{0.5}Ni_{0.5}O_2$. Normalized (a) Mn and (b) Ni K-edge XANES spectra. K^2-weighted Fourier transform (FT) magnitudes of (c) Mn and (d) Ni K-edge EXAFS spectra.

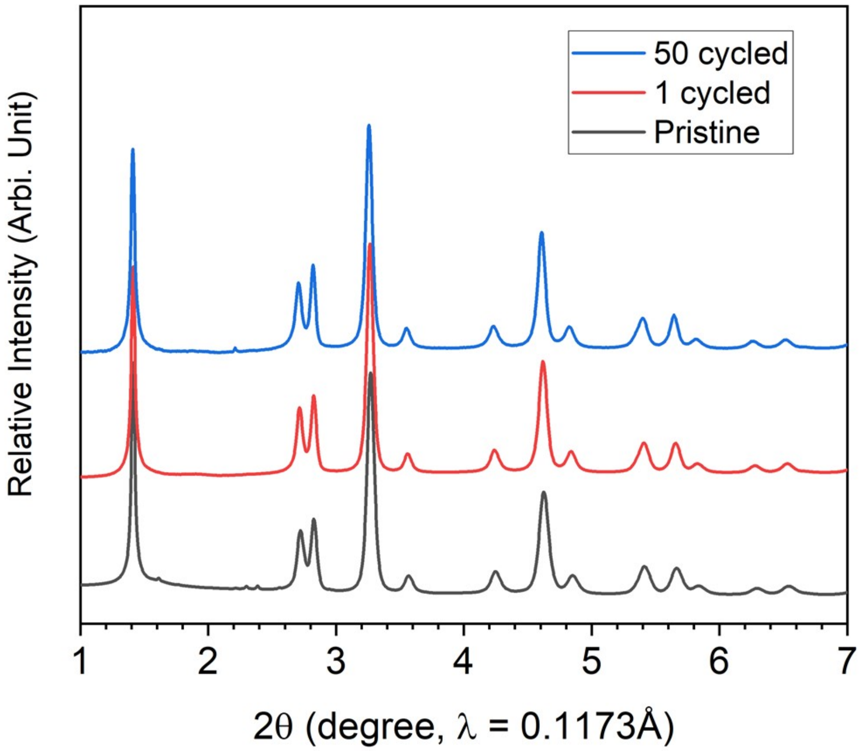
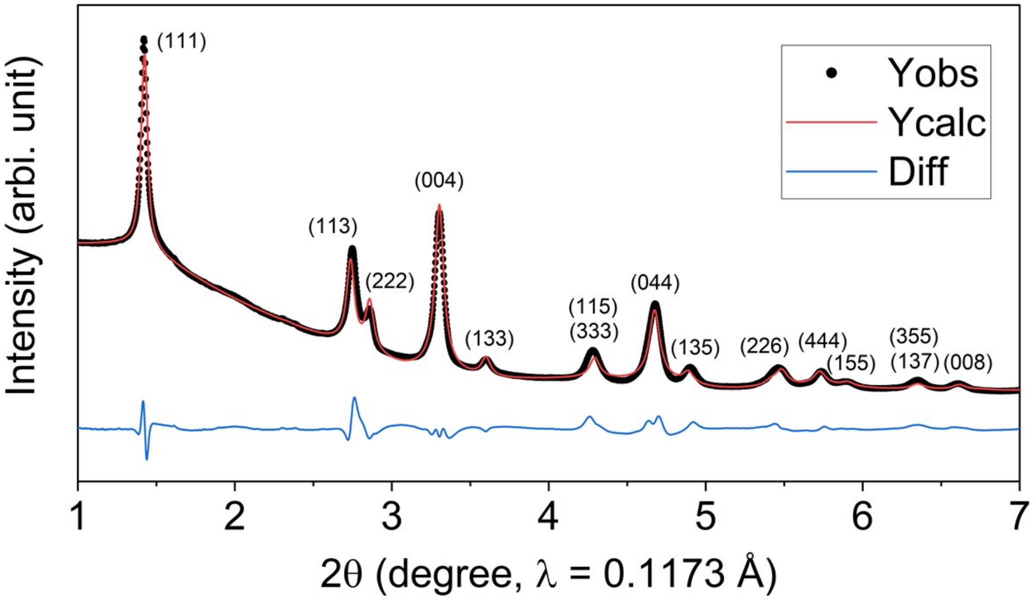


Fig. S3 *Ex situ* synchrotron XRD patterns of LT-$LiMn_{0.5}Ni_{0.5}O_2$ electrodes in their discharged state. Bottom to top: pristine electrode; after 1 cycle, and after 50 cycles (v = 2.5 – 5.0 V; i = 15 mAh/g).



Atom	Site	x	y	z	Occ	B_{eq}
Li1	*8a*	0.125	0.125	0.125	0.81	1
Li2	*16d*	0.5	0.5	0.5	0.166	1
Mn1	*16c*	0	0	0	0.083	1
Mn2	*16d*	0.5	0.5	0.5	0.417	1
Ni1	*16c*	0	0	0	0.083	1
Ni2	*16d*	0.5	0.5	0.5	0.417	1
O	*32e*	0.2537	0.2537	0.2537	1	2.546

Fig. S4 *Ex situ* synchrotron XRD pattern and Rietveld refinement results of a delithiated LT-$Li_{1-x}Mn_{0.5}Ni_{0.5}O_2$ electrode using a spinel model (LT-$Li_{2-y}MnNiO_4$, y ~1.0) collected at 4.2 V. Space group *Fd-3m*; *a* = 8.1307 Å; R_{wp} = 3.73%.

Table S1 Reaction potentials (vs. Li^0) and corresponding redox couples in spinel cathodes.

	Tetrahedral Li ($0 \leq x \leq 1$)	Octahedral Li ($1 \leq x \leq 2$)
$Li_xMn_2O_4$[18]	4.1 V Mn^{3+}/Mn^{4+}	3.0 V Mn^{3+}/Mn^{4+}
$Li_xMn_{1.5}Ni_{0.5}O_4$[19]	4.7 V $Ni^{2+}/Ni^{3+}/Ni^{4+}$	3.0 V Mn^{3+}/Mn^{4+}
LT-$Li_xMn_{0.5}Ni_{0.5}O_2$* [This work]	4.5-4.7 V $Ni^{2+}/Ni^{3+}/Ni^{4+}$? O^{2-}/O^{1-}? Ni-O (hybridized state)?	3.6 V Ni^{2+}/Ni^{3+} 3.0 V Mn^{4+}/Mn^{3+} (minimal)

*Lithiated-spinel component only