doi:10.1017/S1431927611008828
Microsc. Microanal. 17 (Suppl 2), 2011
© Microscopy Society of America 2011

# 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

J.G. Wen,* J Bareño,** C.H. Lei,* I. Petrov,* and D.P. Abraham**

* Frederick Seitz Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, IL 61801

** Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL 60439

Excess-lithium layered oxides – $Li_{1+x}(TM_aMn_b)_{1-x}O_2$ 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 $[1\bar{1}00]$ zone axis, which reveal the coexistence of $Li_2MnO_3$-like and $LiCoO_2$-like areas within (0001) transition metal planes. When viewed along $[1\bar{1}00]$, the projected atomic columns in TM (0001) planes appear as -TM-TM-Li- for $Li_2MnO_3$ and -TM-TM-TM- for $LiCoO_2$, with the closest distance between columns being ≈ 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 ≃ 2. With the aberration-corrected JEOL 2200FS microscope, which provides a ≲ 0.1 nm, probe size, TM layers in $Li_2MnO_3$ 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 ($\Delta Co/Mn \approx$ 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 $Li_2MnO_3$–like and $Li(Fe,Mn)O_2$ –like nanodomains. [3]

## References

[1] M.M Thackeray et al. *J. Mater. Chem.* **17** (2007) 3112.

[2] J.G. Wen et al. *Solid State Ionics* **182** (2011) 98.

[3] We are grateful to S.-H. Kang, N. Karan, and Mali Balasubramanian for materials and valuable discussions. We acknowledge use of the Center for Microanalysis of Materials (CMM) at the Frederick Seitz Materials Research Laboratory, University of Illinois at Urbana-Champaign (Illinois), which is partially supported by the U.S. Department of Energy under grant DE-FG02-07ER46453 and DE-FG02-07ER46471. Argonne, a U.S. Department of Energy Office of Science laboratory, is operated under Contract No. DE-AC02-06CH11357.

https://doi.org/10.1017/S1431927611008828 Published online by Cambridge University Press

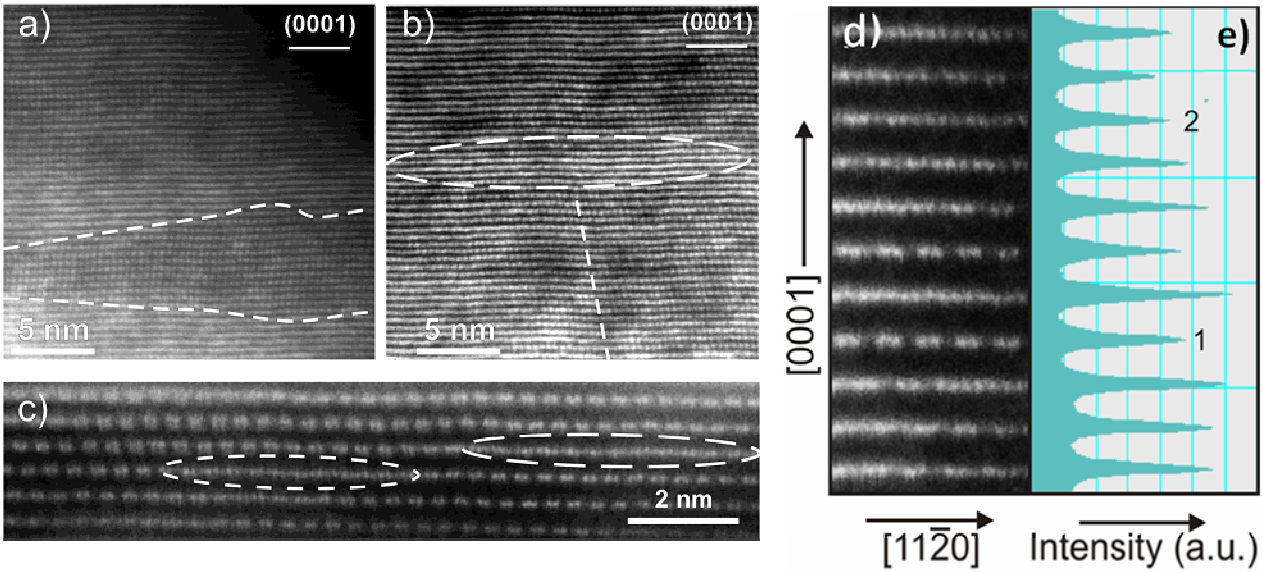


FIG. 1. HAADF images of $Li_{1.2}Co_{0.4}Mn_{0.4}O_2$ along $[1\,\bar{1}\,00]$. a) and b) are recorded on 2010F (with a probe size of about 0.18 nm), while c) and d) are recorded on 2200FS with a probe aberration-corrector (probe size smaller than 0.1 nm). e) Plot of HAADF intensity integrated along the (0001) plane.

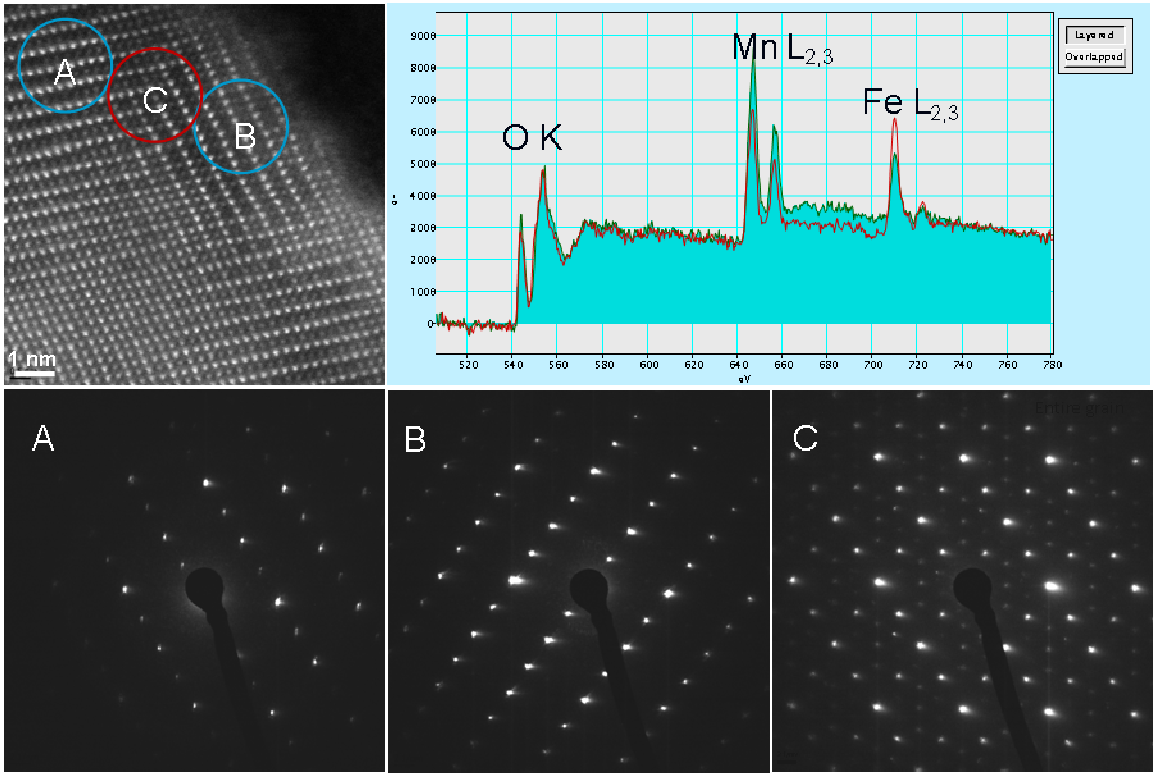


FIG. 2. Coexistence of layered and spinel nanodomains in $Li_{1.2}Fe_{0.4}Mn_{0.4}O_2$. The HAADF image (upper left) shows layered regions (A, B) with different orientations and spinel regions (C), confirmed by corresponding nanobeam diffraction patterns (bottom panels). EELS spectra (top right) show Fe enrichment at the spinel regions and Mn enrichment at the layered regions.

https://doi.org/10.1017/S1431927611008828 Published online by Cambridge University Press