

Laboratory EDXD and High Energy Synchrotron Radiation for *In-situ* Structural Study of Lithium-ion Electrode Materials

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Abstract

The study of structural changes occurring in active electrode materials upon cycling is becoming more and more important in order to understand the factors that limit the cyclability of such compounds.

In fact, the structural stress that can be induced by the intercalation-deintercalation process is known to be one of the most important cause for limited cycle-life, especially when large variations are observed. For that reason, recently, great attention was devoted to "low-strain" materials that show a very reversible intercalation process.

The best way to perform such measurements is *in-situ*, in order to minimize the unavoidable systematic errors induced by sample handling.

We adopted two different techniques for structural *in-situ* measurements: laboratory Energy Dispersive X-ray Diffraction (EDXD) and High Energy Synchrotron X-ray Diffraction (HESXD).

EDXD, originally proposed by our group for *in-situ* electrochemical measurements [1, 2], consents to easily and reliably obtain the real-time evolution of the lattice parameters with high sampling rate.

HESXD was carried out at the European Synchrotron Radiation Facility (ESRF) in Grenoble (France), using the High Energy beamline. Such a choice consented to utilize a monochromatic 87 keV energy X-ray beam, so that very precise results could be obtained.

In this work we report the structural variation upon cycling of several electrode materials for lithium-ion batteries, using results obtained with both the techniques.

In particular, the almost negligible structural variations of the so-called "zero strain" [3] cubic $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$ anodic material were studied using synchrotron radiation. In spite of the fact that the maximum variation of the cubic lattice parameter is lower than 0.1%, we could obtain a high precision curve describing its change upon the intercalation and deintercalation processes. These synchrotron radiation results confirmed the ones already reported using laboratory EDXD [4]. Furthermore, the high precision of the measurement consented the observation of a new interesting feature that is consistent with the study reported by Scharner et al. [5].

Layered Ni-Co-Li oxides having the general formula $\text{LiNi}_y\text{Co}_{1-y}\text{O}_2$ have been extensively studied in order to replace the expensive LiCoO_2 in commercial lithium ion batteries. [6] $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ was already studied from the structural point of view by our group using EDXD. [7]

One of the main drawbacks of such compounds is their instability at high temperatures for low lithium content

values which causes serious safety concerns. [8, 9] Recently proposed doped compounds of general formula $\text{LiNi}_{1-x-y}\text{Co}_x\text{M}_y\text{O}_2$ do not show such thermal problems. [10] Furthermore, these compounds showed a better capacity retention upon cycling. In order to clarify the reason for this last property, the structural variation upon cycling of two compounds (namely $\text{LiNi}_{0.80}\text{Co}_{0.16}\text{M}_{0.04}\text{O}_2$ where M = Al, Mg) were studied. The results will be discussed and compared with those previously reported on the undoped $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$.

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