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Bulk and Surface Structural Changes in High Nickel Cathodes Subjected to Fast Charging Conditions

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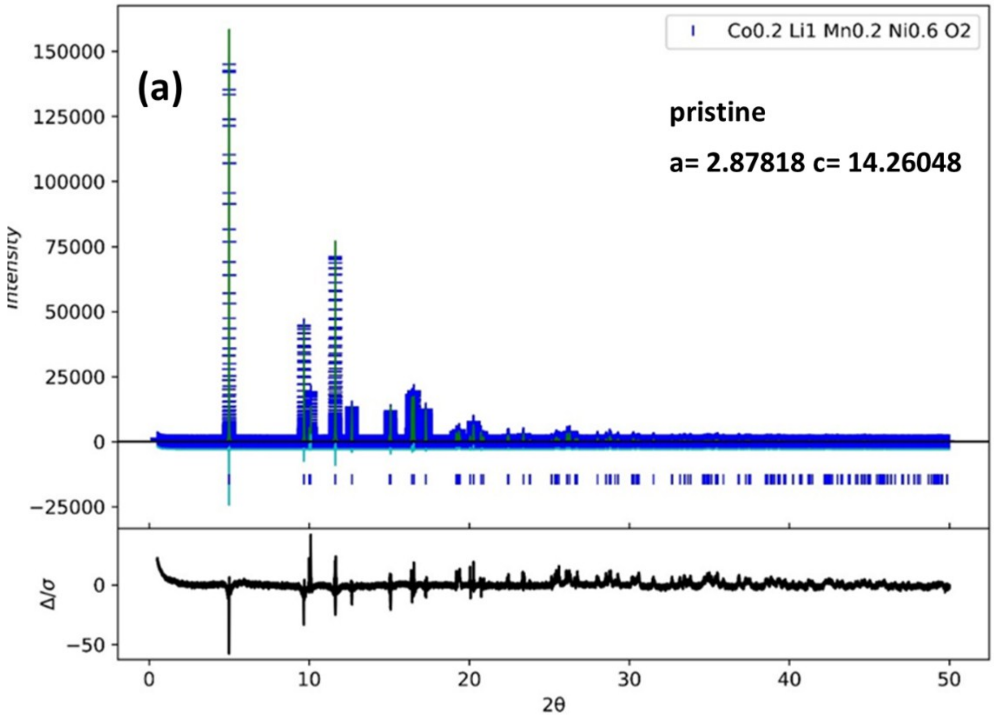
Experimental

Electrode fabrication and cell build were completed at the U.S. Department of Energy (DOE) Battery Manufacturing R&D facility at Oak Ridge National Laboratory. The cathode slurry contained 94 wt.% $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ powder (Targray), 3 wt.% acetylene carbon black (Denka Black), and 3 wt.% polyvinylidene difluoride (Solvay 5130) in *N*-methyl-2-pyrrolidone (NMP). The anode slurry contained 94 wt.% Superior SLC 1520T graphite, 1.5 wt.% carbon black (Timcal Super C65), and 4.5 wt.% polyvinylidene difluoride (Kureha 9300) in NMP. The loading was 2.4 mAh/cm^2 for NMC622 and 2.9 mAh/cm^2 for graphite. The electrolyte was 1 M $LiPF_6$ in ethylene carbonate: ethyl methyl carbonate (EC:EMC) = 30:70 wt% for all cells, and no electrolyte additives were used.

All pouch cells were tested at 30 °C with 5 psi stack pressure. Cycling performance of NMC622/graphite single layer pouch cells was measured after cell formation and degassing. The cell was charged and discharged at a constant rate of C/3 to get the maximum capacity within the voltage range between 2.5 V and 4.2 V. Then a charging and discharging rate of +6C/-1C or +1C/-1C between 2.5 V and 4.2 V with a constant-current hold at 4.2 V were used for comparison.[1] A total time limit was imposed to guarantee that the duration of the charging step did not exceed the intended time for each C rate (10 minutes for 6C charging, 1 hour for 1C charging) at the upper cutoff voltage. Half coin cells were built for further testing. The cathode was punched from disassembled cycled NMC622 pouch cells, and the anode was Li metal. The electrolyte composition was the same as the pouch cells, and the half coin cells were delithiated and lithiated at a constant rate of C/10 between 2.5 V and 4.2 V.

X-ray powder diffraction (XRD) data were collected at the beamline 11-BM (Advanced Photon Source, Argonne National Laboratory) using synchrotron radiation of energy 115.227 keV (λ = 0.412798 Å).

Soft X-ray absorption spectroscopy (XAS) samples were mounted on an aluminum sample holder with double-sided carbon tape in an Ar-filled glovebox and transferred to the load-lock chamber in a double-sided container, using a glove bag purged with argon for the transfer. Soft X-ray absorption spectroscopy (XAS) measurements were performed at the 31-pole wiggler beamline 10–1 at the Stanford Synchrotron Radiation Lightsource SSRL using a ring current of 350 mA and a 1000 L mm spherical grating monochromator with 20 μm entrance and exit slits, providing $\sim 10^{11}$ photon s^{-1} at 0.2 eV resolution in a 1 mm^2 beam spot. Data were acquired under ultrahigh vacuum (10^{-9} Torr) in a single load at room temperature using the total electron yield (TEY), where the sample drain current was collected.[2] All spectra were normalized using the current from freshly evaporated gold on a fine grid positioned upstream of the main chamber. Hard XAS measurements (Ni K-edge XAS) were performed in transmission mode using a Si (220) monochromator at the SSRL, beamline 4-1.[2] The absorption energy was calibrated by using the first inflection points in the spectra of the Ni metal foil reference at 8333 eV.



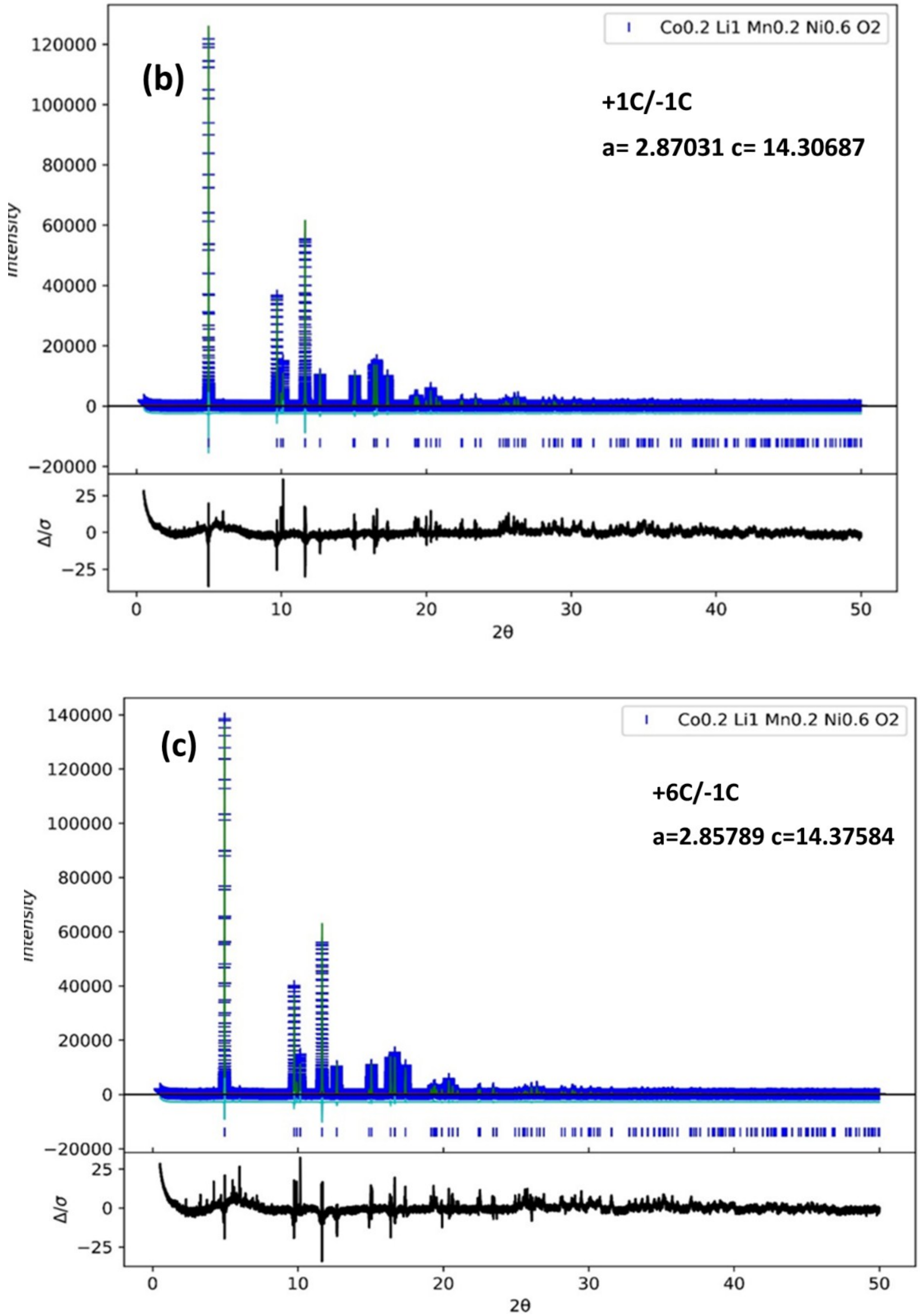


Figure S1. Synchrotron XRD refinement results of (a) Pristine NMC622 (b) NMC622 cathode after 200 cycles +1C/-1C (c) NMC 622 cathode after 200 cycles +6C/-1C

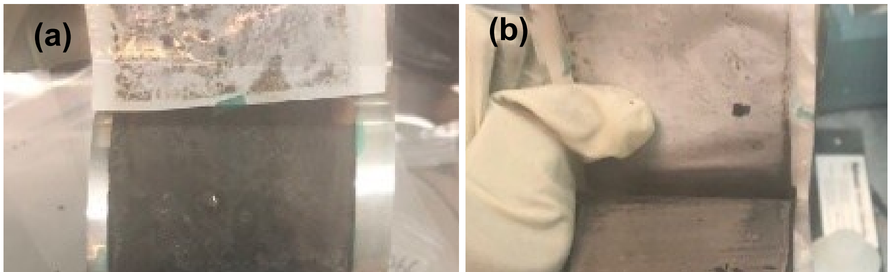


Figure S2. Full cell graphite anodes (a)+1C/-1C, (b)+6C/-1C rate between 2.8 V and 4.2 V after 200 cycles.

[1] C. Mao, R.E. Ruther, J. Li, Z. Du, I. Belharouak, Identifying the limiting electrode in lithium ion batteries for extreme fast charging, Electrochem. Commun. 97 (2018) 37–41. doi:10.1016/j.elecom.2018.10.007.

[2] M.M. Rahman, Y. Xu, H. Cheng, Q. Shi, R. Kou, L. Mu, Q. Liu, S. Xia, X. Xiao, C.-J. Sun, D. Sokaras, D. Nordlund, J.-C. Zheng, Y. Liu, F. Lin, Empowering multicomponent cathode materials for sodium ion batteries by exploring three-dimensional compositional heterogeneities, Energy Environ. Sci. 11 (2018) 2496–2508. doi:10.1039/C8EE00309B.