

Development of Li-rich layered oxides as concentration-gradient for high energy density lithium-ion batteries

Ségolène Pajot^{1,2,3}, François Weill¹, Michel Ménétrier¹, Adrien Boulineau³,
Gunay Yildirim², Loïc Simonin³ and Laurence Croguennec¹

¹ ICMCB-CNRS, Bordeaux University, Bordeaux INP, F-33608 Pessac, France

² CEATech Aquitaine, F-33607 Pessac, France

³ Univ. Grenoble Alpes, F-38000 Grenoble - CEA, LITEN, F-38054 Grenoble cedex 9, France

The Li and Mn-rich layered oxides are currently attracting a strong interest from the scientific community, as being one of the most attractive class of positive electrode materials for Lithium-ion batteries. Indeed, the Li and Mn-rich layered oxides $\text{Li}_{1+x}\text{M}_{1-x}\text{O}_2$ ($\text{M} = \text{Mn}, \text{Co}, \text{Ni}$) exhibit very high reversible capacity at an affordable cost. A common feature for all the Li and Mn-rich layered oxides is their long voltage “plateau” (i.e. high capacity), observed only at the end of the first charge. This behavior has been explained by the reversible participation of oxygen anions in the redox processes. While it is clear that the largest advantage of the Li-rich layered oxides lies in their outstanding capacities, they suffer from a continuous voltage decay upon cycling. It is induced by irreversible structural modifications occurring at the outer part of the particles (that determines the potential measured) and inducing densification of the metal-oxygen framework.

One of the tracks we are following to modify the surface chemistry of the Li and Mn-rich layered oxides, and to stabilize reversible anion participation to the redox processes is the achievement of concentration gradients within the particles (aggregates). The goal is to promote the formation of the Li and Mn-rich layered oxides in the bulk and, moving to the surface, to enrich the layered oxides composition with Ni and Co: the target is to combine high energy density and chemical stability as it was reported for Ni-rich layered oxides.

The synthesis of carbonate precursors $\text{Mn}_{0.52}\text{Ni}_{0.29}\text{Co}_{0.19}\text{CO}_3$ showing a concentration gradient is achieved via a coprecipitation method and requests to adjust several synthesis parameters including the temperature, the pH, the feeding rate and the stirring speed. A thermal treatment is then performed with optimized Li/M ratios, lithium carbonate being the lithium precursor, and at different temperatures in order to promote lithium diffusion within the particles but also to maintain the concentration gradient after calcination. The average composition of the final lithiated oxide is $\text{Li}_{1.1}\text{Mn}_{0.47}\text{Ni}_{0.26}\text{Co}_{0.17}\text{O}_2$.

In-depth characterization of the composition and structure, from the surface to the core, was achieved combining X-ray diffraction, elemental chemical analyses by ICP, and different techniques of microscopy (EPMA, EDS and FIB-STEM). Electrochemical performances and the thermal stability in the charged state of the battery will be also discussed for this series of materials.