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Report:

The aim of this work was to use operando PDF analysis to study the lithiation mechanism of silicon-germanium alloys, which recently showed promising performance as negative electrode materials for Li-ion batteries. The previous study of the lithiation/delithiaton of $Si_{1-x}Ge_x$ electrodes showed the formation of amorphous phases during the first discharge. At the end of first discharge, a crystalline phase with a lattice parameter between those of $Li_{15}Si_4$ and $Li_{15}Ge_4$ has been identified by our team by operando XRD measurements. During the charge, this crystalline phase disappeared gradually and an amorphous phase is observed again. The crystalline structure of the pristine material $Si_{0.5}Ge_{0.5}$ is not recovered back. The amorphous intermediate phases formed upon lithiation/delithiation are still unidentified. The PDF analysis is suitable to study materials with short range order, as it is the case of the amorphous phases that are formed upon cycling of $Si_{1-x}Ge_x$ material. The possibility to probe the electrochemical *in situ* reaction by PDF analysis is complex but it can bring a lot of information on the alloy mechanisms, as well as on the possible species formed upon cycling.

Experimental techniques:

In order to have the greatest resolution on diffraction data with large Q values, data recording was done using an incident energy of 70 keV. Total scattering patterns were acquired with a 2D detector Perkin Elmer XRD 1611CP3 from the beam line ID22. 2D images were collected every 5 seconds and converted into Q space versus intensity plots by using the pyFAI library (Fast Azimuthal Integration using Python). After standard corrections, the data were Fourier transformed to obtain PDF using PDFGetX3. PDF fit were performed with PDFGui software using crystal structures from ICSD database.

Operando electrochemical measurements were performed using the *in situ* cell composed respectively of one beryllium window, active electrode material (Ge and $Si_{0.5}Ge_{0.5}$ self-supported), separator soaked in the $LiPF_6$ (1M) EC/PC/3DMC + 1 % VC + 5 % FEC electrolyte, lithium disc counter electrode and a second beryllium window. The cell, schematised in Fig. 1, was assembled in an argon-filled glove box. The electrochemical measurements were carried out on an MTI BST8-WA 8 channels potentiostat in galvanostatic mode at a current of C/7 for $Si_{0.5}Ge_{0.5}$ electrodes and C/5 for Ge electrodes.

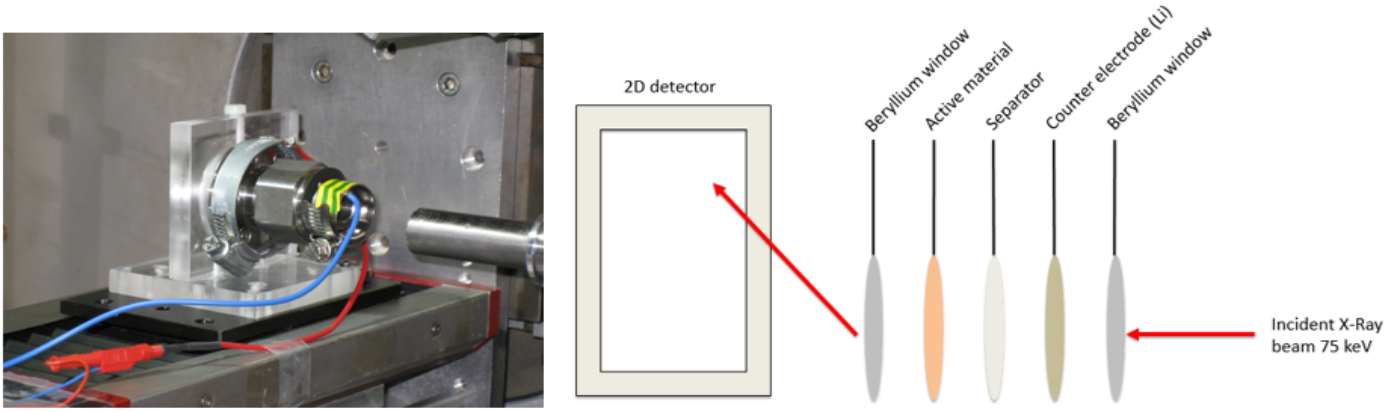

Figure 1: On the left, photo of the *in situ* cell with the holder. On the roght, schematic view of the *in situ* cell and the components

All the components of the cell (beryllium windows, separator soaked with the electrolyte, lithium counter electrode, carbon additive contained in the electrode) were analysed separately in order to remove their contribution from the total scattering pattern.

Acquisition:

Firstly, the empty cell was tested in the absence of active material to see how the signal from the cell behaved and if the acquisition was correct. The acquisition consisted on recording 100 images of the sample on a single point. The presence of beryllium windows gave a bad image resolution with highly intense spots (Figure 2c and 2d) instead of defined diffraction rings as it was a case for the LaB_6 reference (Figure 2a and 2c), caused by the large grain texture of the beryllium windows . These data, unfortunately, cannot be used for the operando measurement since the contribution of the spots, once integrated on the whole surface of the detector, cannot be subtracted from the experimental data, and therefore the information on the electrode material cannot be discriminated.

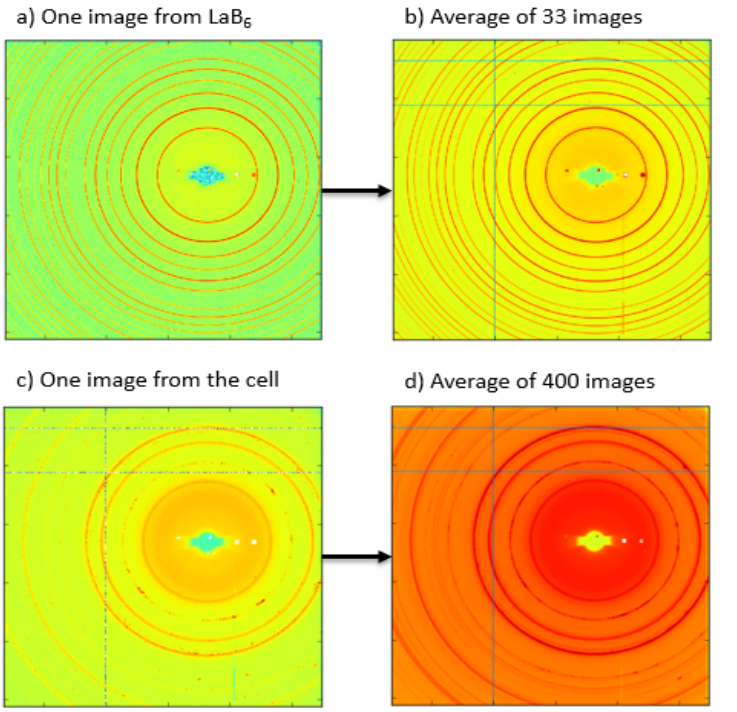

Figure 2: Typical images recorded for LaB6 reference (a and b) and for the cell (c and d)

In order to reduce the effects of these spots, and to improve the resolution on the image plate, it was decided to map collect an average image on the sample by mapping a grid of 10 by 10 points. On each point, 4 images were recorded and the average of 400 images gave an improved image resolution but with a higher background (Figure 2d). Then, the $Si_{0.5}Ge_{0.5}$ electrode material was analysed operando with a current rate of C/7. The cell was assembled as previously described with a quartz fibre separator. The mapping of sample was done together with the electrochemical measurements.

A first discharge of the electrode was collected in 38 hours and 38 grids were saved. Overall, 45 grids were recorded with the beginning of the charge (lithium desinsertion). The blank of the cell was measured just after removing the electrode from the cell. This operation was performed in the glove box and the cell was reassembled and analysed with a record of 600 images in one grid. The measurement of the blank cell, however, did not provide the expected background, since it was not possible to place both windows and cell exactly at the same place. Therefore, the contribution of the windows and of the lithium anode did not exactly match that obtained in the operando cell. Under these conditions, it is not possible to obtain the signal

of the electrode alone. Several tests were performed to obtain an acceptable measurement of the blank cell, but none of them was successful.

As a conclusion, we think that the use of beryllium window has to be banished in operando experiments on this beam line. In fact, the signal of such materials gives a highly textured scattering contribution which impedes the retrieval of the pure PDF signal of the studied material. In our future experiments that concern operando study of battery materials, we will change the material of the windows of the cell to an amorphous one, such as glassy carbon. Since such materials could react under the potential conditions employed in the operando cell, these windows must be protected by a thin layer of Nickel.

Moreover, the quartz separator used for the first in situ measurement also strongly contributed to the total scattering pattern. It was thus replaced in the measurement of the second and of the following cells by an amorphous glass fibre separator (Whatman). Ge electrodes were also analysed operando versus lithium with a current rate of C/5. The first discharge of the Ge electrode was recorded in 22 hours on 28 grids of 400 images. It was also collected a second in situ measurement of $Si_{0.5}Ge_{0.5}$ electrode material with the Whatman separator: this sample was cycled at C/4, but the electrochemical cycling was not satisfactory. Electrodes of Ge and $Si_{0.5}Ge_{0.5}$ were also analysed ex situ using an adapted sample holder.

Data processing:

As it was said previously, the signal of the two beryllium windows strongly contributes to the total scattering patterns, which makes the rigorous subtraction of the background signal virtually impossible. Similar problems were found for the lithium metal counter-electrode. The signal from the active electrode material was very weak compared to all these components. As we could judge on the structure function S(Q), the background subtraction was not satisfactory: in these conditions it was not possible to extract the PDF g(r) of the pure active material.

In this report, the data for the pure Germanium electrode, expected to be easier to analyse, are presented. In fact, for the $Si_{0.5}Ge_{0.5}$ alloy electrode, the treatment is more difficult due to the simultaneous presence of the two elements.

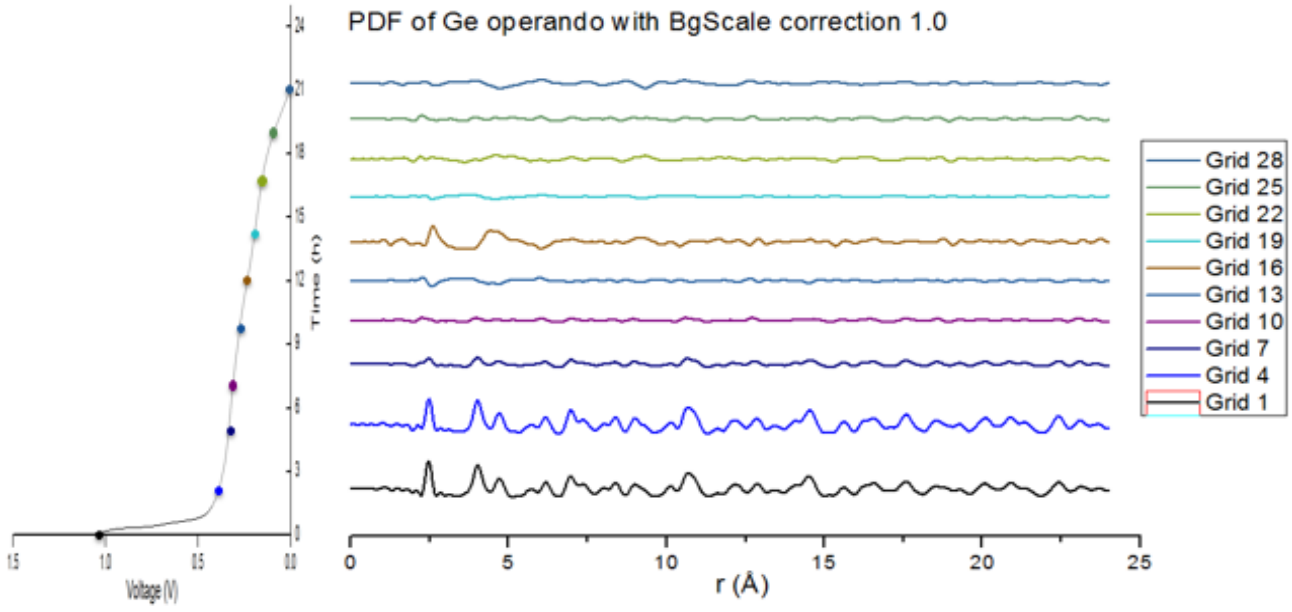

Figure 3: On the right, first discharge curve obtained for Ge electrode during in situ measurements. On the right, selected PDFs of Ge electrode corrected with background 1.0. collected during the first discharge, colors of the curves correspond to the colors of the points on the electrochemical curve.

Concerning the Germanium sample, structure functions and PDF were calculated. If the background subtraction is not applied, the evolution of PDF with the level of lithiation cannot be used since it is dominated by the signal of both windows and lithium counter-electrode. The PDF with background subtraction by a constant scale factor 1.0 applied on each grid is presented on figure 3. To simplify the figure, only one out of three grids is plotted with constant vertically offset. The corresponding electrochemical curve is also presented with the corresponding color points. The subtraction works on the first recorded grids, and,

the three first ones peaks match almost perfectly the peaks of Germanium calculated by the PDFgui software. After ten grids, however, inconsistencies were observed as if the background signal changed during the measurement (Figure 3). This discontinuity observed from the eleventh grid could be assigned to the injection of electrons to the beam at the same time, which indeed strongly influences the background signal. It is also the case for the twenty fifth grid. An additional problem may come from the non-linear response of the plate detector, especially in the presence of intense diffraction spots as those produced by the beryllium window. These data, therefore, cannot be analysed in the expected way.

The only possibility to process the collected data is, in our opinion, to use differences between PDF. Therefore, the spectrum of the first grid, which correspond to the signal from the pristine electrode material together with the cell, was subtracted in all the others grids. Thereby all species that form during cycling will give positive peaks, whereas all species which disappear upon cycling will give negative peaks. The evolution of PDF difference curve is represented in figure 4. The discontinuities due to the injections clearly jumps out, especially that at the twenty-fifth grid. The negative peaks appearing in the r (Å) difference PDF match well those of germanium.

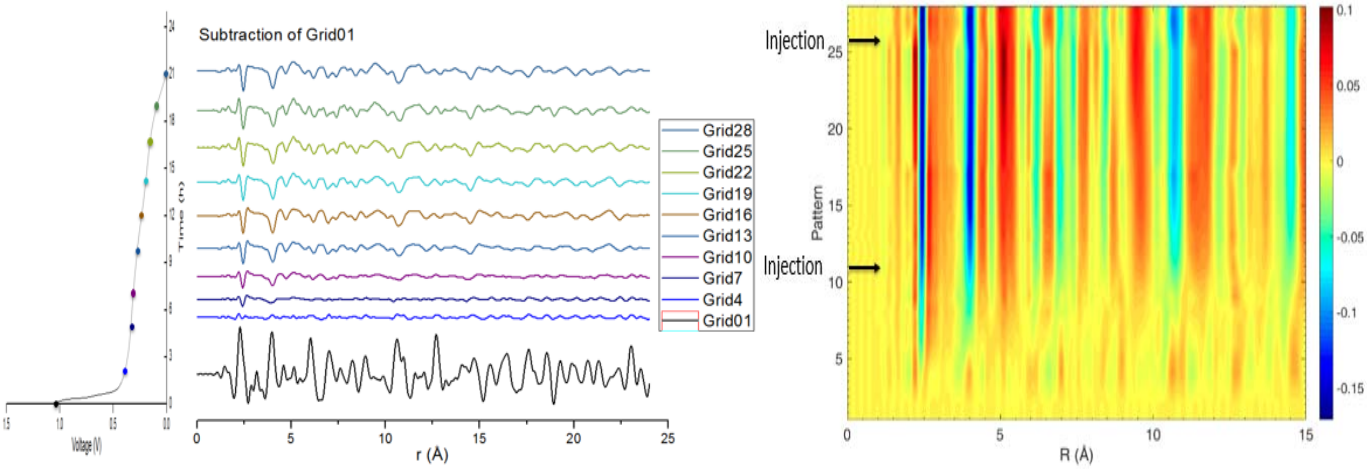

Figure 4: Selected PDFs differences from the first grid of Ge electrode collected during the first discharge. On the right, cartographic view of the evolution of PDF difference.

The decreasing of the beam intensity and the injections every 12 hours disturb data acquisition and make data processing very tricky. The operando study needs several hours or days, and the inconstancy of the beam intensity cannot be rightly corrected with the monitoring. It seems that the background changes slightly after every injection, and influences the subtraction and the correct interpretation of the signal. One solution will be to record the first discharge of the electrode material in less than twelve hours, which means applying a higher current rate, which could be harmful for the good electrochemical behaviour of the studied materials.

For future experiments, we plan to work first on pristine materials and ex situ samples. Data recording will be faster and injections will not influence the acquisition. Our in situ need upgrading, and the replacement of the beryllium windows with glassy carbon ones is planned in order to facilitate the subtraction of the background. According to the PDF signal from the counter electrode, the solution proposed is to make a ring-shaped lithium counter-electrode. In this way, the electrochemical reaction will take place on the whole material but the beam will be focused only within the ring, and the signal from the lithium will be removed from the total scattering pattern. The use of amorphous Whatman separator will be privileged instead of Quartz separator.

PDF method is a new tool to probe the local atomic structure in amorphous materials or nanoparticles where conventional Bragg diffraction analysis fails. This first beam time for electrochemical operando PDF measurements at the ESRF was rewarding, to our knowledge it was the first operando PDF analysis with electrochemical measurements in this synchrotron. Many improvements were realized to simplify data processing, in particular concerning background subtraction. The use of PDF needs to be further extended to *operando* studies, it will allow bringing new insights on material evolution during cycling.