

## Operando Raman study of $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ ( $1 > x > 0.1$ )

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$\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  (NCA) is nowadays one of the highest performing members of the family of layered mixed transition metal oxides employed as active material for Li-ion batteries. However, NCA degrades upon long-term cycling partly via surface reconstruction and structural fatigue. We evaluate the Raman spectra of NCA during cycling for obtaining mechanistic information of the active material by exploring its lattice dynamics.

The Raman spectra of a NCA particle are collected while the composite electrode is galvanostatically cycled using a newly developed spectro-electrochemical cell. The experimental conditions are optimized for sampling more than 200 spectra per cycle. Figure 1 shows the clear evolution of the two main NCA Raman bands ( $E_g$  at  $485\text{ cm}^{-1}$  and  $A_{1g}$  at  $560\text{ cm}^{-1}$  [1]) as a consequence of electrode potential. A custom-made data analysis script treats and fits each spectrum and the peak parameters (positions, heights and widths) render highly detailed spectral trends. The unprecedented time resolution allows direct comparison with gas evolution analysis, structural and electrochemical data.

The Raman peak position trends relate to the electrochemical redox peaks found in cyclic voltammetry while the Raman peak heights reach maxima when molecular oxygen is released from the lattice. Contrary to what has been conventionally proposed, our findings suggest that the Raman peaks are highly sensitive to the evolution of the material's electronic structure as a consequence of  $\text{Li}^+$  release/uptake. The highly detailed spectral trends offer unique insights into the cycling dynamics and degradation processes of NCA.

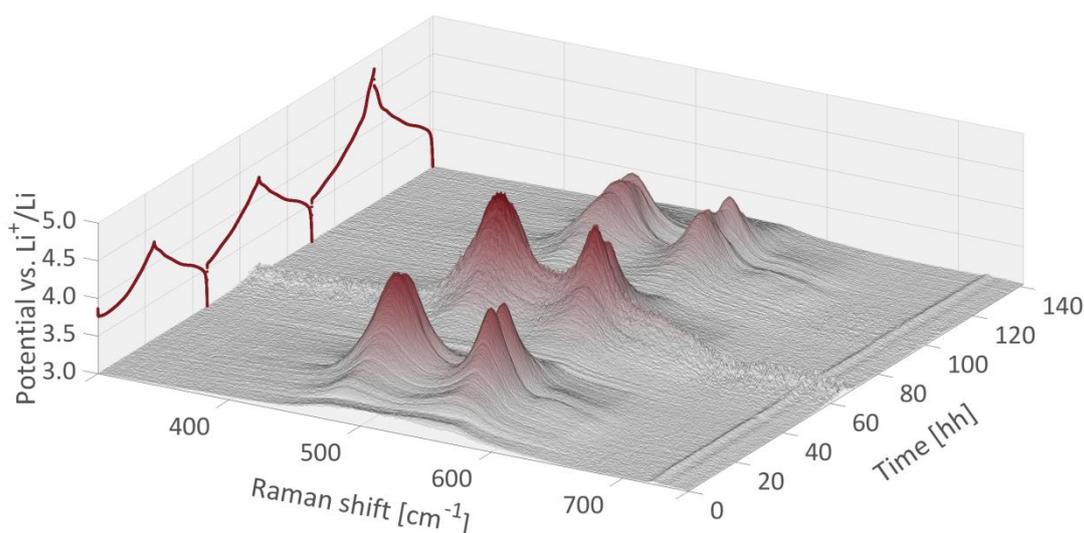


Figure 1. Spectral landscape of NCA during cycling. The corresponding galvanostatic potential profile is plotted in the left, inner plane.

### References:

[1] C. Julien et al. Phys. Chem. Chem. Phys. 4 (2002) 4226–4235.