PULSSE project:
energy storage and synchrotron radiation

Whether the aim is to power an electric car, operate a mobile phone or laptop computer, use photovoltaic cells or a wind turbine, this always involves the production, consumption, and storage of energy with the same central element: batteries.
The ANR PULSSE[1] project, which has just been accepted, involves four beamlines at SOLEIL. Its purpose is to show that synchrotron radiation is useful in characterising the materials of these batteries. We meet Guy Ouvrard, project leader.

Guy Ouvrard, officially the director of the IMN[2] since January 2008, was visiting SOLEIL on that day for the PULSSE kick-off meeting, where he was going to meet his colleagues from the LRCS[3], IMN and SOLEIL who are involved in this project with him. He was greeted by Stéphanie Belin, scientist on SAMBA beamline, who is in charge of the PULSSE project for SOLEIL. We took the opportunity to ask for a few explanations...

The "Lithium-ion" batteries

"Programme for the use of synchrotron light in the field of energy storage". Energy storage: a tall order. Guy Ouvrard says: "Initially, we will be dealing with the materials of lithium-ion batteries, and our work may eventually deal with fuel cells."
Batteries and cells are obviously of major economic importance, alongside research on alternatives to fossil fuels, which is more topical than ever.
Guy continues: "A lot of work is currently being done to characterise these materials. When a battery is operating, the Li^+ ions go from one of the electrodes, through the electrolyte, and then to the other electrode (see inset). The electrons travel the same direction, through the external circuit. The electrode materials must therefore be able to accept ions and electrons reversibly and many times because the battery will be subjected to about a thousand recharging cycles.
Two aspects must therefore be studied. On the one hand, the insertions and de-insertions of Li^+ ions will cause changes to the structure of the material. These changes can be minor, particularly if the material has sites where these ions can be inserted. In other cases, such as in phosphate batteries which we are starting to hear a great deal about, major changes can occur in the material; this is an example of a biphased system, $LiFePO_4/FePO_4$[4].
Moreover, the battery is the seat of an oxidation–reduction reaction (see inset). The number of electrons supplied by this reaction corresponds to the capacity of the battery, which is a reservoir of electrical energy. The energy depends on the redox potential; the higher the potential, the greater the capacity, and the more full the reservoir!"

Studying battery materials using x-ray absorption spectroscopy

To study a battery in operation, then, we need a technique that provides both structural and electrochemical information. X-ray absorption spectroscopy (XAS) seems to be a relevant method, and one that Guy knows very well, having used it for more than 20 years:
"The part of the spectra at the absorption thresholds, i.e. XANES[5], gives information about the redox processes, and EXAFS[6] gives information about the structure. EXAFS has the additional advantage over x-ray diffraction that it allows amorphous phases to be studied. Crystallinity can be significantly reduced when battery materials are modified and, when that happens, you cannot see very much by diffraction, whereas EXAFS still provides some data. This means that x-ray diffraction and EXAFS can be complementary."
Beyond the technique itself, the relevance of the information we wish to acquire about these batteries depends a lot on the test conditions. Guy continues:
"Nearly all the studies conducted up to now on batteries by XAS were carried out on batteries out of operation. But what interests us is their performance when operating, because it is when operating that they can break down!
Two approaches are generally used: a battery is dismantled after use, and a sample of the lithiated material is extracted and placed in the beam. This is an ex situ test. The other option is the in situ test: the battery, which was specifically designed to be studied by synchrotron, is placed in the beamline. A charge or a discharge is performed, and then absorption measurements are carried out (after waiting for the system to return to equilibrium). These conditions are in fact fairly similar to the ex situ situation."

"In operando" measurements

In 2002, Guy Ouvrard carried out initial studies on batteries in operation at LURE. This was a collaboration with François Baudelet, who is now in charge of the ODE beamline at SOLEIL. These dispersive EXAFS experiments gave very different results from those obtained with batteries at equilibrium. These results have not yet been fully explained, but they demonstrate the interest of *in operando* studies.
Why, then, are there not more studies like this?
"Because when the battery is working, the system is changing, and when it is changing, we no longer know what we are measuring!"
The solution? "The characterisation method must be much faster than the phenomenon being studied (by a factor of 100 to 1000). The phenomena under investigation vary in duration from about an hour for a charge or discharge, to the order of ten seconds for polarisation-relaxation reactions, which occur for example when the battery is switched off."
Measurements during operation therefore require good temporal resolution. Spatial resolution is also important, though:
"The electrodes are complex composite components made of grains about ten microns in size mixed with a polymer (such as PTFE) which acts as a binder to make the system easier to handle. This gives an object with a rubbery texture, laminated to a thickness of less than a millimetre. The aim is to study the material in as much detail as possible by looking at what happens amongst the grains of active material. Moreover, averaged data (obtained either by scanning a large surface of a sample at high resolution or by studying it at a lower resolution) are also necessary to ensure that the results can be generalised to the whole battery."
Overall, there are many constraints and conditions that restrict the number of techniques that can be used to carry out these studies. That is why the PULSSE project was born.

1 PULSSE : programme pour l'utilisation de la lumière synchrotron dans le domaine du stockage de l'énergie (programme for the use of synchrotron light in energy storage).

2 IMN : Institut des Matériaux Jean Rouxel – Nantes

3 LRCS : Laboratoire de Réactivité et Chimie du Solide - Amiens

Cells, accumulators and batteries

Cells and accumulators are sources of electrical energy obtained by the direct transformation of chemical energy via electrochemical reactions, which involve oxidation–reduction (or 'redox') reactions. An **oxidation–reduction reaction** is a process by which electrons are transferred from one species to another. The species that gives up electrons is called the reducing agent, and the species that receives electrons is the oxidising agent. The cell in which the reaction occurs consists of two electrodes (positive and negative) and an electrolyte that conducts the ions and blocks the electrons produced during the reaction.

When the system is based on an electrochemical process that is reversible at each electrode, it is rechargeable. This is an **accumulator**.

It supplies electrical energy to an external circuit when the oxidation–reduction reactions continue spontaneously. In this case, the accumulator acts as a generator and injects a current into this external circuit. The direction of this current is imposed by the oxidation–reduction reactions. The accumulator **is discharged**.

If it is connected to the ends of a generator that imposes a current in the opposite direction, the system then operates in the opposite way from its spontaneous direction of operation. The electrochemical reactions are inverted and the starting materials are reconstituted; the oxidation–reduction reaction is forced by the addition of energy in the form of an electric current. This is the **charge** of the accumulator.

The cyclability of the accumulator (one **cycle** represents one charge and one discharge) characterises its lifetime.

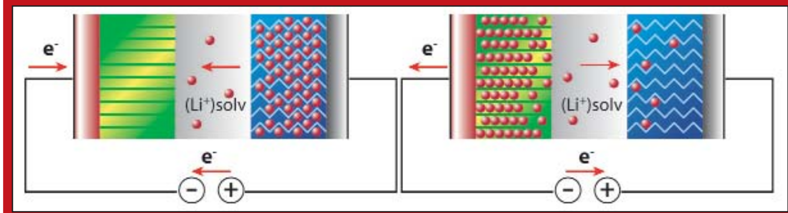

Diagram of a Lithium battery in operation.
Left: discharged state. Right: charged state.
(From “Les clefs du CEA”)

Lithium battery: When discharging, the negative electrode releases Li^+ ions, which migrate through the electrolyte to intercalate themselves into the crystalline network constituting the positive electrode. At the same time, this ion migration is compensated for by the passage of the same number of electrons in the external circuit, producing the electrical current.

A **cell** is not rechargeable. In a classic cell, the materials constituting the electrodes are consumable, and degrade as the cell operates (oxidation of the anode and reduction of the cathode), until the process finally becomes inactive when the cell is exhausted.

In a fuel cell, the structure (electrodes and electrolyte) does not react, and remains invariant over time. The cell continues to function along as it has a supply of reactants (the reducing fuel and the oxidising combustion agent), arriving from the external reservoirs.

The **hydrogen cell**: hydrogen (pure or from methanol or natural gas) is the fuel. It will combine with the oxygen in air in the presence of a catalyst (platinum in this case), generating water, heat, and electricity. This reaction is the opposite of the electrolysis of water.

Combining beamlines to combine techniques

"The idea of PULSSE is to combine experiments on four SOLEIL beamlines, working in x-ray diffraction or XAS to study these materials. LUCIA provides the spatial resolution. ODE provides the temporal (as well as spatial) resolution. The Quick EXAFS experiments will take place on SAMBA. In addition, x-ray diffraction will be carried out on CRISTAL."

Guy says:

"The purpose of this project is not to study 'the material of tomorrow' which will revolutionise energy storage, but to show the scientific community that it is important and wise to use SOLEIL to characterise battery materials. That way, in the second phase within the next five years, we will be able to say 'we have a tool that can be used for these characterisations'. In other words, it is important to take the time to validate a characterisation procedure beforehand. This saves time later, when studying new materials.

Industrial clients, in particular, cannot afford to waste time working on the fundamental aspects of the problem, but they will certainly enjoy the benefit if this work has already been done.

A lot at stake but not much competition

In view of the growing interest in battery technology and energy storage in general, there seems to be strong motivation for this type of project, but...have any other teams had the same idea, on other synchrotrons, for example?

"The project lies at the intersection of two scientific disciplines: solid electrochemistry, an area in which France is well placed, and x-ray absorption spectroscopy. Both of these techniques are cutting-edge, and it is hard to find teams ready to work on both problems at the same time. There are not many electrochemists who are experts on x-ray absorption, and likewise few spectroscopists specialise in electrochemistry. Big laboratories, which are typical of French research structures, have the advantage of gathering diverse and varied skills in one place. In North America, for example, it is usual to have just one research subject per laboratory, which is less favourable to the emergence of projects like PULSSE."

How the project will be conducted:

"Beam time has not been made contractual. We will request it via the usual procedure of project proposals. One week of beam time per line per year would already enable us to collect a considerable amount of data! Last December, I worked on ODE for three days as a consultant. By recording one spectrum every 300 ms for 30 hours... let's just say that I haven't processed all the data yet!"

To help process and analyse data, PULSSE has provided two postdocs: one based at IMN for three years, and the other at LRCS for two years. SOLEIL has also made a commitment to purchasing an automatic battery control system. Naturally, non-PULSSE teams will also be able to benefit from this investment.

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4 $LiFePO_4$ is a low-cost material because it contains no rare metals, and it is non-toxic. This cathode is also very stable and releases no oxygen (the cause of Li-ion fires and explosions), which makes it safer.

5 XANES : X-ray Absorption Near Edge Structure. XANES provides information about the state of oxidation and the local geometry around the atom being studied.

6 EXAFS : Extended X-Ray Absorption Fine Structure. Provides information about the local environment of the atom being studied, the co-ordination numbers and the bond lengths.