# Structural study and diffusion of lithium in materials for $Li_yMn_{1.5}Ni_{0.5}O_4$ (LMNO) battery cathodes

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Li-ion battery technology is essential for many applications and currently represents the most mature technology for zero-carbon urban transport. The spinel-type compound $Li_yMn_{1.5}Ni_{0.5}O_4$, has an excellent capacity available quickly[1], and a high operating potential 4.7 V thanks to the use of redox couples ($Ni^{2+}/Ni^{3+}$) and ($Ni^{3+}/Ni^{4+}$) during the insertion/disinsertion of $Li^+$. Composed of non-critical transition metal elements, these materials were identified as good candidates for high-power applications [1]. Contrary to the description commonly proposed in the literature [2], recent measurements of neutron diffraction coupled to a DFT study show the existence of a single polymorph with variable plane defect densities as a function of nickel content and synthesis temperature [3].

The objective of this study is to elucidate precisely the structural, electronic, magnetic and electrochemical properties of $Li_yMn_{1.5}Ni_{0.5}O_4$ (y = 0, 0.5 or 1) spinel cathode materials (LMNO) as well as to assess the energy barriers that $Li^+$ ions must overcome during their diffusion. This data is essential for designing new, efficient Li-ion batteries. To this end, we use the density functional theory with GGA functionals (PBE, …), functionals corrected by the Hubbard-DFT+U model and hybrid functionals (HSE06, …) to study the properties of these transition metal oxides. The projected electronic state densities (PDOS) and the structural parameters (cell parameters, bond lengths) are systematically analyzed and compared to the literature.

We will show that if the functional GGA PBE correctly reproduces the geometrical characteristics and the stability of the half-lithiated material (y=0.5), it does not reproduce the lithium intercalation voltages of these materials. The addition of the Hubbard correction (DFT+U) allows to obtain an average operating voltage in agreement with the experiment but leads to worse structural characteristics and semi-lithiated compound (y=0.5) would be unstable, which is inconsistent with the experimental results [1–3]. The use of a hybrid HSE06 functional gives a better description of structural and electronic properties, but with significant computational costs.

Finally, the migration of $Li^+$ ion in the spinel structure of these materials occurs from a tetrahedral site (Td) to another Td site via an empty octahedral site (Oh). Two different channels are identified based on the distribution of $Ni^{x+}$ and $Mn^{4+}$ ions surrounding this empty Oh site. Energy barriers of Li diffusion obtained using the elastic band method (cNEB) [4] is found to be compatible with experimental results and literature [5].

**Keywords:** Lithium diffusion, Spinel cathode materials, LMNO, Operating Voltage, DFT

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