

## *In situ* studies of electrodic materials in Li-ion cells upon cycling performed by very-high-energy x-ray diffraction

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A very high-energy synchrotron radiation source (87 keV) was utilized for *in situ* sampling of the structural changes occurring in the electrodic materials of a Li-ion cell during charge–discharge cycling. The real-time evolution of their crystal lattice was obtained as a function of the degree of Li intercalation. As a result, new information on two electrodic materials, Li–Ti “zero strain” and Li–Ni–Co oxide, both of extreme interest for generation of rechargeable batteries, was gained. The actual change of the Li–Ti oxide lattice parameter upon cycling was observed in greater detail than before, and provided evidence of unexpected behavior in some intervals of the cycle. In the Li–Ni–Co sample, a new phase formed during the early stages of cycling that remained stable in the subsequent cycles was revealed. © 2001 American Institute of Physics.  
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Over the last several years the technological evolution of portable devices, like mobile phones and laptops, has revolutionized the way of communicating and further improvements are expected in the near future. However, the development of rechargeable batteries used to supply such devices has not followed the same trend. To improve the performance of batteries, a deeper knowledge of the mechanisms ruling the charge–discharge processes is required. In particular, the observation of the structural changes occurring in electrodic materials is of key importance to understand the reasons for the decrease in battery capacity and the final onset of irreversible effects that produce deterioration of battery performance.

The method by which to observe these structural changes is usually time-resolved *in situ* x-ray diffraction carried out during the charge–discharge cycles. The main obstacle to such an investigation is that the cell walls, the electrolytic solution, and the sample itself intensely absorb x-rays and rather weak diffraction signals are generally obtained even using synchrotron radiation as the primary beam. To decrease the absorption problems, cells with very thin walls, possibly made of light materials, have been used and also the electrolyte has often been reduced to a very thin liquid layer (down to 20  $\mu\text{m}$ ).<sup>1</sup>

An alternative approach based on increasing the radiation energy has been exploited in the last few years utilizing either the opportunities offered by the third generation synchrotrons: 11 keV reported in 1993,<sup>1</sup> 24.5 keV in 1996,<sup>2</sup> 30 keV in 1997,<sup>3</sup> or the white radiation of a laboratory energy dispersive x-ray diffractometer (up to 55 keV, reported by Ronci *et al.* in 2000).<sup>4</sup>

In the last case, the absorption effects were considerably reduced and cells having very simple designs could be uti-

lized using metallic lithium as a counter electrode and a liquid solution of choice (e.g., 1 M LiClO<sub>4</sub> in EC-DMC 1:1) as an electrolyte. A further advantage is that no movement is required for data acquisition, so the collection conditions are unchanged during the entire cycle and the measurements are highly reproducible and reliable. However, the laboratory energy dispersive technique suffers from the drawback that the photon flux is much lower than that available at a synchrotron source and, furthermore, its resolution is rather poor.<sup>5</sup>

In the present work, a monochromatic 87 keV x-ray beam of the ID15 beamline at the European Synchrotron Radiation Facility was used. In our experimental setup (see Fig. 1), the advantages of the laboratory energy dispersive method because of the immobility of the system during data collection and the use of hard x-rays are preserved or, better, improved, while the problems connected to it are solved. The

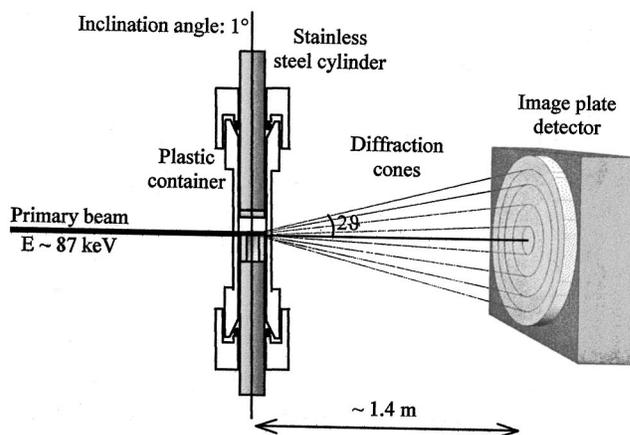


FIG. 1. Sketch of the electrochemical cell and of the experimental setup. The active part of the cell under measurement is a membrane, cast on a 10  $\mu\text{m}$  thick Al foil. The membrane is composed of the intercalation material powder grains that are blended with a binder and carbon powder (to guarantee electrical contact). Further details on the cell can be found in Ref. 4.

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ID15 x-ray beam, because of its high energy, seems to fulfill these experimental requirements. First of all, the absorption problems are completely overcome, since attenuation of the beam through the cell is less than 1%. The use of an image plate (model MAR 345) allows complete collection of Debye–Scherrer rings, therefore increasing the counting statistics. In fact, because of the high penetrating ability of this radiation, no shadow due to the asymmetric positioning of the cell is produced by the sample on the detector, as would be expected if softer x-rays were used, so the data analysis is simplified.

In addition, the use of high-energy radiation can balance the decrease in resolution due to the large size of the irradiated sample area, which is a consequence of the grazing angle geometry adopted to maximize the signal (diffraction from the sample) to background (diffraction of the substrate and environment) ratio. Indeed, when the energy is increased, Bragg reflections are produced at lower diffraction angles. As a consequence of the sample–detector distance increase (required to observe the same momentum-transfer range), the irradiated part of the sample appears smaller when seen by the detector. In this way, the effects of the grazing incidence geometry are balanced and the ideal Fraunhofer diffraction conditions (point-like sample) are more easily attainable. Such advantages made this experimental setup suitable to perform high quality measurements and allow one to obtain relevant new results in two different experiments.

The first experiment consisted of measuring the variations in the lattice parameter of the spinel  $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ , a very interesting material for battery technology. It is defined as “zero-strain” because of the extremely small changes it exhibits upon cycling when used as an electrode material in lithium ion cells.<sup>6</sup>

The overall variation of its (cubic) lattice parameter  $a$  during a whole cycle (which involves the insertion–deinsertion of one lithium equivalent for formula unit) was found to be about 0.1%.<sup>7</sup> Furthermore, it was demonstrated that the process occurs through the equilibrium of two different phases having the same crystallographic structure and very similar lattice parameter values.<sup>7</sup>

By means of energy dispersive x-ray diffraction, the time-resolved evolution of the  $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$  structure upon cycling was recently shown.<sup>8</sup> On the basis of these measurements, a linear negative (positive) trend of  $a$  was observed upon lithium intercalation (deintercalation) and the presence of partial irreversible behavior during the initial cycle was suggested. However, the statistical scattering of the sampled values of the evolving lattice parameter did not permit us to reach definitive conclusions. In particular, it was not possible to state whether the lattice parameter  $a$  again reached its initial value at the end of the first cycle or not.

By processing the high statistics and high-resolution diffractograms collected at ID15 (Fig. 2), it was possible to answer this question and even to study in detail the profile of the lattice parameter curve (Fig. 3). The profile shows an unexpected change of slope at the very beginning of the discharge and at the end of the charge process. This was not expected because two-phase equilibrium should result in a linear variation of the measured lattice parameter

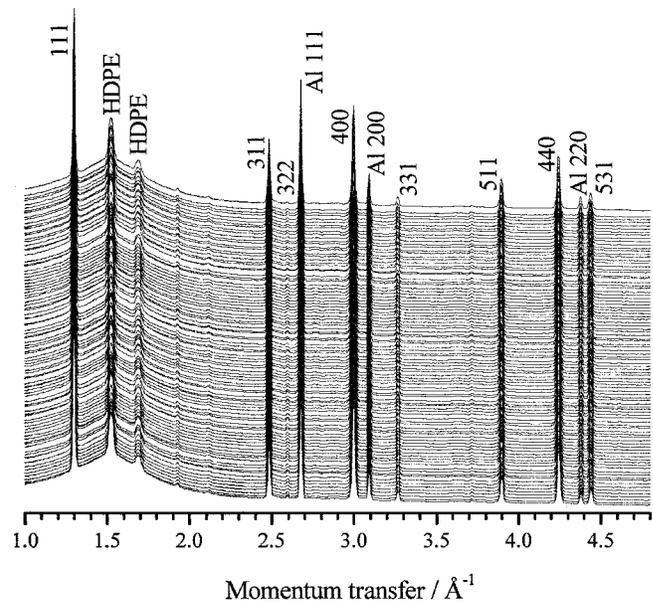


FIG. 2. Selection of diffractograms of  $\text{Li}_{1+x}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$  collected upon the first discharge ( $x=0-0.29$ ). The peak's shift is not visible and only accurate data processing reveals the small changes in the lattice parameter. The hump present below  $2.5\text{Å}$  is a contribution by the high density polyethylene cell walls (that produce also the two reflections labeled HDPE) and of the electrolytic solution to the scattered intensity. The polyethylene peaks are used as a reference to monitor the variations of the x-ray beam energy due to thermal drift of the monochromator.

$\bar{a} = [(1-x)a_1 + xa_2]$ , where  $0 \leq x \leq 1$  is the amount of intercalated lithium in  $\text{Li}_{1+x}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ .

The overall lattice parameter variation  $\Delta a \sim 0.006\text{Å}$  was confirmed to be very small, with a relative variation of  $\Delta a/a \sim 0.07\%$ . This almost negligible structural modification upon cycling is considered to be the main cause of the very good cycling properties of this compound.

With regard to the possible presence of partially irreversible processes, we found that the initial and the final values ( $8.3576 \pm 0.0003$ ) and ( $8.3582 \pm 0.0003$ )  $\text{Å}$ , respectively, are not essentially different. However, a clear difference can be observed by comparing the slope of the two above mentioned initial and final parts of the curve and, in particular, by comparing the values of the two relative maxima. This shows

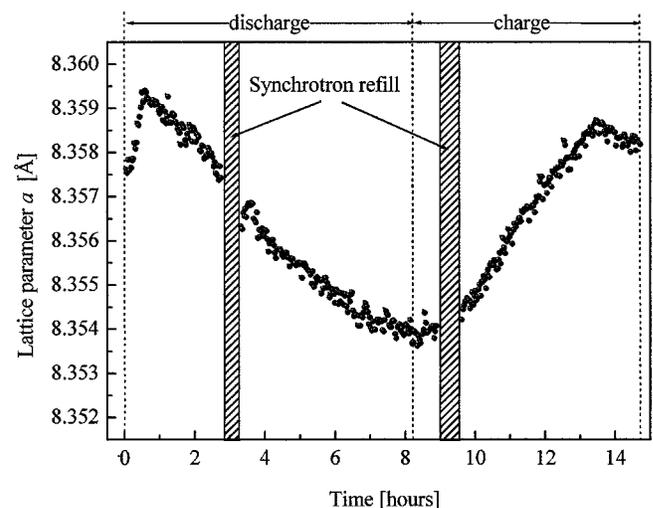


FIG. 3. Evolution of the lattice parameter of  $\text{Li}_{1+x}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$  during the first cycle.

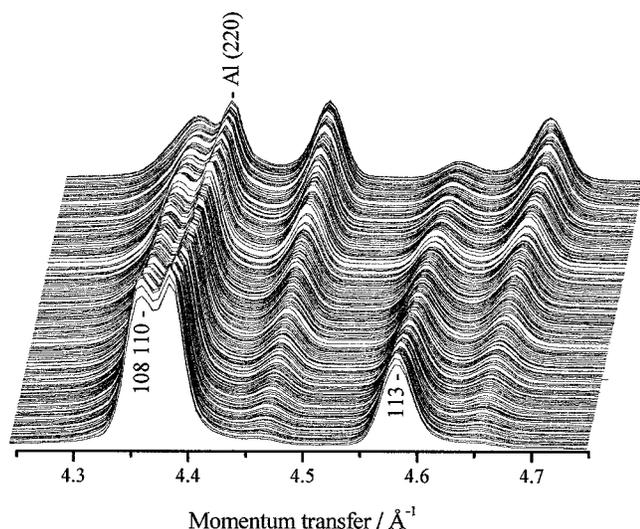


FIG. 4. Map of the reciprocal space region of interest for  $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$  observed while charging the battery from  $x=1$  to 0.5.

evidence that  $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ , commonly considered an almost ideal material, shows a structural variation qualitatively similar to other common electrode materials (see, for instance, Refs. 9 and 10), although on a much smaller scale.

The second experiment was carried out on a sample of  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ .<sup>11,12</sup> This electrode material belongs to the Li–Co–Ni oxide family, whose components are widely used in lithium-ion battery technology<sup>13,14</sup> because of their favorable electrochemical properties.

An unanswered question concerning this family of compounds is whether the first charge process occurs with the formation of different phases [like in  $\text{LiCoO}_2$  (Refs. 14–16 and  $\text{LiNiO}_2$  (Refs. 17–19)] or the initial single phase is preserved, as reported in several works on Ni-rich Li–Ni–Co oxides.<sup>20–22</sup> In Fig. 4, part of the sequence of diffractograms (the portion containing the 108, 110, and 113 reflections) collected during the first part of the charge process is shown. The growth of new peaks at about 4.47 and 4.66  $\text{Å}^{-1}$  is evident and it clearly demonstrates the appearance of a second phase upon deintercalation of the first 0.5 lithium

equivalents. This result, as far as we know never reported before for the  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  compound, may help in understanding the well-known partial irreversibility of the first charge–discharge cycle.

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