

## Irreversible structural transformation of Li-rich NMC electrodes during cycling: the role of manganese

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Li-rich layered oxides  $\text{Li}_{1+x}\text{M}_{1-x}\text{O}_2$  ( $\text{M} = \text{Mn, Co, Ni}$ ) can be considered as good candidates for use as positive electrode in LIBs regarding on their high specific capacity (250mAh/g), only achieved by loading at high potential ( $> 4.3$  V). Under these charging conditions, a voltage plateau appears at the end of the charge and an extra capacity is obtained. However, the first cycle is performed with a significant irreversible capacity and coulombic efficiency ranges between 85-90 %. Moreover, Li-rich compounds undergo notable capacity loss and voltage decay during cycling. These drawbacks prevent these materials to be commercialized so far and need further understanding. Redox phenomena at the origin of voltage plateau, have been extensively studied in literature [1]. However, even if irreversible capacity is often related to irreversible structural transformations undertaken by these compounds during the plateau, some questions still remain. What is the exact nature of this structural transformation? Are all chemical elements involved in the same way into the irreversible structural changes? How does this transformation impact redox mechanisms?

In this work, *operando* X-ray diffraction (XRD) and high resolution electron microscopy (HREM) were combined to *operando* X-ray absorption spectroscopy (XAS) to study the structural modifications undertaken during the first charge-discharge cycle. DFT calculations have used to validate proposed structural models.

Our results confirm that these compounds must be considered as nano-composites  $\text{Li}_2\text{MnO}_3$ - $\text{LiMO}_2$  from both structural and electrochemical viewpoints. As shown by *operando* XRD, irreversible structural modifications occur mainly during the plateau. They concern particularly  $\text{Li}_2\text{MnO}_3$  since its characteristics diffraction peaks are no longer observed in XRD patterns at the end of the charge. Furthermore, only manganese spectra are notably modified during the plateau as observed in *operando* XAS. HREM shows that structural transformations undertaken at the end of the charge corresponds to a 3D migration of cations into lithium layers, which are partially delithiated. DFT calculations performed on  $\text{Li}_2\text{MnO}_3$  delithiation process have shown that 3D migration of manganese atoms is coupled with a 2D one inside transition metal layers.

A structural model containing 2D and 3D defects, validated by DFT and HREM image calculations, was used to simulate XAS spectra. From comparison between experimental and calculated XAS spectra, we can conclude that cationic migration mainly involves manganese atoms. These results suggest that new electrochemical phenomena observed during discharge (irreversible cycle) could be related to an irreversible change of the local structure of the manganese (defects 2D, 3D) during the plateau. Moreover, that may also explain why manganese atoms are more redox-active during discharge as probed by *operando* XAS.