

**MS40-2-8 Stoichiometry and C-rate impact on NMC/graphite lithiation : an in situ and operando study**  
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S. Tardif <sup>1</sup>, T. Jousseume <sup>1</sup>, J.F. Colin <sup>1</sup>, M. Chandesris <sup>1</sup>, S. Lyonnard <sup>1</sup>  
<sup>1</sup>CEA - Grenoble (France)

**Abstract**

Recent developments in the Li-ion technology have triggered a paradigm shift in the automotive industry and the rise of the electric vehicle (EV). Yet, to fully eclipse fossil fuels, electrochemical batteries must improve their energy capacity, power density, safety and cost efficiency. Focusing here on the electrode materials, the layered compound family  $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$  (NMCxyz) holds great promise. Increasing the Ni content allows to extract more lithium in a potential window compatible with standard electrolytes. However, it also results in a destabilisation of the crystal structure, leading to irreversible capacity losses. A clear understanding of the lithiation mechanism as a function of the Ni content is thus much needed to later optimize the electrode design for better performances. A second factor for irreversible capacity losses is the charge rate. Whereas fast charging is of paramount importance for the EV, the large electric currents implied can lead to and/or enhance the heterogeneous behaviour of the electrode, resulting in premature aging. Rate dependence and material phases evolution are closely related by the chemical potential [1]. That is why the coupled analysis of these two aspects is necessary and the comparison of dynamic (*operando*) and static (*in situ*) mechanisms could distinguish new models from literature [2].

In this study, we followed the lithiation and delithiation mechanism in graphite and NMC electrodes with three different stoichiometries (Ni fraction from 0.6 to 1) in the exact same experimental conditions (setup, cycling conditions) to evidence the lithiation mechanisms. Synchrotron operando X-ray diffraction (XRD) was performed to have both high temporal resolution, angular resolution and wide-angle range required for a precise description of the lithiation and delithiation of the investigated materials. Both graphite and NMC materials were analysed by pattern-matching to follow their crystallographic structure, and thus the lithiation pathway. The comparison was further performed with the dynamics at lower rates (i.e. equilibrium or quasi-equilibrium, as investigated on a Cu-K $\alpha$  diffractometer with Bragg-Brentano geometry).

We highlight similarities and differences in the insertion mechanisms of the different NMC materials, as a function of the C-rate. We also reveal the impact of the charge rate on the intercalation mechanism of NMC as well as of graphite, showing the importance of the layered compound nature, and supported by numerical simulations. For the first time, the confrontation of lithiation models under either dynamic (with no electrochemical reactions pause) or static (system at equilibrium) conditions broaden our knowledge of lithium insertion thanks to the parallel utilisation of *in situ* and *operando* techniques.

**References**

[1] Tardif, S. et al, J. Mater. Chem. A, 2021, 9, 4281-4290 [2] Park, J. et al, Nature Materials, 2021