

INVESTIGATION OF POSITIVE ELECTRODE MATERIALS FOR LITHIUM BATTERIES BY MEANS OF X-RAY AND NEUTRON DIFFRACTION

C. MASQUELIER¹, M. MORCRETTE¹ AND G. ROUSSE²

¹ LABORATOIRE DE RÉACTIVITÉ ET DE CHIMIE DES SOLIDES, UMR CNRS 6007, AMIENS (FRANCE)
² ILL, GRENOBLE (FRANCE)

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In situ X-ray diffraction studies allow the following of the structural changes associated with lithium extraction from positive electrode materials for Li batteries. Two recent examples are presented here.

The “layered” rock salts compositions LiCoO_2 and LiNiO_2 as well as the spinel $\text{Li}[\text{Mn}_2]\text{O}_4$ have been extensively studied for use as positive electrodes for rechargeable lithium batteries. Their interest lies in the delivery of voltages close to 4V vs Li^+/Li when lithium is extracted reversibly. Other families of compounds, *i.e.* polyanionic structures built up from MO_6 octahedra ($M = \text{Fe}, \text{V}, \text{Ti}$) and PO_4^{3-} or $\text{P}_2\text{O}_7^{4-}$ polyanions have also been identified as alternative electrodes, among which are LiFePO_4 , LiMP_2O_7 and the NASICON family $\text{Li}_x\text{M}_1\text{M}_2(\text{PO}_4)_3$ [1]. A review of electrode materials for lithium batteries is given in ref [2].

Besides the need to identify new

materials for electrochemical devices, it is also a challenge to understand the topotactic lithium insertion/de-insertion mechanisms (associated with reduction or oxidation of the transition element at the positive electrode) that occur within these materials. Lithium batteries have ever increasing industrial and technological importance. Additionally, they do indeed offer a rather nice tool for solid state electrochemists because the redox processes involved often lead to subtle phase transitions and to metastable new forms of materials with “exotic” oxidation states or compositions [3]. These processes may also lead to structural instabilities that are penalising for the integrity of the host material over extensive charge/discharge cycles. In this

regard, X-ray and neutron diffraction are powerful – and complementary – techniques for the investigation of positive electrode materials for lithium batteries as they benefit from the crystalline nature of the material used. Powder neutron diffraction is used for highly reliable crystal structure determinations of *pristine* materials containing lithium into which local disorders, local distortions, phase purity etc... play a major role for their effective use in a battery system. On the other hand, *in situ* X-ray diffraction that use either standard equipment in the laboratory or high-resolution synchrotron radiation, has been used by several groups for the investigation of structural changes during cell operation. For this purpose, specially-designed cells for diffraction in either reflection or transmission geometry, were developed following J. Dahn’s pioneer concept [4].

The intent of this communication is to demonstrate the use of neutron and/or X-ray diffraction for the investigation of positive electrode materials in lithium batteries. For this purpose we have chosen to present two typical examples that have recently been addressed: $\text{Li}_x\text{Mn}_2\text{O}_4$ and Li_xCoO_2 .

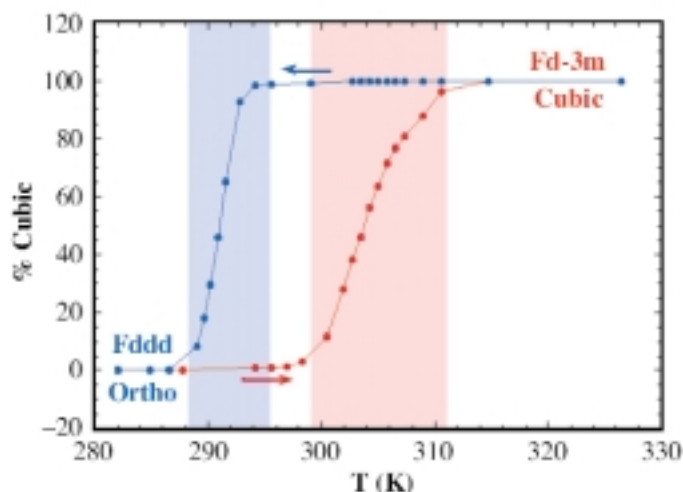
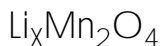


Fig. 1: Ratio between cubic and orthorhombic forms of LiMn_2O_4 as a function of temperature, determined by synchrotron diffraction (LURE, WD4C). From [6].

Fig. 2: Parts of *in situ* synchrotron diffraction patterns (ESRF, BM16) as a function of x during electrochemical extraction of lithium from $\text{Li}_x\text{Mn}_2(\text{O}_{3.74}\text{F}_{0.26})$. From [5].



Palacin *et al.* [5] reported an *in situ* synchrotron study carried out at the ESRF (Beamline BM16, transmission geometry through a Bellcore Plion “plastic” cell) on the structural phenomena that occur during lithium extraction out of a fluorine-substituted spinel $\text{LiMn}_2(\text{O}_{3.74}\text{F}_{0.26})$. Besides the “classical” features previously observed in the 4.1 V – 4.2 V region for $\text{Li}_x\text{Mn}_2\text{O}_4$, two extra phenomena of interest were observed at the beginning and then at the end of the charge process:

i) The pristine material, with average oxidation state for manganese equal to +3.4, is indeed a mixture of two phases: a minor cubic spinel phase and a major orthorhombic form that had just been discovered from combined electronic, X-ray (at LURE, Orsay) and neutron (at LLB, Saclay) diffraction. The orthorhombic distortion of the spinel results from a charge-ordering transition on Mn^{3+} and Mn^{4+} sites that occurs very close to room temperature when the concentration of Mn^{3+} present in the spinel phase is above the critical level of 50% [6] (Figure 1). The *in situ* data presented in Figure 2 (beginning of charge) nicely revealed that this distortion disappears exactly for 0.18 lithium extracted from $\text{LiMn}_2(\text{O}_{3.74}\text{F}_{0.26})$, *i.e.* when the average valence of manganese reaches 3.5+.

ii) On charging above 4.4 V, Palacin *et al.* also observed an apparent irreversible capacity of $\Delta x = 0.08$, associated with extra electrochemical phenomena at 4.5 V (on oxidation) and at 3.3 V (on reduction). A complementary study [7] was undertaken that allowed, with the help of high-resolution transmission electron microscopy, to identify the formation of a new $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ double hexagonal (DH) structure isotypic with LiFeSnO_4 (Figure 3). The transition between spinel $\text{Li}_x\text{Mn}_2\text{O}_4$ (ABCABC... stacking) and DH- $\text{Li}_x\text{Mn}_2\text{O}_4$ (ABACABAC... stacking) was explained in detail [6] through a translation mechanism of Kagome (OC_3) and Te_2OC type blocks that are common to both structures (Figure 3).

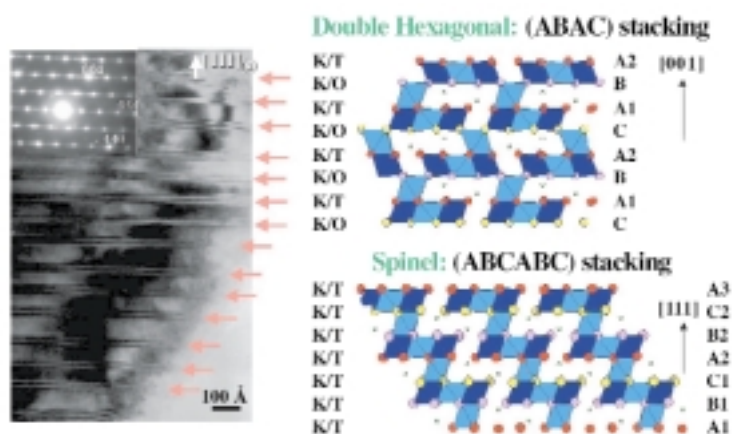
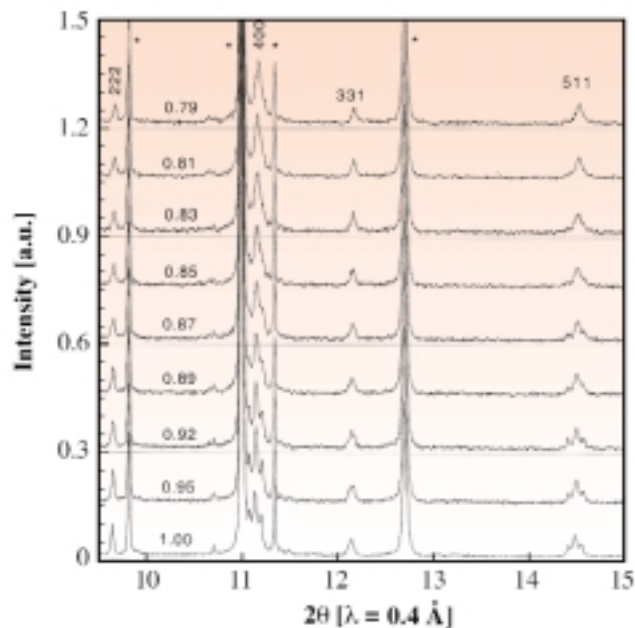


Fig. 3: TEM image of stacking faults along $[111]_{\text{spinel}}$ due to the intergrowth of the double hexagonal structure. The structural relationships between Spinel and DH arrangements are drawn. From [6] and [7].



Another interesting *in situ* experiment was carried out at the ESRF, to understand the structural behaviour of $\text{Li}_{1-x}\text{CoO}_2$ when charged (lithium extracted) to high values of x , *i.e.* up to a voltage close to 5V vs Li^+/Li . This was the subject of a recent communication [8] whose main outlines are recalled here. The originality of the experiment was the use of the microdiffraction beam line ID11, where the 0.2×0.2 mm beam was small enough to pass through the grids of the Al and Cu current collectors of a PLion plastic cell. The diffracted beam was collected on a 2-D image plate detector that permitted very short acquisition times (~ 10 seconds per pattern!).

Several processes of de-intercalation of lithium can be distinguished in

Figure 4: the incremental capacity peaks at 3.92 V, 4.05 V, 4.18 V and 4.55 V are the signature of transitions between phases at various stages of charge. A very large number of diffraction patterns were collected between 8° and 20° for a wavelength of 0.3757 \AA (Figure 5). Besides the interesting evolution of lattice parameters vs x in Li_xCoO_2 (Figure 6), successful Rietveld Refinements allowed the determination of the atomic positions in each of the phases formed [8]. Of particular importance for the cycling behaviour of Li_xCoO_2 is the region close to $x = 0.5 / V = 4.18 \text{ V}$ where a monoclinic phase, M1, extends from $x = 0.55$ to 0.47. This region corresponds to the maximum of the c equivalent lattice parameter, *i.e.* to the maximum distance between CoO_2 close packed layers. At deeper extents of charge, *i.e.* at potentials higher than 4.28 V vs Li^+/Li , irreversible

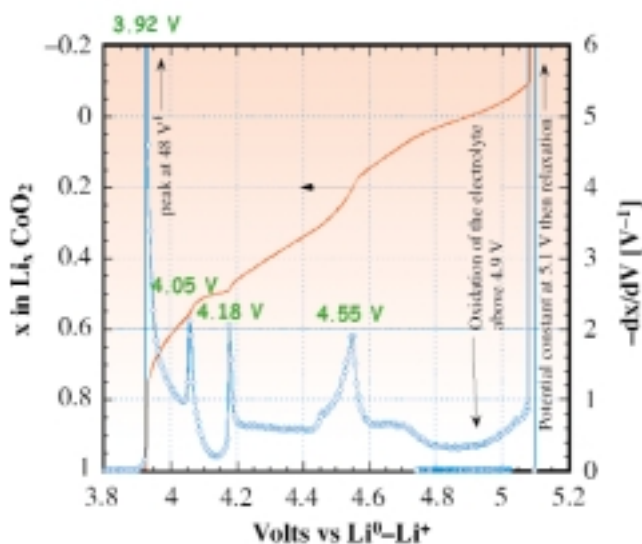


Fig. 4: Potentiostatic intermittent extraction of lithium from LiCoO_2 at an equivalent rate of C/20. From [8].

transformations occur and hence, the practical composition range for cycling Li_xCoO_2 in a real battery system when x is between 0.5 and 1.

CONCLUSION

The two examples developed in this paper show the effective use of *in situ* synchrotron X-ray diffraction to help understand and solve problems associated with structural changes that occur upon lithium extraction from positive electrode materials. Despite its great potential use for Li-containing materials, neutron diffraction is still limited for *in situ* studies due to the small quantity of active material and to the large amount of hydrogen-containing components within the battery. Both techniques are complementary and should be used more systematically alongside the essential *in situ* and/or *ex situ* experiments on “in-house” X-ray diffractometers. ■

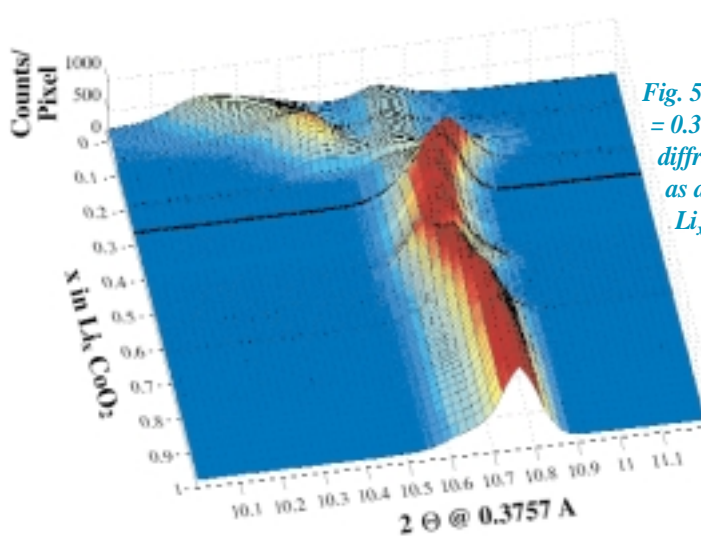


Fig. 5: Synchrotron ($\lambda = 0.3757 \text{ \AA}$) diffraction patterns as a function of x in Li_xCoO_2 . From [8].

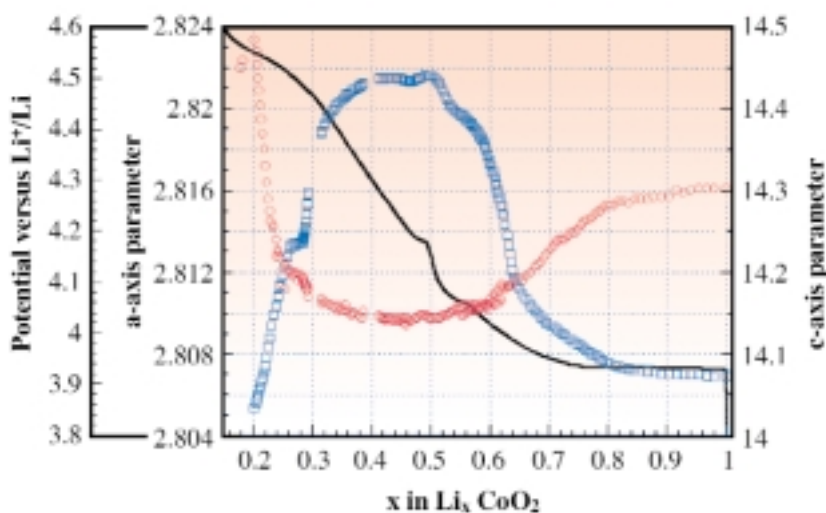


Fig. 6: Evolution of cell parameters (rhombohedral description) as a function of x in Li_xCoO_2 . From [8].

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