FROM BULK TO NEAR-SURFACE INVESTIGATIONS OF $LiNi_{0.5}Mn_{1.5}O_4$ USING *OPERANDO* TECHNIQUES (NEUTRON/X-RAY/RAMAN/OEMS)

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The Li-ion technology still needs improvements to fulfil the requirements for electric mobility, especially in terms of energy density. $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) is a promising cathode material thanks to its high potential during cycling and thus its high energy density [1]. However, it suffers from stability problems in long-term applications, especially in full-cell configuration against a graphite electrode. The understanding of the main and side reaction mechanisms is crucial to develop this cathode further and to this, *operando* techniques are the most suitable ones to follow the structural and/or surface changes occurring during the lithiation/delithiation processes.

For the structural changes and especially to follow the lithium, a cylindrical cell for neutron powder diffraction measurements was developed. A representative result from such *operando* diffraction experiments is shown in Figure 1, left. During cycling, LNMO undergoes a solid-solution reaction from pristine to half-delithiated states followed by a two-phase reaction occurring from half to fully delithiated states with a total shrinkage of the lattice parameter of ca. 6 %. Similar results were obtained from our in house *operando* XRD measurements.

The near-surface region of the LNMO was investigated using *operando* Raman spectroscopy (Figure 1, right). The assignment of the peaks and their intensities were confirmed by first principle calculations. Finally, *online* electrochemical mass spectrometry (OEMS) was used to follow the gas evolution from LNMO during cycling. All these results, combining information from bulk and surface, will be discussed, to demonstrate that LNMO could be a cathode of choice for future of Li-ion batteries.

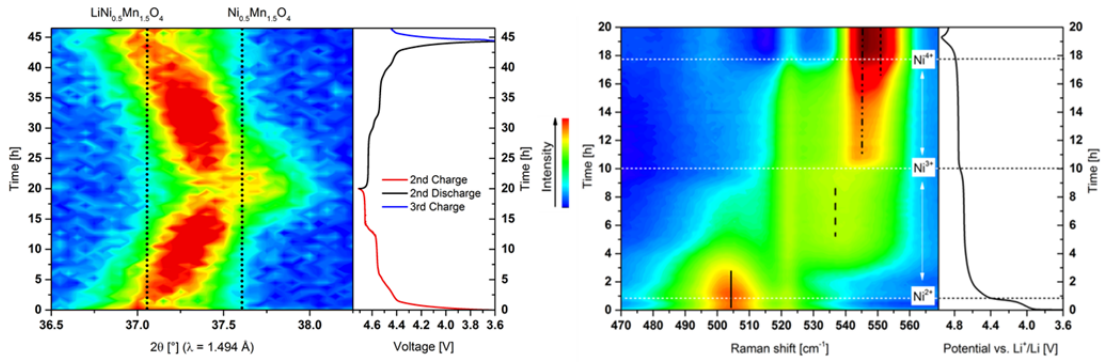

Figure 1: Contour plot obtained from *operando* (left) neutron diffraction measurement of (222) LNMO peak; (right) Raman spectroscopy measurement of LNMO.

[1] A. Manthiram, K. Chemelewski, E.S. Lee, Energy Environ. Sci. 7(2014) 1339-1350.