

## Structural and Chemical Evolution of Li and Mn Rich Layered Oxide Cathode and Correlation with Capacity and Voltage Fading

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Lithium-rich, magnesium-rich (LMR) cathode materials have been regarded as one of the very promising cathodes for Li-ion battery applications. However, their practical application is still limited by several challenges, especially by their limited electrochemical stability and rate capability. In this work, we present recent progresses on the understanding of the structural and composition evolution of LMR cathode materials with emphasis being placed on the correlation between structural/chemical evolution and electrochemical properties. In particular, using  $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  as a typical example, we clearly illustrate the structural characteristics of the pristine materials and their dependence on the materials processing history, cycling induced structural degradation/chemical partition and their correlation with degradation of electrochemical performance. The fundamental understanding obtained in this work may also guide the design and preparation of new cathode materials based on ternary system of transitional metal oxide.

The advanced lithium ion batteries (LIBs), featured with high capacity, high operating voltage and high rate capability, are required for both portable electronic devices and electric vehicle applications. As one of the key components of a LIB, the cathode is a limiting factor for high energy density LIBs. Intense investigations have been conducted to search for the advanced cathode materials. Among various candidates, the lithium-and-manganese-rich (LMR) cathode materials has been regarded as a promising material which can deliver a much higher energy density than the traditional cathode materials such as  $\text{LiMn}_2\text{O}_4$  spinel and  $\text{LiCoO}_2$ . For example, the typical LMR cathode ( $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6}]\text{O}_2$ ) can deliver a discharge capacity exceeding  $250 \text{ mAh g}^{-1}$  after initial charging. The pristine LMR cathode materials have a layered-layered structure, which can be written as  $(x\text{Li}_2\text{MO}_3 \cdot (1-x)\text{LiMO}_2)$ ,  $0 < x < 1$ ,  $\text{M} = \text{Mn, Ni, Co, et al}$ ). As one of the most popular LMR cathode materials,  $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  (represented by 20N-LMR) can be expressed as (50%  $\text{Li}_2\text{MnO}_3$  + 50%  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ ). Upon cycling, the most discernable change of the 20N-LMR particles is the formation of a surface reconstruction layer (SRL) which was also observed in Ni-Mn-based cathodes [1, 2]. It has been generally accepted that cycling induced SRL have the following features: 1) Formation of oxygen vacancies; 2) Transition metal (TM) cations hopping into Li-sites; 3) TM cations being reduced to low valence state; and 4) Lattice structure transformation. Selective area electron diffraction (SAED) patterns confirmed the formation of the SRL (as shown in Figure 1 (a-d)), where extra spots are come from the newly developed SRL (highlighted by red and blue circles). Figure 1 (e-j) show that TM cations have occupied the octahedral sites in Li-slabs within the SRL. With increasing cycle numbers, the thickness of the SRL increases gradually. The SRL structure is actually an ordered structure, which means extra ordering was introduced during cycling as compared with pristine layered structure. Figure 1 (j) shows a snapshot of the SRL development, where there are three

distinguished structures from the outmost layer to inner bulk. By comparing experimental images with simulation structural models, Yan et al (Yan, et al., 2014) proposed the outmost layer are  $M_3O_4$ -type spinel and the middle transition layer matched best with a tetragonal structure with space group of  $I4_1$  (the ICSD No. is 164994). For pristine 20N-LMR, samples synthesized by the CP and SG methods show Ni-rich layer on particle surface, which is detrimental to the electrochemical stability of the LMR cathode. Suppression on the Ni segregation gives rise to significantly enhanced electrochemical performances, as reflected by the largely improved cycling stability and mitigated voltage fade the sample synthesized by HA method. Systematic TEM investigations on the samples with different cycle numbers revealed that the structural degradation of cathode particle initiated from particle surface and propagated into inner bulk accompanied by a progressive chemical composition changes. Such structural and chemical change results in material's degradation as well as cell performance degradation. The better understanding on the correlation between the structure, especially the surface structure of cathode material and its electrochemical properties may also provide useful clues for improving the performances of other electrode materials used in rechargeable battery systems [4].

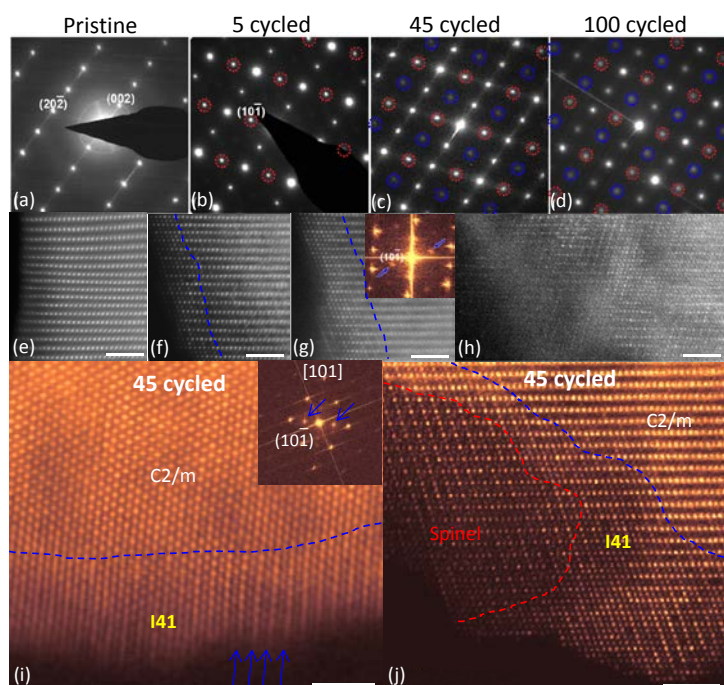


Figure 1. (a-b) [010] zone axis SAED patterns. Extra diffraction spots appeared in cycled samples, which are highlighted by red and blue circles. Red circles indicated the formation of ordered structure. Blue circles come from double diffraction. (e-h) High resolution STEM-HAADF images to show the cycling induced structure change on particle surfaces. Pristine samples (e) shows homogeneous structure from surface to bulk. Dashed lines in (f, g) highlight the thickness of the SRL. In (h), the whole areas were transformed. (i) [101] zone axis STEM-HAADF image and its fast Fourier transformation image. (j) [010] zone axis STEM-HAADF image to show spinel structure and  $I4_1$

structure in a 45 cycled sample. The scale bars are 2 nm in (e-j) [3].

## References

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- [4] The work was conducted in the William R. Wiley Environmental Molecular Sciences Laboratory (EMSL), a national scientific user facility sponsored by DOE's Office of Biological and Environmental Research and located at PNNL.