

Structural Changes Induced by Cycling/Aging in Oxide Materials for Lithium-Ion Batteries

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Rechargeable Li-ion cells present the highest energy and power density of any commercial battery technology. These cells constitute the main power source of modern consumer electronics, and are being increasingly considered for space satellites, medical devices, and distributed energy storage applications. In addition, considerable materials research is being conducted at Argonne to extend Li-ion battery technology to hybrid electric vehicles (HEVs), plug-in HEVs, and battery electric vehicles (EVs), wherein the challenge is to achieve extended driving range (i.e., energy), high charge/discharge rates (i.e., power), and long calendar life (i.e., stability) in a safe and cost-efficient manner. Commercial lithium-ion cells employ spinel- LiMn_2O_4 , olivine- LiFePO_4 , and ordered-rock-salt- LiCoO_2 as active materials in the positive electrode; graphite, spinel- $\text{Li}_4\text{Ti}_5\text{O}_{12}$, and silicon are used, or are being considered, as active materials in the negative electrode.

Among the layered ordered-rock-salt compounds, $\text{Li}_{0.8}\text{Co}_{0.2}\text{O}_2$ (with some Al doping) is a front runner for high-power lithium-ion HEV batteries. TEM examination of these oxide particles from cycled/aged cells show structural differences (see Fig. 1) between the surface and bulk – the particle bulk has the expected ordered R3m structure, whereas the particle surface has the Fm3m structure. Elemental analysis data show that the particle surfaces have a higher Ni:O and Co:O ratio than the bulk, which indicates oxygen loss from the particle surface during cell aging. This oxygen loss creates a $\text{Li}_x\text{Ni}_{1-x}\text{O}$ surface layer that has a lower Li ion conductivity (higher impedance) than the particle bulk, thus degrading the rate (power) performance of the oxide/electrode.

Another family of layered compounds – $\text{Li}_{1+\delta}(\text{TM}_x\text{Mn}_{1-x})_{1-\delta}\text{O}_2$, where TM stands for a transition metal (e.g. Fe, Ni, Cr, Co) or a combination of them (e.g. $\text{Li}_{1+\delta}(\text{Ni}_x\text{Co}_y\text{Mn}_{1-x-y})_{1-\delta}\text{O}_2$) – is of intense interest because of their high capacity and thermal stability. [1] There is ongoing debate in the literature on whether these compounds form homogeneous solid solutions or there exist Li_2MnO_3 domains within a $\text{Li}(\text{TM}_x\text{Mn}_{1-x})\text{O}_2$ matrix. A critical aspect of this debate is the intrinsic structure of Li_2MnO_3 [= $\text{Li}(\text{Li}_{1/3}\text{Mn}_{2/3})\text{O}_2$]. Our microscopy data (see Fig. 2) show that the Li-ions exhibit an ordered arrangement in the TM layer – the Li^+ is surrounded by six Mn^{4+} neighbors forming the structural unit $[\text{LiMn}_6]$ which is the building block of Li_2MnO_3 . These $[\text{LiMn}_6]$ building blocks are also observed in other $\text{Li}_{1+\delta}(\text{TM}_x\text{Mn}_{1-x})_{1-\delta}\text{O}_2$ compounds (for example, $\text{Li}_{1.2}\text{Co}_{0.4}\text{Mn}_{0.4}\text{O}_2$ and $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$). Therefore, these oxides are often described as containing a composite structure of ordered or partially disordered Li_2MnO_3 domains intergrown and integrated with the LiTMO_2 structure. Our presentation will focus on structural changes during cycling/aging, which degrade the capacity and energy density of the oxide electrode.

References

[1] J. Bareño et al., *Adv. Mater.*, **22**, 1122 (2010)

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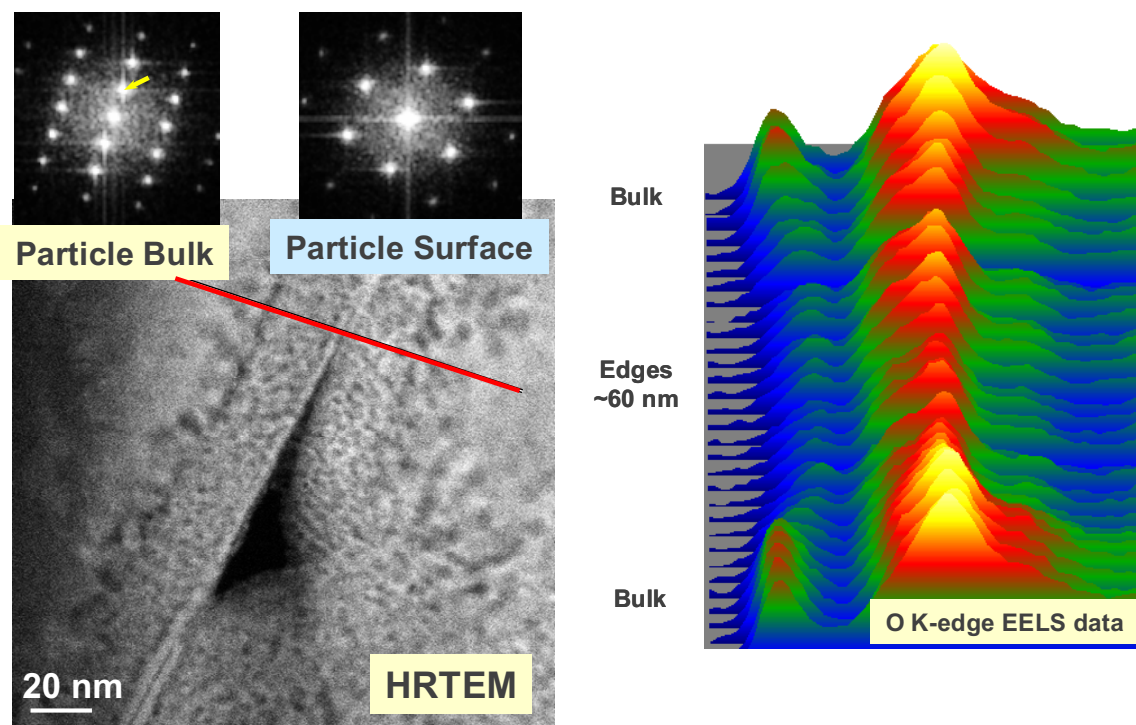


Fig. 1. HRTEM image on $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ particles from a high power fade cell. The corresponding FFT patterns and O K-edge EELS spectrum show structural differences between the surface (Li_xNiO , rock salt-like) and bulk (ordered-rock-salt like) of the particles.

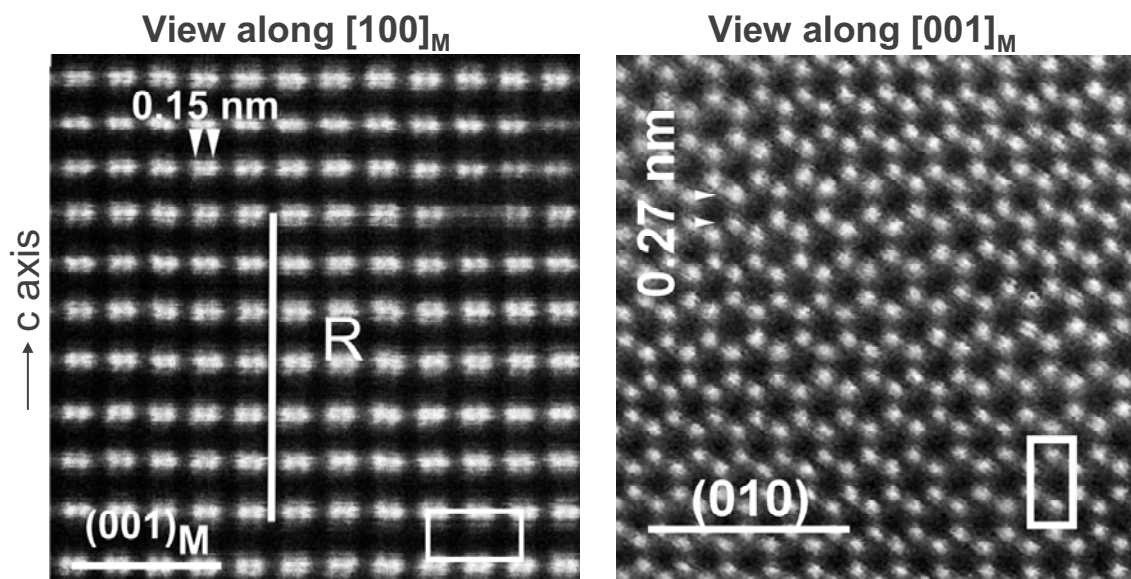


Fig. 2. HAADF images from a Li_2MnO_3 sample along the $[100]_M$ and $[001]_M$ (M =monoclinic) zone axes. Bright-spots in image are TM columns and Li columns appear dark. The $[100]_M$ image shows a -Li-Mn-Mn-Li- arrangement, whereas the $[001]_M$ image shows Li-ions surrounded by six Mn neighbors – both images indicate the ordering of Li-ions in the TM planes.