Raman spectroscopy of NMC and first principles study of Li_xNiO_2 cathodes for Li ion batteries

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A better understanding of the cathode active materials based on Ni-Mn-Co-oxides plays a crucial role in the improvement of lithium-ion batteries. The assessment of the structural order in LiMO, (M = Ni, Mn, Co) by XRD is difficult to achieve, due to the close positions of the characteristic peaks. However, Raman spectroscopy would help in this task, providing an easiest way to identify the presence of orthorhombic and spinel phases in the cathode materials. Complementary, calculations of the equilibrium structure of some cathodes containing Li at different percentages have also been performed. Since the dominant transition metal both in the (811) core and in the (631) shell of the core-shell NMC cathodes used in BAT4EVER project is nickel, we have deeply investigated $LiNiO_2$ lithiated structures in the layered R-3m structure. Atomistic simulations of the battery materials can shed light on those properties of the materials difficult to assess experimentally.

In this work, we report the different phases identified in the cathode materials provided by the BAT4EVER partners by means of Raman spectroscopy, as well as the study of the change in the structural, electronic and magnetic properties of Li_xNiO_2 at various Li concentration x within the first principles density functional theory (DFT) framework. The analysis of the Density of States hints to the formation of a band gap in agreement with the experiment, where an insulating behavior with a gap of 0.5 eV was measured, but never found before in calculations of $LiNiO_2$ in the R-3m structure. The analysis of the formation energies of various configurations of Li_xNiO_2 found that the total energy is highly sensitive to the arrangement of the Li vacancies.

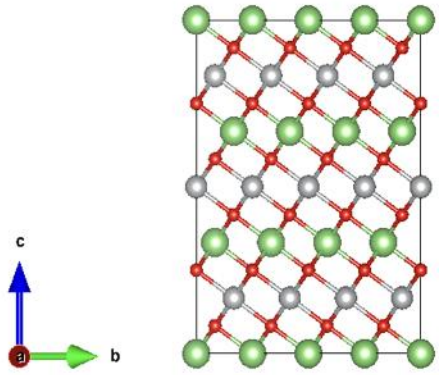

Figure 1. Structure of LNO in the hexagonal R-3m space group with 192 atoms unit cell.