

In-situ / operando experiments on energy materials at synchrotron / neutron centers

Energy converters and energy storage devices have to manage electronic and ionic and thermal transport and need thus a sophisticated architecture of functional and structural components, such as electrodes, electrolytes, current collectors, end plates, sealing.

X-rays and neutrons are excellent probes for studying the electronic structure and crystallographic structure and microstructure of materials, transport processes, kinetic processes and dynamics. The inner life of a battery, fuel cell or solar cell can be very “busy”, and for physicists, chemists, materials scientists and process engineers it can be quite interesting to look into such devices.

What makes one material good for a battery, or better than another material for a battery? Why are the good materials often expensive; can we replace them by cheaper materials? Why is the life time of this fuel cell type so short? Why does it require high purity fuel to propel such fuel cell type? How can we mimic nature for solar energy conversion? How can we do that with cheap materials?

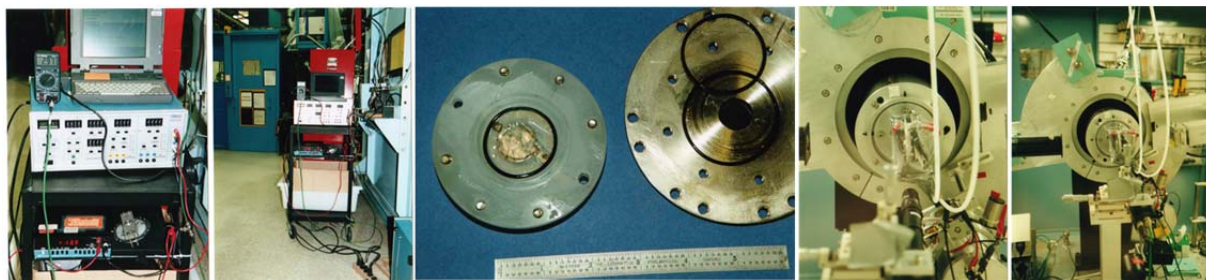
At some point, scientists and engineers who address these questions, have to employ x-ray and neutron methods in order to understand how the above mentioned devices, their components and materials “work”. Sometimes it is really necessary to investigate these materials while they are actually working or under operation. This is possible with neutrons and x-rays, provided some technical adjustments are made.

The six pictures shown above are snap shots from *in-situ* and *operando* experiments that we did in 2011 and 2012 in Switzerland, France, and the United States: On-line monitoring of the sulfur chemistry of a high temperature ceramic fuel cell; proton conductors under high compressive strain and temperature; a lithium battery under operation; a photo-electrochemical cell under water splitting condition; a proton conductor in operation together with impedance measurements; a hydrogen gas sensor – sensing hydrogen.

While these devices, components or materials were put under their true operation conditions, x-rays, neutrons, and photoelectrons were probing them and giving us structure information and dynamics information that would have not been possible few years ago.

The experiments shown above needed many years of preparation and have consumed a considerable amount of public funding as well as enormous personal sacrifices from the involved technicians, engineers and scientists to make it work. These experiments are of the “we-are-the-first” – type and have not even been published yet.

There is little exaggeration when I say that these experiments are currently the most advanced on the globe.



In-situ and operando lithium battery electrochemistry at synchrotron beamlines

Like any electrochemical energy converter and storage device, batteries are structurally and chemically very complex devices. Battery technology has made tremendous progress in the last two decades, partially because of advancement in understanding how materials work and interact at the molecular level. X-ray and electron spectroscopy aided a lot to this purpose, as is evidenced by the huge number of literature that evolved parallel with the market growth of batteries.

The chemical processes that take place in a battery and that make a battery actually work but also ultimately fail, cannot entirely be monitored – and understood - without looking into the battery during operation. I have therefore designed such cell together with Eric Granlund from the machine shop at UC Berkeley. Craig Horne, Otto Haas and Elton J. Cairns had provided me with important input before I succeeded with this cell design.

The photos above show a stainless steel / polypropylene based in-situ electrochemical battery cell mounted at the diffractometer of Beamline 2-1 at SSRL in Stanford for X-ray diffraction (XRD) and hard X-ray absorption spectroscopy (XANES), in the years 2000 and 2001. I have used this cell also at SSRL BL 2-1 for EXAFS, and for in-situ anomalous small angle x-ray scattering (ASAXS) at the BESSRC-CAT beamline at the Advanced Photon Source in Argonne National Laboratory. Latter was the first ever reported such in-situ ASAXS study.

On the left you see a portable potentiostat connected with our in-situ spectro-electrochemical (battery) cell, controlled by a Macintosh laptop, and connected to a voltmeter showing an open circuit potential for the cell of 2.97 Volt. This is all placed in front of the experimental hutch at Beamline 2-1 of SSRL. The cell itself is mounted at the diffractometer of the beamline, see the two photos on the right. The cell is in a zip lock bag which is floated with Helium so as to provide protection against ambient air, which, in the end turned out to be not necessary. In the middle you see the disassembled cell plus 3 O-rings for sealing; it turned out that those three O-rings provide enough protection and sealing against the ambient environment.

At Empa I have recently designed a similar cell which is smaller and which requires only one O-ring.

A. Braun, S. Seifert, P. Thiyagarajan, S.P. Cramer, E.J. Cairns. *In situ anomalous small angle X-ray scattering and absorption on an operating rechargeable lithium ion battery cell*. *Electrochemistry Communications* **3** (3) 136-141 (2001). <http://www.sciencedirect.com/science/article/pii/S1388248101001217>

A. Braun, S. ShROUT, A. C. Fowlks, B. A. Osaisai, S. Seifert, E. Granlund, E. J. Cairns. *Electrochemical in-situ reaction cell for X-ray scattering, diffraction and spectroscopy*. *Journal of Synchrotron Radiation* (2003), **10**, 320-325. <http://scripts.iucr.org/cgi-bin/paper?S090904950300709X>

In-situ XANES at the Mn K-shell absorption edge

Lithium manganese oxide (LiMn_2O_4) is a well-studied lithium battery cathode material. The manganese in it is a key player because it is subject to redox cycling between Mn^{3+} and Mn^{4+} during charging and discharging. The Mn^{3+} has some tendency to disproportionate into Mn^{4+} and Mn^{2+} , latter of which can be dissolved in liquid environment, such as in contact with a liquid battery electrolyte. This will promote structural disintegration and ultimately battery failure.

Figure 1 below on the left shows the evolution of the electric charge during a deep discharging of a LiMn_2O_4 electrode in the above mentioned in-situ cell. At open circuit potential of 2.97 Volt the average oxidation state of the Mn is $\text{Mn}^{+3.5}$. Upon discharging, Li ions are inserted into the LiMn_2O_3 , thus chemically reducing the Mn towards Mn^{3+} (position “A”) and even more towards Mn^{2+} . We discharged down to 1.23 Volt (position “B”).

During discharging the in-situ cell, we were recording XANES spectra at the Mn K-edge. This is possible because the X-ray beam with energy ranging from 6500 eV to 6600 eV can penetrate the two Beryllium X-ray windows of 380 microns thickness each, plus the 25 mil thick aluminum support on which the 50 micron thick cathode assembly is coated, plus two layers of Celgard polymer battery separator and a thin liquid layer of LiPF6 dissolved in dimethyl carbonate. The figure on the right shows the x-ray absorption spectra of the manganese in the in-situ cell. Any other material in the cell as well as the cell itself leaves no characteristic signature in the spectrum.

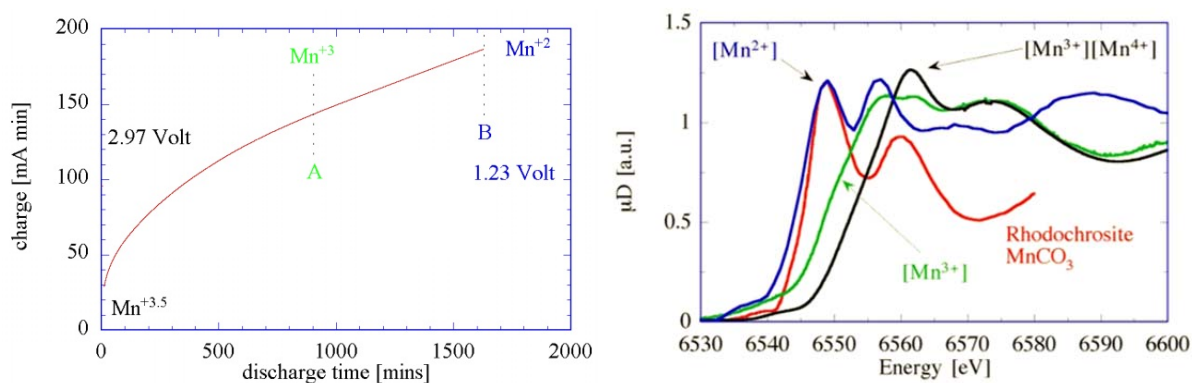


Figure 1: left – Evolution of charge during discharging the in-situ battery cell. Right – Three X-ray absorption spectra recorded at open circuit potential of 2.97 Volt (black), during $\text{Li}_2\text{Mn}_2\text{O}_4$ stage (“A”, blue), and during deeply discharged stage (“B”, green). The red spectrum is recorded from Rhodochrosite mineral for reference.

The black spectrum was recorded in the beginning at open circuit potential. Discharging causes the reduction of the manganese and manifests in a *chemical shift* of the spectrum towards lower X-ray energies, as is shown for the green spectrum which is indicative to Mn^{3+} (position “A”). Further discharging moves the Mn spectrum further down in energy towards Mn^{2+} , shown by the blue spectrum. This was position “B” where the potential was 1.23 Volt. Rhodochrosite is a mineral with Mn^{2+} . Its spectrum is shown here for comparison; it overlaps the white line with the blue spectrum from position “B”.

Anomalous small angle x-ray scattering at the Mn K-edge

Charging and discharging of a battery causes not only changes in the electronic structure and crystallographic structure of the electrodes, but also changes in the microstructure. Small angle scattering with X-rays is probably the only method capable of monitoring microstructural changes in a battery cell.

Given that our in-situ cell is designed for x-ray transmission, the transmitted signal, i.e. the x-ray scattering curve, will contain microstructure information from all materials and components in the beam path. While we have tried to minimize such contributions, there is still a minimum material necessary for the function of the battery cell, i.e. the aforementioned beryllium windows, aluminum foil, polymer binders, lithium metal, in addition to the cathode material of interest. In Figure 2 below I have listed which material was used.

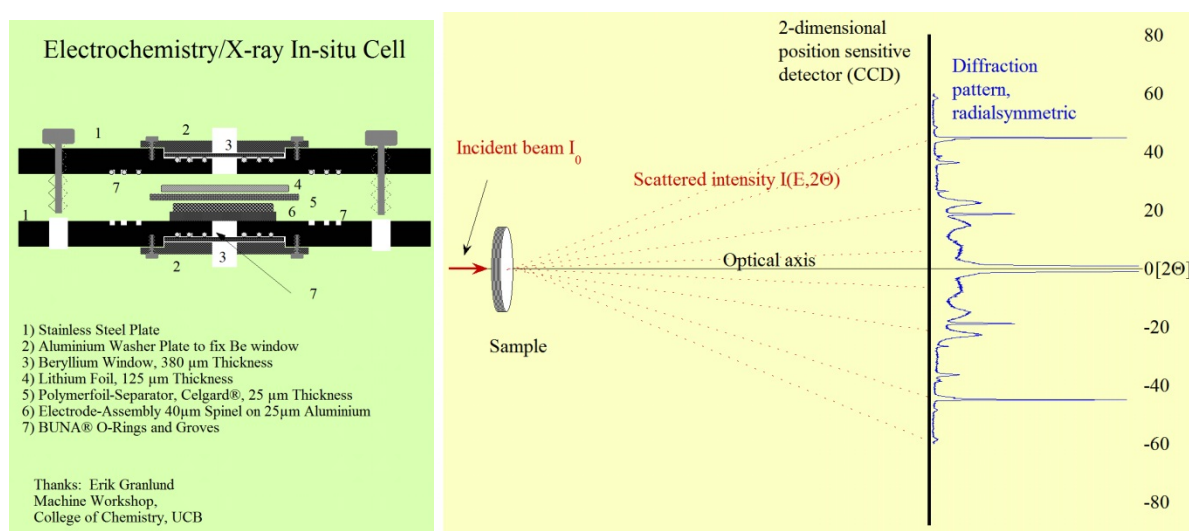


Figure 2: Left – schematic of the in-situ cell and list of materials. Right – schematic of transmission geometry for X-rays, with formation of 2-dimensional scattering pattern with Bragg peaks.

I performed this electrochemical in-situ lithium battery ASAXS (anomalous small angle x-ray scattering) experiment together with Soenke Seifert at BESSRC-CAT in 21-24 June 2000, Advanced Photon Source.

In order to get around the signal of these non-of-interest components, we apply X-ray contrast variation by tuning the X-ray energy to the manganese K-shell absorption edge. Then we record a number of small angle scattering curves for a series of X-ray energies, spanning the pre-edge and absorption edge of manganese, as is shown below in figure 3, right panel.. Here I should note that the data were recorded with a 2-dimensional x-ray detector, a CCD camera (see schematic in Figure 2, right, above). To get one 2-dim SAXS curve took 0.1 seconds (!).

It was only the shutters that slowed data acquisition down to 1second per shot. Adjustment of the X-ray energy to the next step took also some time, but altogether, the experiment for 20 X-ray energies curves took around 1 minute per charging point of the in-situ cell. The evolution of the charge was deliberately chosen slowly. We took about 2000 minutes to charge and partially discharge the in-situ cell.

For the quantitative analysis of the scattering curves, it was necessary to perform a weighted subtraction as shown in Figure 3, right panel. After that, the Porod background was subtracted and a global Guinier fit was applied. We applied two Guinier ranges because we could identify two significant Guinier shoulders; notwithstanding that a more sophisticated analysis could yield better structural data.

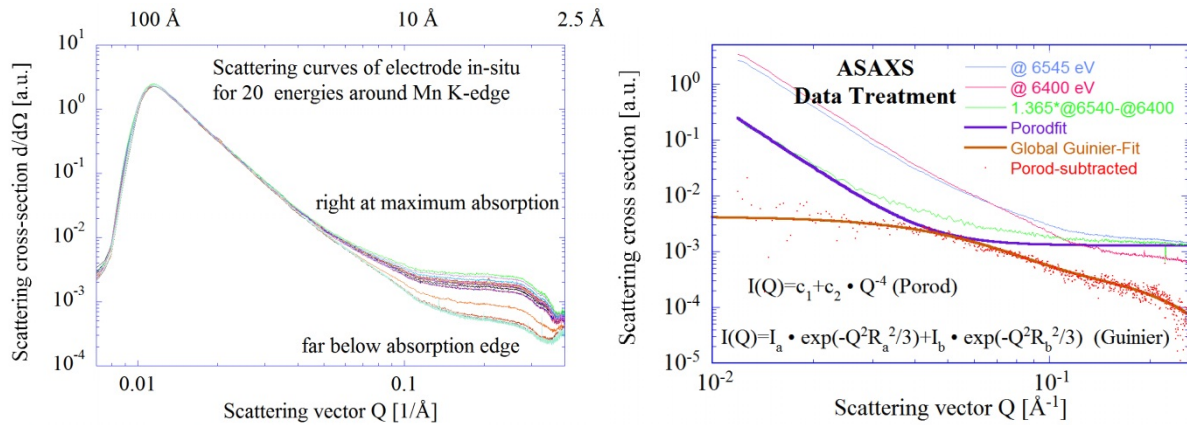


Figure 3: Left – Small angle scattering curves recorded from the in-situ battery cell at 20 Mn resonant energies. Changes are significant for the scattering vectors from 0.03 1/Å to 0.35 1/Å. Right – Example how the ASAXS data reduction was done on two scattering curves recorded at 6400 eV (before pre-edge) and 6545 eV (at the adsorption edge). Weighted subtraction of both with factor 1.365 (from f' and f'' correction), application of Porod fit, subtraction of Porod fit and then a global Guinier fit with two Guinier ranges.

In Figure 4 it is obvious how the ASAXS scattering curves of the uncharged, charged and partially discharged LiMn₂O₄ materials in the in-situ cell differ from each other. The output from the Guinier analysis shows two structural components at around 1 nm and 3.5 nm. Latter grows steadily during charging from 3.5 nm to 5 nm in the very first charging cycle. Such continuous information would not be possible with any other method.

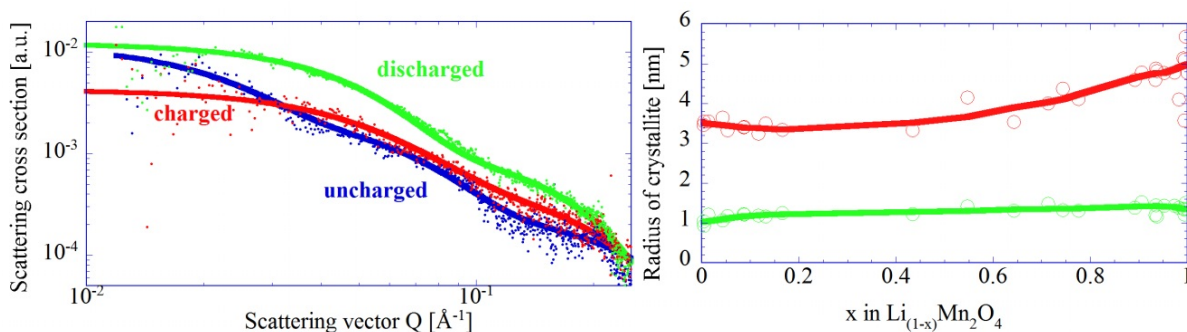


Figure 4: Left – Final ASAXS curves of the battery in the uncharged, charged and discharged state during the first charging cycle. Right – Evolution of nanocrystal size during delithiation (= charging). The change of the nanostructure in the lithium battery cathode particularly for the object size of 3.5 nm is striking.