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ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** **In-situ observation of the lithiation of advanced silicon based anode for Li-ion batteries**	**Experiment number**: MA-2586
Beamline: ID16B-NA	**Date of experiment**: from: 18/06/2015 to: 23/06/2015	**Date of report**: 04/09/2015
Shifts: 15	**Local contact(s)**: Jussi Petteri Suuronen	*Received at ESRF:*

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Report: Proposal reference number N° MA-2586

In the constant urge of enhancing the energy density of lithium batteries for electrical and hybrid vehicles applications, new materials are daily tested. One of these materials of interest is the silicon which with its very high specific capacity and safer use, compare to conventional carbon-based electrode, would allow developpement of attractiver batteries. However the lack of developpement in this field is mostly due to the important volume expansion and cracking of silicon particules occuring during lithiation/delithiuation process within cycling. Capacity fading and so decreasing cycle life time are results of such a comportement and can be understand by *in situ* characterization of the microstructure evolution of silicon-based anodes.

In this purpose the conception of X-ray transparent cells based on PTFE polymer enabling a good electrochemical behaviour was achieved. Two different kind of cells were imagined for local X-ray tomography imaging and X-ray global tomography imaging, i.e. respectively cells figure 1 A and figure 1 B. Both of the half cells were tested before the schedulded experiment at the ESRF and were succesfully validated with a VMP Origaflex from OrigaLys Electrochem SAS OGF500 used as well during the experiment at the ESRF. It was more suitable to use cells type A for electrochemical behaviour, because they are more representative of a real battery and have a more reproductive electrochemical behaviour than the cells of type B. But the cells type B are better for X-ray imaging, because it is widely recommaded to prefer global tomography in order to have the best imaging quality possible. The two types of cell are complemenatry but cells of type B are mostly used during the experiment.

Different electrode compositions, based on the use of different silicon, different cycling conditions (C-rate) and electrolyte were inverstigated. The main compositiopn of the composite electrode is based of a binder (CMC), an electronic percolant (carbone) and three silicon particules as active material, varing in the shape and size :

- A powder produced by high-energy ball milling of a commercial micrometric Si powder.
- A powder obtained by filtering large particules of the same commercial micormetric Si powder.

- A powder of nanoporous Si kindly furnished by Takeshi Wada form the Tokyo University of Science.

The slurry is then deposited and dried on a substrate, the current collector of the electrode, which can be carbon foam for the cells type A and copper (with pointy head) foir cells type B.

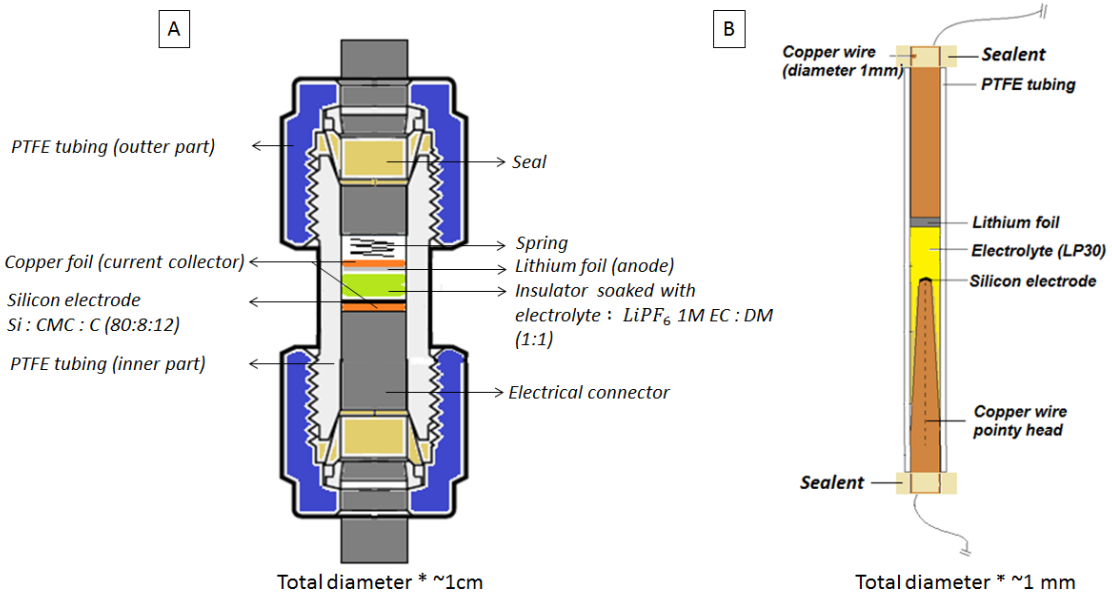

Figure 1 : Schemes of the experimental cells used for X-ray tomography imaging of silicon-based composite anode for lithium-ion batteries, typical assembly on the left (B) with insulator soaked in LP30 elctrolyte (LiPF6 1M in EC : DEC (1 : 1)) and spring, and small configuration on the right (A) with LP30; (*) the total diameter is consider in the field of view of the beam, i.e. in the middle of the cell

Three composition for the electrolyte were investigated, the LP30 (LiPF6 1M in EC : DEC (1:1)), a mixture of LP30 : FEC (10 : 1) and BXF (LiFSI 1M in Pyr13 FSI).

Procedure :

The beam configuration for the experiment was a quasi pink-beam with an energy of 17.5keV and a real pixel size of 4.95nm. The field of view is about 2560x2560x2160 pixels. For the aquisition datas, 2001 projections for 360° rotation, 300 references and dark are made for each of the four positions for each scan. With an expositon time of 300ms (more or less depending of the sample) the scan time was around 1h30min. None of the specific optical tools were used during the experiment. The samples are fixed on a specific support holder made in plastic to avoid any short circuit between the battery and the holder. Each sample tested were imaged at the initial state, i.e. no lithiation, and several time during a cycle, depending of the rate of discharge chosen.

For this experiment the limitating problem is the time of discharge which can be long due to limitation problem for lithium diffusion, therefore the C-rate must not reach high value for these kind of electrodes. Typically a C/9 value (one discharge in nine hours) is in quite good agreement with theoritical data. Hence experimentally sixteen hours are necessary for achieving one cycle adding the time for scaning with ten scans per cycle, the resulting time for one cycle is approximately tewenty seven hours. Aiming to study the effect of the C-rate with higher current value can reduce the time for one cycle to eleven hours for a C/4 rate. By scanning and doing electrochemical cycling in the meantime is also a good way to analyse more samples during the allocated time on the beamline.

Results and perspectives :

As they are more thicker the samples type A are used as last resort or for preparing at first the experimental settings. Six samples of type A were tested for setting the experimental parameters and only two of them were tested within cycling. More focus was done on the cells of type B with twentyfour samples tested. Within those twentyfour, all intial states were made, but only eight of them were able to show a good electrochemical behaviour after the intial scan, hence that 2/3 of the samples were not viable for electrochemical and structural evolution analyses. They are used to improve image analyse and segmentation procedure between the different parts in the electrode by thresholding on the grey level value. It is possible also to appreciate the difference between the different types of silicon and the global structure of the electrode

at the initile state. But the remaining 1/3 of the tested samples showed insertion of lithium and volumetric expansion of silicon particules, more quantitative analyses still need to be done.

The limiting aspect of the cells of type B was the formation of tiny bubles after the first scan. Those bubles within time are gathering and block the ion diffusion through the cell. Maybe they came from electrochemical formation of CO_2 by forming the SEI on the surface of the electrode. But those bubles are not forming clearly in the cells of type A.
It might be the insertion of an inert gas during the initial assembeling step of the cells in gloves box, as they do not have spare space at all to stock them. And they might migrate by electrolyte displacement or convection, enhanced by heating of the beam. Different techniques were used to try to remove them but in the end the bubles were still there. The fact that they are converging in the middle of the cell prevent against a good quality of imaging, and moreover unable electrochemical cycling by placing the cell in opencircuit.
In the light of these results further progress must be done to control electrochemically the capillary cell and prevent bubbles formation or at least contain the gathering by using a polymer insulator in the middle of the cell. The fibers will spread the bubles and prevent for open circuit configuration in the cell. To validate this new configuration test in X-ray tomography and cycling must be done.

Other results :

In parallel other works were carried out to study the microstructrue of iron manganese alloy, six composite type samples were analyzed with different compositions and two different microstructure sizes.
Only one reconstruction was successful $Fe_{40}Cr_{10}Mg_{50}$ with a thick microstructure and 50 nm voxel size see figure 3 A, other reconstructions were done ($Fe_{40}Cr_{10}Mg_{60}$, $Fe_{56}Cr_{14}Mg_{30}$ and $Fe_{32}Cr_{8}Mg_{60}$) with a small microstructure and 50nm size voxel figure 3 B but either way resolution is not sufficient or there was vibrating problem during the scan.