Direct Observation of Cation Ordering in Li\(_{1.2}\)TM\(_{0.4}\)Mn\(_{0.4}\)O\(_2\) (TM: Co, Fe)
Lithium-Ion Battery Materials Using Aberration-corrected TEM

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Excess-lithium layered oxides – Li\(_{1+x}\)(TM\(_x\)Mn\(_{1-x}\))\(_2\)O\(_3\) with TM = Co, Ni, Fe, Cr, or a mixture of these elements– have been studied extensively as potential positive electrode materials to replace LiCoO\(_2\) for lithium rechargeable batteries. Cation ordering in some of these compounds has been reported by XRD, NMR, HR-TEM, and electron diffraction.[1] Here, we report direct observations of cation ordering in Li\(_{1.2}\)TM\(_{0.4}\)Mn\(_{0.4}\)O\(_2\) (TM: Co and Fe) using advanced transmission electron microscopy techniques including aberration-corrected high-resolution high-angle annular dark field (HAADF) imaging, nano-beam diffraction, and electron energy-loss spectroscopy (EELS).

Fig. 1 shows HAADF images of Li\(_{1.2}\)Co\(_{0.4}\)Mn\(_{0.4}\)O\(_2\) along the [0001] zone axis, which reveal the coexistence of Li\(_2\)Mn\(_3\)-like and LiCoO\(_2\)-like areas within (0001) transition metal planes. When viewed along [0001], the projected atomic columns in TM (0001) planes appear as -TM-TM-Li- for Li\(_2\)Mn\(_3\) and -TM-TM-TM- for LiCoO\(_2\), with the closest distance between columns being \(\approx 0.14\) nm. At high collection angle (cut off angle \(> 100\) mrad in the experiment), the intensity of the HAADF image electrons is dominated by incoherently scattered electrons and proportional to \(Z^n\), where \(n \approx 2\). With the aberration-corrected JEOL 2200FS microscope, which provides a \(\leq 0.1\) nm, probe size, TM layers in Li\(_2\)Mn\(_3\) appear as a sequence of two bright dots (heavy atomic columns) followed by a dark spot (light, Li-rich atomic columns). TM layers in the LiCoO\(_2\) structure appear as a sequence of three bright dots (heavy atomic columns), which smear into a continuous streak at lower image resolutions. The integrated intensity along (0001) TM planes (Fig. 1e) is higher at planes showing three-dot structure than at adjacent two-dot layers, suggesting lower Li content at regions showing LiCoO\(_2\)-like structure, while EELS spectra show a small Co enrichment (\(\Delta\text{Co/Mn} \approx 10\) %) at the same regions.[2]

Fig. 2 contains a HAADF micrograph and nanobeam electron diffraction patterns, which show that Li\(_{1.2}\)Fe\(_{0.4}\)Mn\(_{0.4}\)O\(_2\) contains nanosized areas of layered (A, B) and spinel (C) structure. EELS data revealed local enrichment of Fe at the spinel regions. Our data indicate significant Li-Mn clustering at TM planes of this sample, resulting in a coherent mixture of Li\(_2\)Mn\(_3\)-like and Li(Fe,Mn)O\(_2\)-like nanodomains. [3]

References
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FIG. 1. HAADF images of Li$_{1.2}$Co$_{0.4}$Mn$_{0.4}$O$_2$ along [001]. a) and b) are recorded on 2010F (with a probe size of about 0.18 nm), while c) and d) are recorded on 2200FS with a probe aberration-corrector (probe size smaller than 0.1 nm). e) Plot of HAADF intensity integrated along the (0001) plane.

FIG. 2. Coexistence of layered and spinel nanodomains in Li$_{1.2}$Fe$_{0.4}$Mn$_{0.4}$O$_2$. The HAADF image (upper left) shows layered regions (A, B) with different orientations and spinel regions (C), confirmed by corresponding nanobeam diffraction patterns (bottom panels). EELS spectra (top right) show Fe enrichment at the spinel regions and Mn enrichment at the layered regions.