HAADF STEM imaging of new spinel-like phases in Ni-rich layered oxide Li-ion cathode materials

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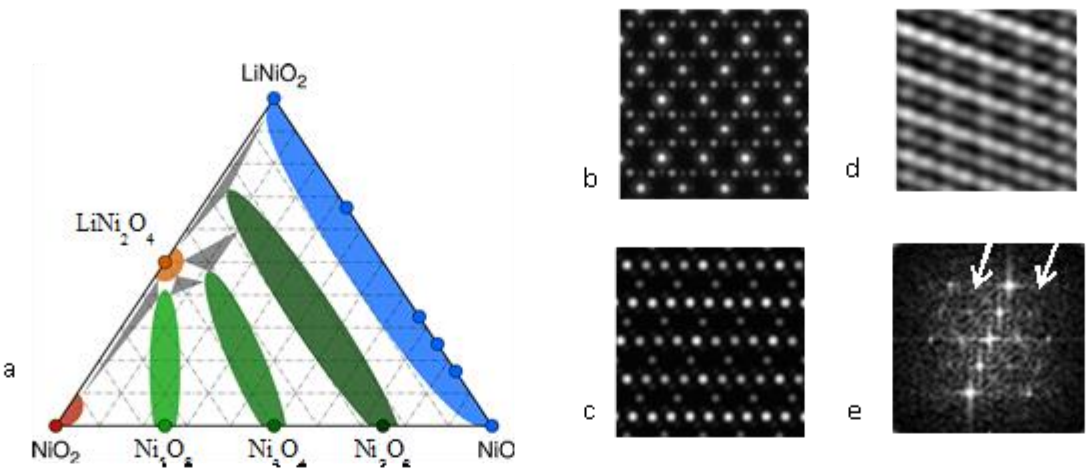
Ni-rich layered oxides (R-3m) such as $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) or $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC811) are amongst the highest capacity cathode materials currently being used commercially. Despite their high structural stability at high state of charge (fully delithiated state), these layered cathodes experience surface oxygen loss and surface structural changes upon reaction with the electrolyte. It has long been argued that oxygen loss leads to the formation of surface phases with rocksalt structure and with possibly spinel or spinel-like phases as an intermediate phase. The Ni-Li-O ternary phase diagram was recently computed using first-principle simulation based techniques which is shown schematically in Figure a. In addition to the known $LiNiO_2$ (R-3m), NiO_2 (R-3m), NiO (Fm-3m) and spinel LiN_2O_4 (Fd-3m) phases, the results predict the existence of three new phases along the oxygen loss path between NiO_2 and NiO. These phase are β–$Ni_{1.25}O_2$ (R-3m), γ–$Ni_{1.50}O_2$ (Cmmm) and d-$Ni_{1.75}O_2$ (Fm-3m). One common feature in these three phases is the gradual filling of the vacant Li 3b layer with Ni^{2+} which is ordered on alternate Li vacant sites. This periodic ordering gives rise to extra reflections which are qualitatively identical to the extra reflections in the spinel phase. In this study, we have searched for the presence of these spinel-like phases in two model $LiNi_{0.8}Al_{0.2}O_2$ (LNA) and $LiNiO_2$ (LNO) systems by combined high angular annular dark field scanning transmission electron microscopy (HAADF-STEM) and electron energy loss spectroscopy (EELS).

HAADF-STEM was performed in a FEI Titan G2 80-200 STEM with a Cs probe corrector at Sandia National Laboratories. The spatial resolution of the STEM system was 0.07 nm. EELS and chemical analysis were performed in an aberration corrected FEI Titan microscope (TEAM I at Lawrence Berkeley National Laboratory) using a GATAN Enfina EELS spectrometer with an energy resolution of 0.8 eV. The ADF-STEM images using the multislice approach were obtained with JEMS program.

ADF-STEM image simulations of spinel LiN_2O_4 (Fd-3m) and β–$Ni_{1.25}O_2$ (R-3m) are shown Fig b and c respectively. The common feature of the three new phases is the cation filing and ordering along the Li (3b) plane only while cation ordering is occurring on two {111} planes in spinel. Although all the phases give rise to similar extra "spinel-like" reflections, the unidirectional aspect of this ordering can be clearly observed by ADF STEM imaging. A HAADF STEM image of such a phase is shown in Figure d with in figure e the corresponding FFT with the extra reflections marked by arrows. Chemical analysis obtained from EELS reveals a reduced oxygen phase with Ni/O ratio of 0.6 which is close to β–$Ni_{1.25}O_2$ (R-3m). Further detailed analysis on image simulations, contrast and comparison with observed structures will be presented.



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