

In-situ X-Ray Diffraction of Layered  $\text{Li}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_2$   
upon Electrochemical Cycling

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Layered oxide material  $\text{LiCoO}_2$  is among the most promising material for an application as cathode material in 4V lithium batteries. Partial substitution of cobalt for iron could be an interesting alternative due to reduced cost and toxicity, and implication of the  $\text{Fe}^{3+/4+}$  redox couple.

The  $\text{Li}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_2$  ( $0 \leq x \leq 1$ ) solid solution has been prepared by ion exchange and examined by x-ray diffraction, chemical analysis [1] and magnetic measurements [2]. We present here the results of an in-situ x-ray diffraction study on this solid solution. The purpose of this study was (i) to establish the influence of iron partial substitution on the  $\text{Li}_x\text{CoO}_2$  phase diagram, especially regarding the multiple phase transitions present for  $0 \leq x \leq 1$ , (ii) to check whether or not iron is oxidized during this process. The measurements were carried out using plastic batteries (Telcordia technology) on the BM 16 line of ESRF, with a wavelength of 0.3096 Å. 70-80 X-ray diffraction scans were recorded along each electrochemical charge. Batteries were cycled between 3.0 and 5.2 V (see figure 1).

The  $y = 0.1$  and  $y = 0.2$  samples show little difference with respect to unsubstituted  $\text{Li}_x\text{CoO}_2$ . As shown in figure 2, diffraction indicates a two-phase range at the beginning of charge, followed by a single-phase domain for  $0.6 > x > 0.3$ , and the emergence of a different, lithium-poor phase with much smaller c lattice parameter at the end of charge.

For  $y = 0.4$ , the two-phase regime is maintained all the way to  $x = 0.4$ . The capacities obtained show that iron is involved in the oxidation process. This will be confirmed by EXAFS and XANES measurements, the results of which will be shown at the conference.

References :

- [1] M. Holzapfel et al., *JSSC* **156** (2001), 470.  
[2] Chappel et al., *JSSC* **154** (2000), 451.

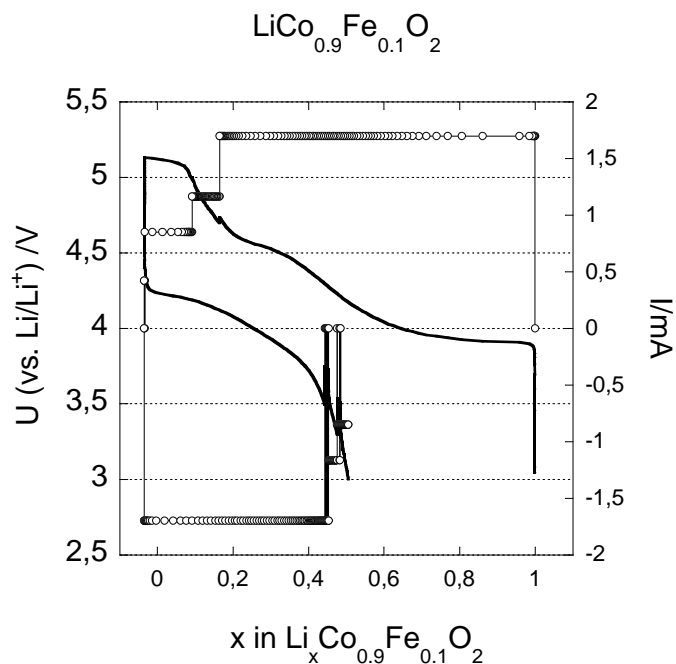


Fig.1. Electrochemical behaviour of a plastic battery containing  $\text{Li}_x\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_2$ .

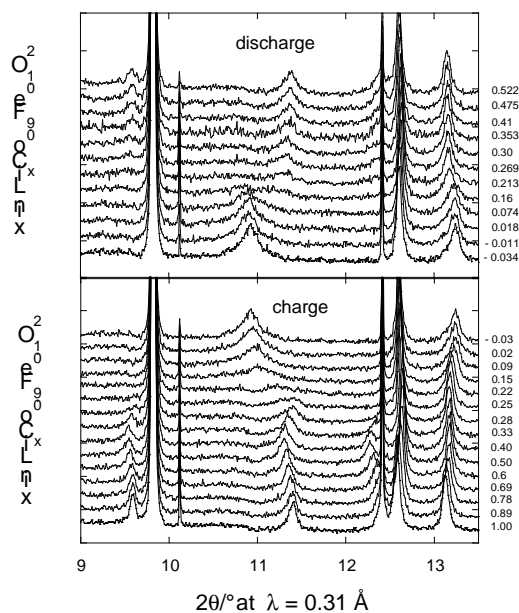


Fig. 2 . ESRF scans along the charge and discharge of  $\text{Li}_x\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_2$ .