

AN OVERVIEW OF THE BEHAVIOR OVERLITHIATED Li(Li,Mn,Co,Ni)O₂ LAYERED OXIDES IN LITHIUM-ION BATTERIES

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The materials belonging to the (1-x)LiMO₂.xLi₂MnO₃ system (M = Ni, Mn, Co) exhibit the largest capacity among all other layered oxides. These materials are overlithiated layered oxides (Li₁(Li_yMn_{1-y-u-t}Co_uNi_tO₂)) with a significant amount of lithium in the transition metal site. Depending on the starting composition, Mn ions can be tri- or tetravalent while Ni ions can be di- or trivalent. In the literature there is a strong debate about the existence of a solid solution or the presence of a composite structure.

A very general study of the synthesis and of the electrochemical characterization of the Li_{1.20}Mn_{0.54}Co_{0.13}Ni_{0.13}O₂ phase has been undertaken for several years in our lab. During the first charge, when all cations are oxidized to the tetravalent state, an overcharge of the cell leads to a structural modification that can be schematically described as a Li₂O extraction occurs that cannot explain alone the oxidation process. Either oxidation of cations to a higher oxidation state or of oxygen is required. All experiments to detect cation oxidation state higher than four failed, so the oxidation of oxygen has been considered.

The contribution of oxygen to the redox activity in this material family is considered from several years. It was suggested in 2009 by Koyama *et al.* from first principle calculation in Li₂MnO₃ [1], and more recently by Ito *et al.* from an XAS study on the Li_{1.20}Mn_{0.56}Co_{0.07}Ni_{0.17}O₂ phase [2]. In our lab we have clearly shown its occurrence in the case of the electrochemical (or chemical) cycling of the Li_{1.20}Mn_{0.54}Co_{0.13}Ni_{0.13}O₂ phase [3-4]. Sathiya et al. [5] also confirmed it in the case of the Li₂Ru_{1-y}Sn_yO₃ system.

From all characterization we performed on can conclude that during the high voltage plateau in the first cycle, there is a partial densification on the external part of the particles followed by an oxygen oxidation in the bulk of the lattice without oxygen migration. This redox process is completely reversible in discharge. The contribution of nickel and cobalt and oxygen reduction leads to the huge specific capacity of this material family.

A general overview of all reactions mechanisms will be presented.

References:

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