Imaging and Spectroscopy of Pristine and Cycled Li$_2$MnO$_3$

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Li-ion batteries have yet to reach their full application potential due to their inherent cycling performance issues, such as voltage instability and capacity fading [1], while fundamental questions remain unanswered regarding the mechanisms responsible. However, Mn-based layered oxides continue to be promising candidates for cathodes in high-energy-density Li batteries given their high voltage and high discharge capacities [2]. A significant impediment to gaining insight into these layered oxides lies in their complexity and inhomogeneity. Thus, the focus of the present contribution will be on the parent material, Li$_2$MnO$_3$, which shows cycling characteristics similar to its more complex offspring. Scanning transmission electron microscopy (STEM) and spectroscopy are used to characterize structural and electronic properties of both pristine and cycled material.

An aberration-corrected JEOL JEM-ARM 200CF STEM instrument, capable of 0.73 Å spatial and 0.35 eV energy resolution was used to examine Li$_2$MnO$_3$. STEM-based methods are quickly becoming the most promising characterization tools for these and similar materials, owed largely to the wide-range of techniques available on advanced STEM instruments, including the direct imaging of both heavy and light elements, and both energy-dispersive X-ray (EDX) and electron energy loss (EEL) spectroscopies. Imaging modes such as high/low angle annular dark field (H/LAADF) and annular bright field (ABF) are exploited to image heavy atomic columns, strain contrast, and light atomic columns, respectively. Additionally, electron energy loss spectroscopy along with calculations based on density functional theory are used to probe the local electronic structure by monitoring the O K- and Mn L-edges, which can be used to track changes to both the O content and the Mn valence.

Some imaging and spectroscopy results acquired from pristine material are presented in Figs. 1 and 2. Fig. 1 contains an Li$_2$MnO$_3$ LAADF/ABF image pair taken along the [010] direction and an atomic model viewed along the same orientation. The [010] zone axis allows for the direct imaging of O columns, which are adjacent to the Mn/Li mixed planes, and Li columns, which are sandwiched by the O columns; both O and Li are visible in the ABF image. An EEL spectrum acquired on pristine Li$_2$MnO$_3$ is presented in Fig. 2. As noted above, using key features such as the O K-edge pre-peak intensity and the Mn $L_{3/2}$ ratio and L_3 onset, we can track the electronic structure of Li$_2$MnO$_3$. Thus, the focus of this presentation will be on the structural and electronic evolution of the pristine layered oxide explored by combining spectroscopy and atomic-scale imaging with various *in situ* microscopy techniques and *ex situ* electrochemical cycling. Specifically, features such as atomic ordering of Mn/Li atoms, O vacancy evolution, and Mn valence changes will be of particular interest.

References
[1] J. Zheng, M. Gu, P. Zuo, C. Wang, J.-G. Zhang, *Nano Lett.* **13** (2013) 3824-3830.
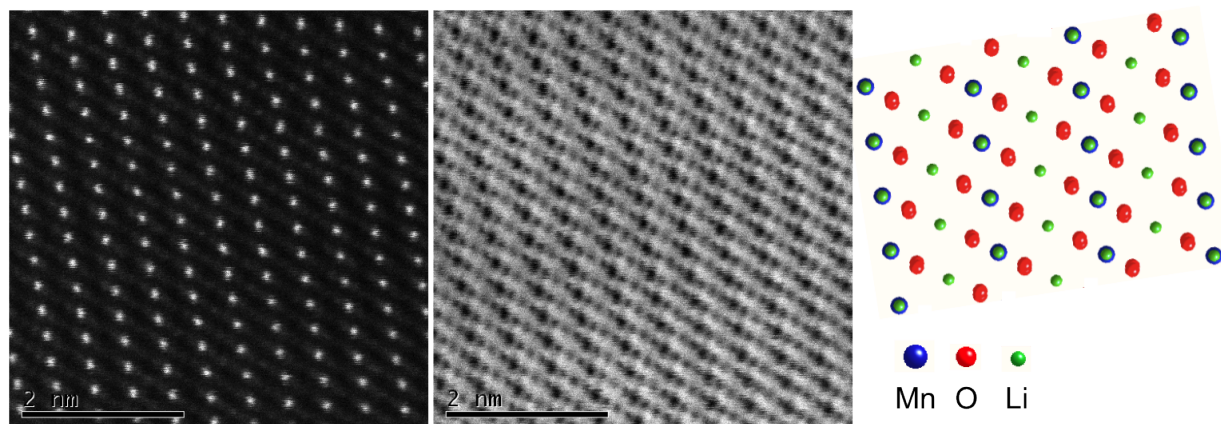[2] M.M. Thackeray, C.S. Johnson, J.T. Vaughey, N. Li, S.A. Hackney, *J. Mater. Chem.* **15** (2005) 2257-2267.

Figure 1: LAADF/ABF image pair of pristine Li_2MnO_3 acquired along the [010] direction, along with a similarly-oriented atomic model. In the LAADF image, the mixed Mn/Li columns appear as bright, with very faint intensity denoting O columns adjacent to these planes. We note the imaging of both O and Li columns in the ABF image.
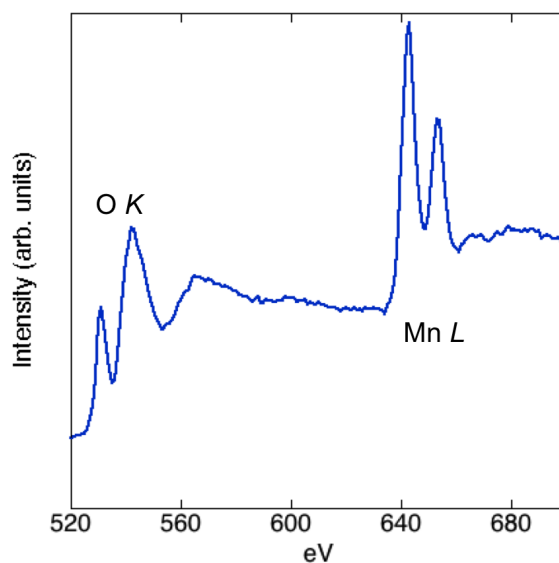

Figure 2: EELS results acquired on pristine Li_2MnO_3 of the O K- and Mn L L-edges. Features relevant to classifying the electronic evolution of cycled material include the O K-edge pre-peak intensity and the Mn $L_{3/2}$ ratio and L_3 onset.