Ab initio study of Li-rich layered transition metal oxides for Li-ion battery applications

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In the last decades, remarkable industrial and academic research efforts have been focusing on lithium-ion batteries (LIBs) for portable electronics and electric vehicles (EV). Generally speaking, LIBs are more expensive than other battery chemistries, but they provide the highest power and energy densities as well as longer cycle. However, this technology requires further development in terms of safety and performance to establish itself in the automotive market. Thus, new materials and chemistries at the positive/negative electrode sides as well as at the electrolyte side are necessary to overcome the state-of-the-art and the commercial benchmarks.

Over-stoichiometric Li-rich nickel manganese cobalt (LNMC) oxides are a family of promising positive electrode materials with large specific capacity and high working potential. In addition, them have the capacity to reduce the cost and improve the safety of batteries due to the lower concentration of Co. The main challenge regards the atomic structure and cation ordering of LNMC, as they have not yet been clarified and are a matter of controversy between researchers. However, the lack of fundamental comprehension of the structure and the structure-related physico-chemical properties (such as diffusion, phase stability, defect thermodynamics, structural stability upon delithiation, etc) hinders a knowledge-based exploration of the almost infinite possible stoichiometries in this complex structures. Here we present a systematic description of electronic and structural features of LNCMO disordered over-lithiated oxides with general formula $Li_{1+x}(Ni_{0.25-y}Co_{0.25-z}Mn_{0.5+y+z})_{1-x}O_2$ in function of the Co/Ni-content. We apply a state-of-art quantum mechanical approach, based on density functional theory (DFT) and periodic boundary conditions [5]; in particular, we use DFT+U methods, which corrects for the large self-interaction error (SIE) caused by the approximate form of standard exchange-correlation density functional when applied to strongly localized unpaired electrons, ad in the d manifold of Mn, Co and Ni.