New Insights on the role of Li vacancies and Manganese cation substitution in LNO cathodes

Saleem Yousuf, Md Maruf Mridha, and Rita Magri

The structural and electronic properties of $LiNiO_2$ (LNO) in the R$\bar{3}$m structure are investigated using the spin-polarized Density Functional Theory (DFT) approach and different unit cells. The electronic structure was found to depend strongly on the type of unit cell used in the simulation. Instead of the mono-electron cation redox Ni^{3+} found in literature using smaller cells, the structural optimization using the largest supercell has revealed a charge disproportionation where only Ni^{2+} and Ni^{4+} are present. The occurrence of such charge disproportionation was found before only for the monoclinic P2/c point group[1]. The charge disproportionation is accompanied by a size-disproportionated NiO_6 octahedra. The difference between the total energies of LNO in the R$\bar{3}$m space group and in the monoclinic C2/m, where only Jahn-Teller (JT) distorted octahedra occur and Ni^{3+} cations, becomes only 0.008 eV/atom, smaller than the one calculated using the primitive cells for both systems. The analysis of the density of states hints to a gap opening for the R$\bar{3}$m structure, in better agreement with the experiment.

The delithiation of the R$\bar{3}$m layered LNO leads to the formation of Ni^{3+} cations and more distorted octahedra. Also the substitution of Mn in place of Ni affects greatly the electronic structure as the emergence of Ni^{3+} occurs at full lithiation in contrast to pure LNO. The double-electron redox Ni^{2+} and JT active Ni^{3+} concentrations were found to depend on the Mn concentration. In particular, we found that higher is the concentration of substitutional Mn, lower is the occurrence of JT active Ni ions. This conveys that Mn cation substitution can alter the structural distortion of the structure and help in stabilizing the cathode material, thus leading to a better battery cycle performance.

[1] Hungru Chen,* Colin L. Freeman, and John H. Harding, "Charge disproportionation and Jahn-Teller distortion in LiNiO2 and NaNiO2: A density functional theory study", PHYSICAL REVIEW B 84, 085108 (2011).

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