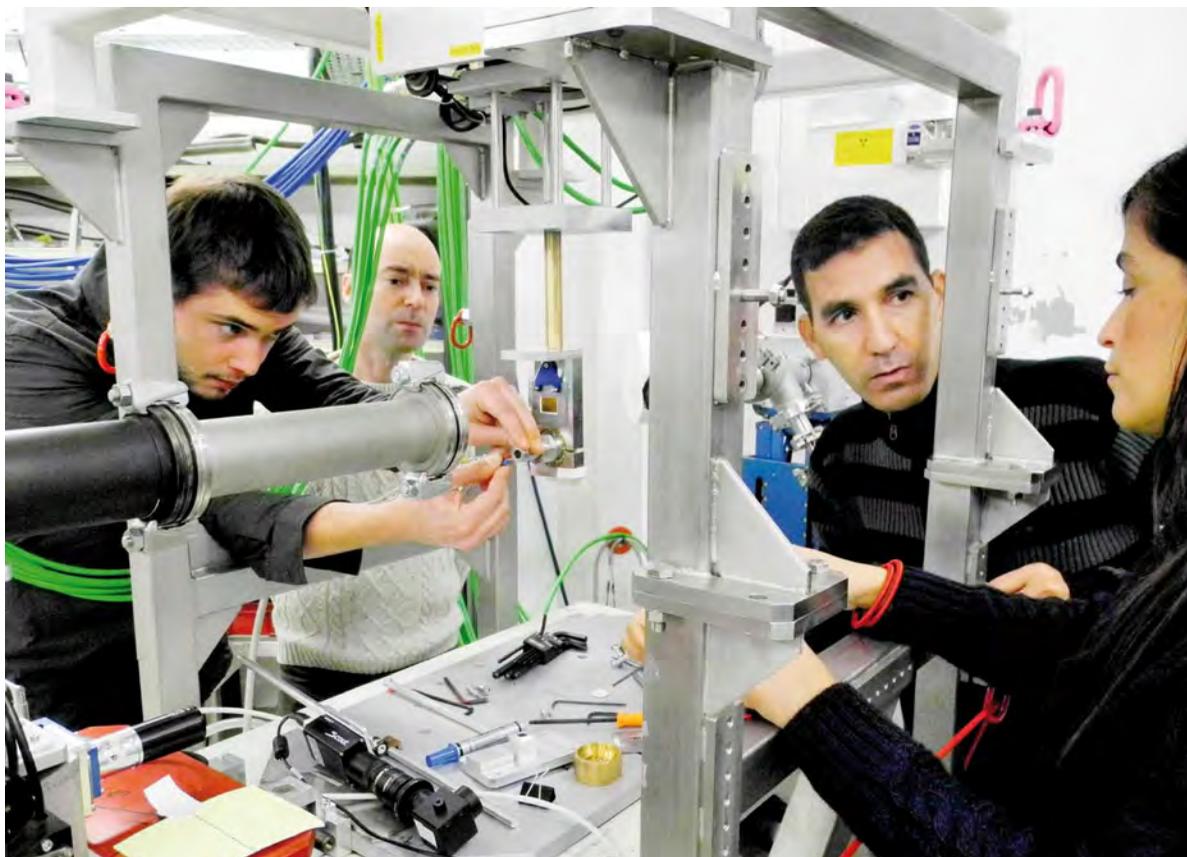


ENERGY

At the core of lithium batteries

How to store electrical energy is the subject of intense economic and scientific research in response to the global energy crisis, diversification of energy sources and changes in the forms of individual transport. A question that brings together four beamlines at SOLEIL, the "Institut des Matériaux" in Nantes and the "Laboratoire de Réactivité et de Chimie des Solides" in Amiens.



Installation of the electrochemical cell on ODE beamline.

From left to right: Stéphane Hamelet (Amiens), Patrick Soudan and Miloud Zerrouki (Nantes) and Stéphanie Belin (SAMBA beamline).

Throughout the world, thousands of researchers are actively looking for batteries that can store the maximum energy possible, at low cost and under the best safety conditions. At present, the greatest number of studies in this field concern lithium batteries (see Rayon de SOLEIL n°16, page 14).

When at rest or in "operando"

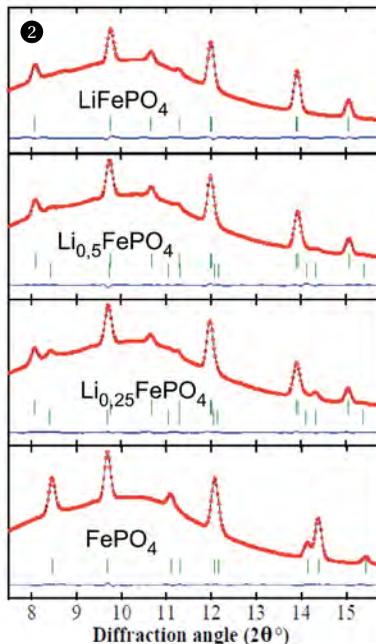
A considerable number of studies have been carried out to determine as precisely as possible, the structural and electronic changes in materials during a lithium-ion battery cycle, both when charging and discharging. Among the methods used there are those that are structural, such as X-ray or neutron diffraction and

transmission electron microscopy and spectroscopic methods, such as infrared spectroscopy, Raman spectroscopy, electron photoemission, Mössbauer spectroscopy and NMR. X-ray absorption spectroscopy (XAS) is a unique form of spectroscopy, both because it allows, depending on the part of the spectrum studied, characterization of the electronic state (XANES) or the structure of the

Figure 1: X-ray diffraction measurements carried out on CRISTAL at the C/2 charging regime on the $\text{LiFePO}_4/\text{FePO}_4$ system. The written compositions correspond to the average composition of the whole electrode.



Figure 2: Electrochemical cell designed for operando experiments



material (EXAFS) on a localized scale and because it requires the use of synchrotron radiation.

To date, nearly all the experiments mentioned above have been performed on disconnected batteries, thus at equilibrium, or on materials extracted from batteries after use. There are very few results available to directly link the electrochemical performance of the battery and the structural and electronic state of the active component.

To fill this gap a project was set up in 2007 to characterize the electrode materials of the battery during operation, by diffraction and X-ray absorption, using the high X-ray photon flux delivered by SOLEIL. These techniques have already shown their ability to analyze the structural changes and charge transfers occurring within the material, depending on the lithium content.

It therefore became possible to examine the behavior of materials specifically during the operation of the battery (operando experiments) and particularly that of the positive electrode, LiFePO_4 , currently regarded as one of the most promising materials for the positive electrodes of lithium batteries. This material is known to

work mainly on a $\text{LiFePO}_4/\text{FePO}_4$ two-phase system.

A "transparent" battery

The first phase of the study was to develop an electrochemical cell capable of collecting diffraction and absorption data, in reflection and transmission mode of detection. This cell, like all lithium batteries, had to be completely air and watertight, and reproduce very accurately the electrochemical behavior of the materials under study. This cell was designed with a hollow piston for the transmission experiments. Sealing was ensured by O-rings and beryllium windows (Figure 1). It reproduced exactly the electrochemical curves obtained in the literature for various compounds, regardless of the C/n charging regime*. One of the major advantages of this experimental device is that it can provide the behavior signature of the material when the electrochemical behavior of the battery becomes abnormal.

Complementarity of the SOLEIL beamlines

Addressing how a battery material actually operates in relation to varying numbers of lithium electrons and

ions in an electrode requires the introduction of the notion of their diffusion, therefore, possible heterogeneities within the electrode, and the behavior of the materials beyond the steady state and during the process of polarization and relaxation. It is therefore important to be able to study the batteries over several time and space scales, requiring the use of the different beamlines involved in this project.

The system studied has a two-phase electrochemical behavior - the two phases in question being LiFePO_4 and FePO_4 - shown by galvanostatic cycling experiments.

On CRISTAL, X-ray diffraction measurements with a C/2 charging regime have confirmed this two-phase stage with the presence of two clearly identified XRD patterns. However, it is quite clear (Figure 2) that when the product is charged, the FePO_4 diffraction peaks are produced later relative to the amount of lithium extracted electrochemically, since for the overall $\text{Li}_{0.5}\text{FePO}_4$ composition of the electrode, one would expect equal amounts of both LiFePO_4 and FePO_4 phases, while on the X-ray diffraction pattern, the initial LiFePO_4 phase is clearly in the majority.

The extent of this delay is even more marked when the regime is high. Since the overall electrochemical composition of the electrode is known, this apparent delay may be explained either by the formation of one or more phases that are not detected by diffraction due to their amorphous nature, or because other parts of the electrode are ahead, i.e., more charged and poorer in lithium than the average for the electrode. The first hypothesis is excluded by the fact that FePO_4 is formed in correlation with the disappearance of LiFePO_4 . The only explanation is therefore a highly heterogeneous electrode.

When diffraction is confirmed by absorption

To test this heterogeneity, X-ray absorption experiments were performed on SAMBA. An electrode was

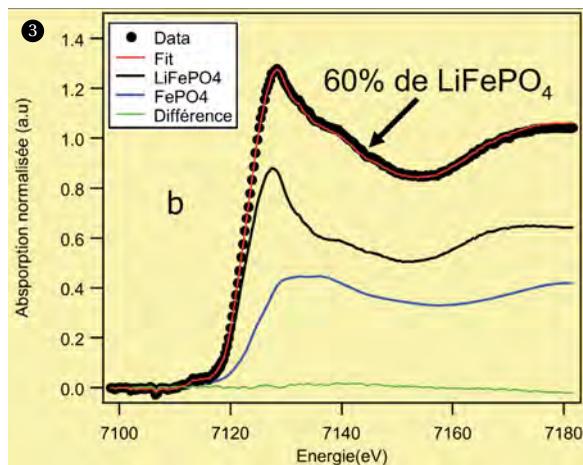


Figure 3: Example of a linear combination calculated for an average $\text{Li}_{0.36}\text{FePO}_4$ composition, based on FePO_4 spectra. The spectra were recorded in the 2C regime on ODE in dispersive XAS mode.

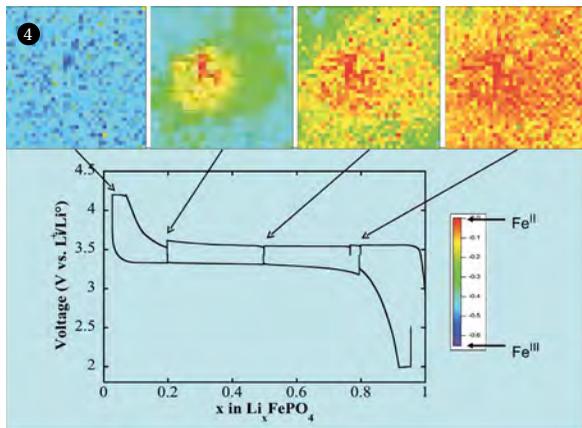


Figure 4: Maps of the distribution of oxidized / reduced iron carried out on a $0.7 \times 0.7 \text{ cm}^2$ electrode surface, in 35×35 points spaced by $200 \mu\text{m}$. Measuring Conditions: charged at 1C, after relaxation of 15 min, for average Li compositions shown by arrows. Measurements were made on LUCIA.

charged up to the $\text{Li}_{0.5}\text{FePO}_4$ composition, then placed in an airtight sample holder in such a way as to allow access to the entire electrode, in order to record XANES spectra on portions of the electrode located at the edges of the electrochemical cell. The biphasic nature of the electrochemical system was indeed confirmed by these measures (presence of isosbestic points), each spectrum being a linear combination of the FePO_4 and LiFePO_4 spectra. However, as additional information, it was observed that some spectra were behind or ahead of the average $\text{Li}_{0.5}\text{FePO}_4$ composition, perfectly illustrating the heterogeneity of the system.

A dynamic X-ray absorption experiment was then carried out using the 2C regime on the ODE beamline. A linear combination of the FePO_4 and LiFePO_4 spectra was calculated from each of the spectra recorded. For example (Figure 3), in the case of $\text{Li}_{0.36}\text{FePO}_4$, the linear combination gives a true composition of the analyzed area of 60% LiFePO_4 and 40% FePO_4 , instead of the expected 36% LiFePO_4 . The delay previously observed by diffraction has thus been confirmed, this time with an observed electrode surface about 1,000 times smaller.

However, this delay is not spatially uniform, as shown by mapping the distribution of Fe^{II} and Fe^{III} in the electrode fraction observable in transmission. Performed on the LUCIA beamline, thanks to its $7 \times 7 \mu\text{m}^2$ beam spot, this analysis was very accurate: the signature for the average degree of oxidation could be analyzed at each point of the sample. The measurements, which only took a few seconds each, were carried out at the absorption near-edge for LiFePO_4 .

Finally, the researchers obtained a map of almost 1,300 points showing the distribution of iron in its oxidized and reduced states when the battery was at rest, and how this distribution changed on a small portion of that surface when the battery was operating through a charge-discharge cycle (Figure 4). These results again illustrate the heterogeneity of the electrode under operation.

Unexpected heterogeneity

Taken together, these results show that the reality of the behavior of a battery electrode, from a structural and electronic standpoint, is far from ideal. Although this conclusion is not entirely surprising given the complexity of the composite structure of the electrodes, it upsets the traditional arguments based on complete homogeneity of the systems.

Many parameters were taken into account, some of them permitting electrochemical behavior and heterogeneity to be correlated: cycle speed, active material particle size, pressure on the electrodes and the

preparation of electrodes. This last point seemed to be quite decisive and corroborated the electrochemical measurements showing that the best performance resulted from a compromise on the nature and proportion of phases included in the formulation of a composite electrode. This is a key element in industrial development aimed at optimizing the formulation for a given active component and pre-selected construction method.

The original objective of this work was to show the potential of synchrotron radiation for characterizing battery materials in operando mode. The results exceeded expectations, thanks to the spatial resolution analysis. X-ray diffraction and absorption experiments, as these are easy to carry out, appear to be excellent methods for characterizing electrodes, at least on a scale of a few microns, which is appropriate for the composites.

Developments are possible on several fronts. The first is to examine the behavior of other electrode materials. Then it would be quite conceivable to systematically test, using the synchrotron, numerous possible combinations of parameters involved in the development of electrodes and to correlate perfectly their heterogeneity and electrochemical performance.

Finally, can we imagine the time when test samples and elements of industrial production will be examined using synchrotron radiation, before finding their way into our laptops and electric cars?

*C/n charging regime: conditions (current strength) applied to achieve the complete charge of the battery in n hours. In the case of 1C, for LiFePO_4 , 100% of the Li^+ ions had migrated to the positive electrode in 1 hour - in 2 hours for C/2, in 30 minutes for 2C.

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