

# A continuous X-ray diffraction study of the electrochemical behavior of a plastic Li-ion cell

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## Abstract

The device developed here for XRD analysis is built on a Guinier–Lenné geometry camera. A monochromatized and focused beam goes through the plastic Li-ion cell protected by a metal–plastic laminate. Each layer of the cell gives diffracted beams, which are collected on an X-ray film on the focus circle. The film is continuously moved up (1–2 mm/h), while the Li-ion cell is charged and discharged, and controlled by means of the Mac-pile system. Both plastic electrodes crystallographic behavior can be simultaneously and continuously observed under the real operating conditions of a commercial battery. Comparison between C/Li<sub>x</sub>NiO<sub>2</sub> and C/Li<sub>x</sub>Ni<sub>0.7</sub>Co<sub>0.3</sub>O<sub>2</sub> batteries is given as an example. Parameters evolution of the two electrodes can easily be correlated with the cycling curves. Studies can also be performed from room temperature up to 100°C. © 1999 Elsevier Science S.A. All rights reserved.

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## 1. Introduction

In situ X-ray diffraction is often needed to study the correlation between Li-ion batteries structural and electrochemical behaviors. Understanding the crystal structure changes of both anode and cathode is often crucial to understand the variation of lithium batteries voltage. Two types of XRD geometry are available for this kind of study: reflection and transmission geometry on a theta-2 theta (or theta–theta) diffractometer. Both types of experiments are made in scanning mode (scintillator or PSD detector) so that the evolution of the structural changes is not continuously followed as a function of the intercalation rate. Moreover, in reflection geometry, only one electrode can be observed for each experiment, the battery must be placed into an leak-free cell with, on the observed side, a beryllium window to let the X-ray go through. Corrosion of the beryllium window may occur and disturb the electrochemical process. The hermetic seal is usually achieved by an o-ring and the supporting electrodes hardware is tied by screws. Finally, the position of the sample is also a critical parameter in reflection geometry, and can dramatically affect the lines position. It is also often difficult to say if the observed transition is a first order or a second order one because of insufficient resolution and counting statistic. Further technical information concerning in situ

X-ray diffraction on lithium compounds can be found in Ref. [1].

## 2. Experimental

### 2.1. Description of the battery

The Bellcore plastic Li-ion technology is very suitable to perform in situ X-ray study over a wide range of potential 0–5 V. Its flexibility allows to adapt the battery to the configuration of the instrument use to perform the study. The battery can briefly be described as an aluminum foil current collector coated with the cathode material, a polymer electrolyte film, and a copper foil current collector coated with the anode material (carbon graphite in a polymer in this case). A lithium thin foil can also be used as anode because of its very low X-ray absorption if needed. The battery is vacuum-sealed in a flexible, air and moisture proof aluminum foil coated with polyethylene on one side and polyester on the other. The overall thickness of the cell is less than 0.3 mm, making it ideal for transmission diffraction work.

### 2.2. Description of the device

Our device is based on an ENRAF-NONIUS Guinier–Lenné camera working in transmission geometry. In this

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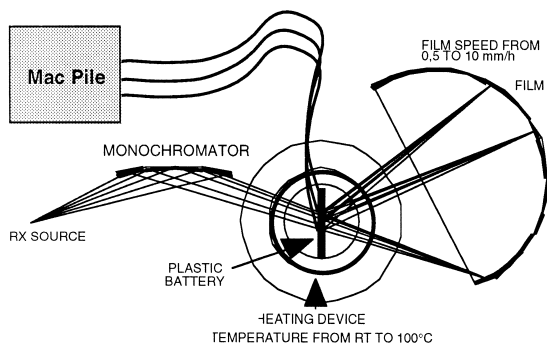


Fig. 1. Schematic representation of the device.

geometry, the lines position is less sensitive to the sample positioning.

The heating device of the Guinier–Lenné camera is replaced by our sample holder. It consists of two Teflon pieces between which the battery is inserted. In this condition, the battery is firmly maintained, and does not move during the experiment. Plane heating resistance can be inserted with the battery into the sample holder in order to perform experiments up to 100°C. The electrical contacts are pressure contacts between the copper strips of the sample holder and the Cu and Al collectors tabs of the battery. The electrochemical control is assumed by means of the Mac-Pile system.

The sample holder is put into the X-ray beam, and the diffracted beams are collected on a film placed on the focus circle. The film (CEA-Reflex 15–18 × 24 cm) is continuously moved up with a speed of 1 or 2 mm/h by means of an endless screw (Fig. 1). Both negative and positive electrodes structural changes can be simultaneously followed during electrochemical cycling.

Collecting diffraction data on a X-ray film presents several advantages. First of all the data are collected in a continuous way, with a film moving and a cycling rate low enough (around C/50) to consider that the battery is always at equilibrium. Moreover, X-ray films are often more sensitive to weak reflections than most detectors. As a matter of fact, each point of the film is exposed to the diffracted beams during 3 h if a 3-mm large analysis slit is used with a 1 mm/h moving film, which are the standard conditions. Then, the cycling curve can easily be correlated with the changes observed on the diffraction film by scaling both of them. Aluminum and copper reflections can be used as internal standard to make sure that the sample did not move during the experiment.

### 2.3. The example of $Li_xNiO_2$

An example of experiment is given for a C/ $Li_xNiO_2$  battery on Fig. 2. In this case, the cell is charged and

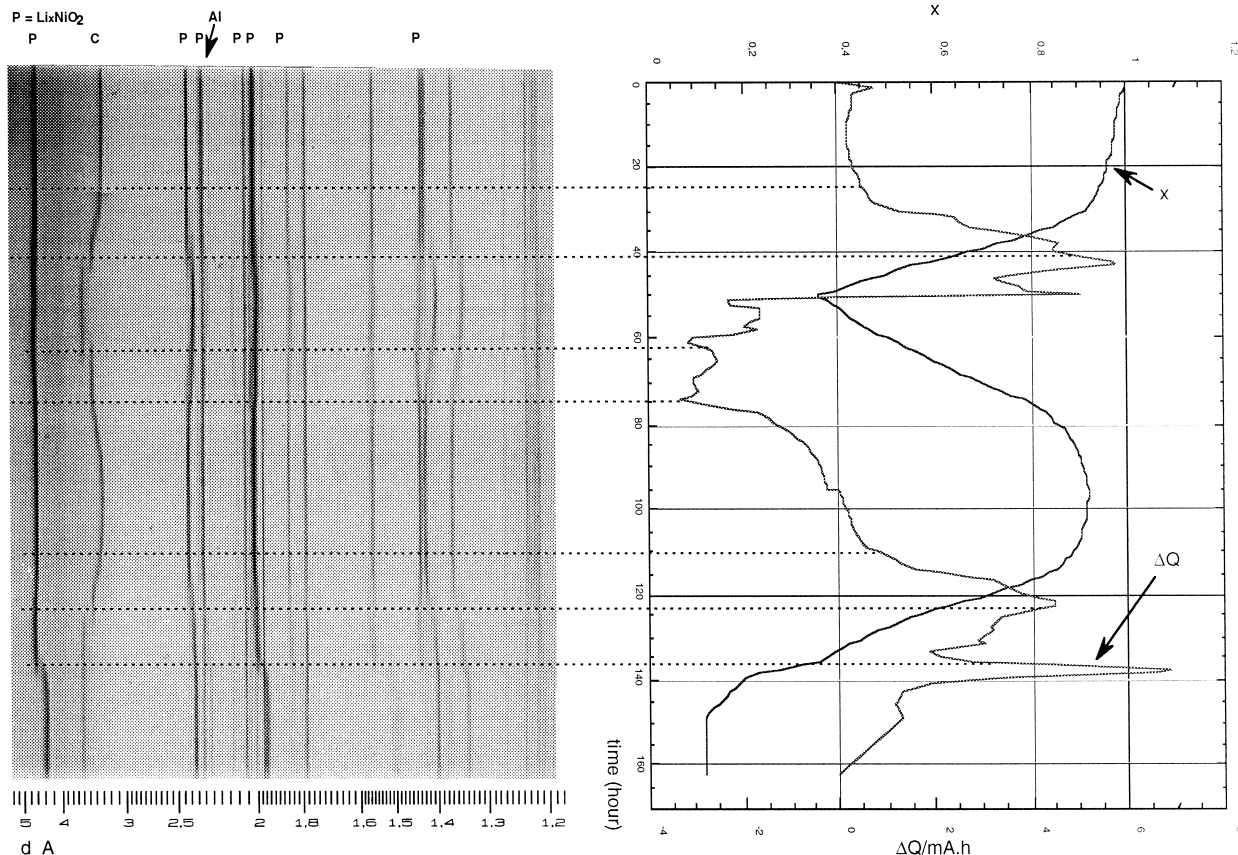


Fig. 2. Correlation between the in situ X-ray experiment and the cycling curve for a C/ $Li_xNiO_2$  battery.

discharged in a potentiostatic mode by steps of 2 mV/h. Both cathode and anode structural changes can be simultaneously followed, and easily correlated with the electrochemical behavior of the battery. The high readability of this kind of representation can be noted. As an example, dotted lines have been superimposed on Fig. 2 in order to show the correspondence between structural changes in carbon and in the electrochemical curves.  $\text{LiC}_{24}$ ,  $\text{LiC}_{12}$  and  $\text{LiC}_6$  phases are observed during the first charge between 25 and 40 h of experiment.

### 3. Comparative study of $\text{Li}_x\text{NiO}_2$ and $\text{Li}_x\text{Ni}_{0.7}\text{Co}_{0.3}\text{O}_2$

Using this continuous in situ X-ray diffraction device, a comparison has been made between  $\text{C}/\text{Li}_x\text{NiO}_2$  (Fig. 3) and  $\text{C}/\text{Li}_x\text{Ni}_{0.7}\text{Co}_{0.3}\text{O}_2$  (Fig. 4) batteries behavior during the first cycle.

It can be noted, as expected, that the carbon behavior seems to be perfectly reversible from a structural point of view between first charge and first discharge in both experiments.

$\text{Li}_x\text{NiO}_2$  undergoes two phase transitions between  $x = 1$  and  $x = 0.3$ . These are hexagonal (H1) to monoclinic (M) and monoclinic to hexagonal (H2). Two coexisting phase regions are found, which correspond to two first-order phase transitions. These results are in complete agreement with those reported by W. Li et al. in Ref. [2]. Continuous reflections shifts can be observed for these three phases as Li is deintercalated. It can be noted that  $(018)_{\text{H1}}$  and  $(110)_{\text{H1}}$  lines positions are different at the end of the first cycle. Such differences may simply confirm the 10% irreversible loss between the first charge and discharge usually observed or reflect the beginning of the deteriora-

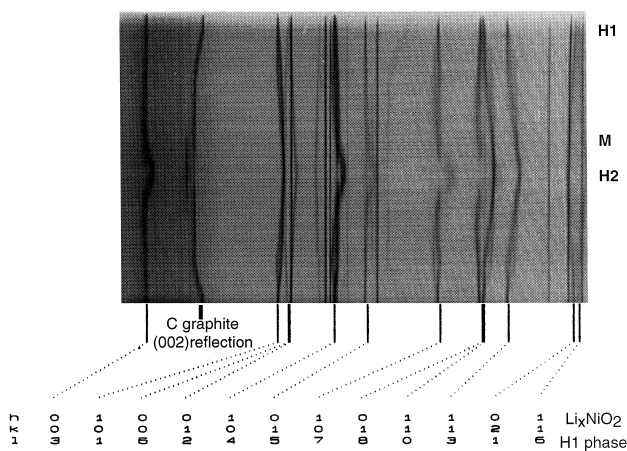


Fig. 3. Continuous evolution of X-ray reflections during the first charge and discharge of a  $\text{C}/\text{Li}_x\text{NiO}_2$  battery.

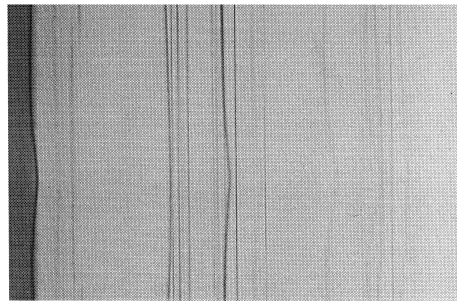


Fig. 4. Continuous evolution of X-ray reflections during the first charge and discharge of a  $\text{C}/\text{Li}_x\text{Ni}_{0.7}\text{Co}_{0.3}\text{O}_2$  battery.

tion of the compound previously reported when the potential reaches 4.2 V. Unfortunately, the quantity of graphite used in this specific experiment is such that phase transitions are observed at the same time on both electrodes, and  $dx/dV$  curves are meaningless. It is the reason why experiments are now performed with plastic electrode cells using Li as the reference electrode in order to measure the contribution of each electrode.

Substitution of nickel by cobalt is known to stabilize the bi-dimensional character of the structure. This point is confirmed by the continuous structural evolution in the behavior of the cathode material in  $\text{C}/\text{Li}_x\text{Ni}_{0.7}\text{Co}_{0.3}\text{O}_2$  battery during electrochemical cycling (Fig. 4). In this case,  $dx/dV$  curves show that deintercalation is not completely monotonous but no biphasic region is observed. Continuous reflection shifts are observed during both intercalation and deintercalation from  $x = 1$  to  $x = 0.3$ .

### 4. Conclusion

This in situ X-ray device allows to follow the structural evolution of the cathode and the anode of a Li-ion battery during electrochemical cycling. It is a powerful method to quickly investigate the structural behavior of an electrochemical system as a function of the intercalation rate. The comparative study between  $\text{C}/\text{Li}_x\text{NiO}_2$  and  $\text{C}/\text{Li}_x\text{Ni}_{0.7}\text{Co}_{0.3}\text{O}_2$  batteries has shown the different behavior of the two cathode materials, which consists of a biphasic transition in the case of pure lithium nickel oxide while it occurs as a monophasic transition in the case of mixed lithium nickel cobalt oxide. Testing  $\text{C}/\text{Li}_x\text{NiO}_2$  and  $\text{C}/\text{Li}_x\text{Ni}_{0.7}\text{Co}_{0.3}\text{O}_2$  batteries showed that this device is well suited for in situ electrochemical first investigations and attack issues related to safety at high temperature.

### References

- [1] Gustafsson et al., *Electrochim. Acta* 37 (1992) 1639.
- [2] W. Li, J.N. Reimers, J.R. Dahn, *Solid State Ionics* 67 (1993) 123.