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Cycling and Aging Studies of Li-Based Cathode Materials via Aberration-Corrected STEM

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The development of next-generation batteries for use in advanced applications (such as hybrid electric vehicles) continues to be a highly-researched topic, in particular with respect to Li-ion batteries. Specifically, the so-called NCM layered oxides ($LiNi_xCo_yMn_zO_2$) represents a promising class of cathode materials for next-generation batteries due to their large theoretical capacities [1,2]. However, their practical potential remains limited given their inherent cycling performance issues, such as voltage instability and capacity fading. Although much is conjectured, seemingly very little is known about how these materials degrade/age, and what precautions can be taken to prevent the changes deleterious to the performance of these cathode materials.

The present contribution will discuss a variety of oxide cathode materials in the context of scanning transmission electron microscopy (STEM) analysis. Specifically, these materials require characterization of chemical compositions/gradients, electronic structure (ion valence), structural disorder, and ion rearrangements. Thus, STEM-based methods are the most promising characterization tools, with techniques available which include the direct imaging of both heavy and light elements, and both energy-dispersive X-ray (EDX) and electron energy loss (EEL) spectroscopies. To that end, we will present a systematic study on the effects of aging, cycling, electron beam irradiation, and other environments taxing to the structural and electrochemical stability of the oxides.

Multiple Li-rich, Mn-bearing cathode materials will be discussed after being exposed to various external stimuli. For example, the process of in situ irradiation via the high-energy electron beam allows for single particle tracking of the processes occurring upon Li and O loss from the material, and is likened to a form of accelerated aging when compared to the structural and electronic changes which occur upon electrochemical cycling. In fact, the overall (generally unintended) effects the electron beam has on a pristine material is an area of microscopy that is often ignored, but is of the utmost importance with this class of materials. When performing spectroscopy with a high-energy electron beam, or even simply while aligning/focusing the probe on the specimen, the electron dose delivered is more than enough to impart irreversible damage. For example, Figure 1 presents an NCM material both before and after a very gentle and brief 1D EELS line scan; not only is the sample surface destroyed, but the crystal structure away from the surface has been transformed to a rock salt-like structure, with transition metals now occupying the Li plane. These, and other effects will be discussed at length.

For these and similar materials, generally a combinatorial microscopy approach is required, consisting of LAADF/ABF imaging, EELS to determine valence, and high-spatial-resolution EDX spectroscopy to determine the nature of intercalation; furthermore, in some cases, the imaging voltage may change between 80/200 kV, depending on the desired output. It is important to note that much of the above analysis would not be possible without the use of advanced STEM instruments, outfitted with both EEL and EDX capabilities. In the present case, the UIC aberration-corrected JEOL JEM-ARM 200CF STEM instrument, capable of 0.73 Å spatial and 0.35 eV energy resolution, equipped with a large angle silicon drift EDX detector, was employed [3].

References
[1] J. Zheng, P. Xu, M. Gu, J. Xiao, N.D. Browning, P. Yan, C. Wang, J.-G. Zhang, *Chem. Mater.* **27** (2015) 1381–1390.
[2] S.-K. Jung, H. Gwon, J. Hong, K.-Y. Park, D.-H. Seo, H. Kim, J. Hyn, W. Yang, K. Kang, *Adv. Energy Mater.* **4** (2014) 1300787.
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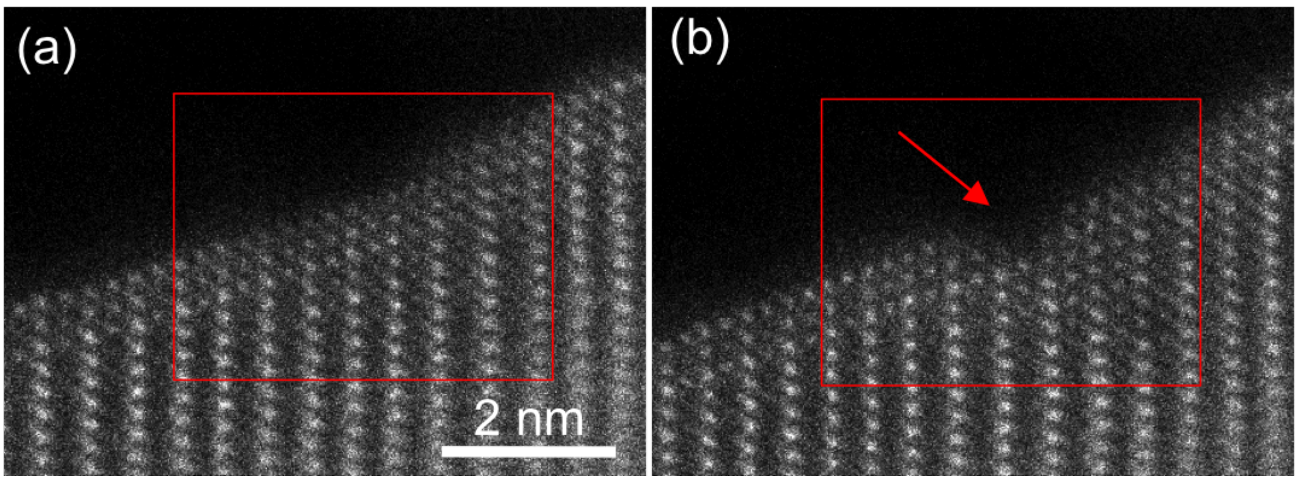

Figure 1: Atomic-resolution STEM images before (a) and after (b) a modest (in beam current) and short (temporally) one-dimensional EEL scan; it is clearly observed that the surface structure is destroyed, while the remaining crystal structure has been altered from a layered to a rock salt-like structure. Therefore, the unintended effects of the electron beam must be carefully accounted for and mitigated during the imaging and spectroscopy of these materials.

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