ESRF	**Experiment title:** *In situ* structural study of silicon anodes in lithium-ion batteries	**Experiment number**: MA-3459
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Shifts: 9	**Local contact(s)**: Hermann Emerich	*Received at ESRF:*

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Report:

This preliminary report describes experiment MA-3459, which was aimed at studying the evolution of the local structure of silicon during *in situ* lithiation as a lithium-ion battery cell anode. We performed two types of *in situ* experimental configurations, although we experienced several challenges. As a preliminary report, the data analysis is still forthcoming due to its complexity, which will become apparent in the detailed descriptions below.

Beamline configuration, alignment

The first shift was spent on beamline configuration, solving issues with monochromators, and alignment using LaB_6. We chose an energy of 50 keV to obtain a high q for pair distribution function analysis, since most of the Si of interest was amorphous or would become amorphous upon lithitaion.

Ex situ - capillaries

We first tested and measured several types of Si sources and other battery materials such as the pouch cell, Li foil, Cu current collector, etc. as reference materials so that we could exclude them later in the data analysis. Capillaries were prepared in advance and mounted onto a goniometer head using beeswax as depicted in Figure 1. However, several hours were lost in the second shift because the position of the tungsten carbide anti-scatter plate was misaligned. The misalignment only became apparent upon analysis of the first datasets followed by more ad hoc reference measurements on an empty capillary that yielded strong crystalline peaks. As a result, the plate had to be re-aligned and several samples had to be re-measured.

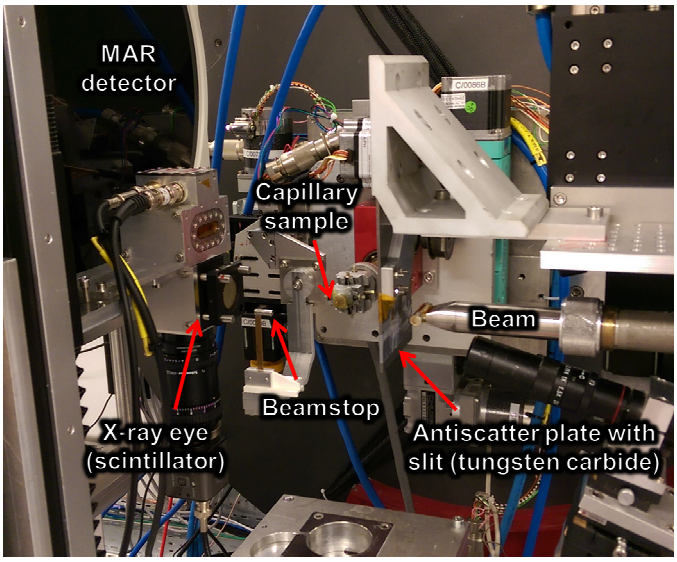

Figure 1. Diagram of the capillary mounted on goniometer head in *ex situ* measurements.

Figure 2. (top left) Planar pouch cell. (top right, bottom right) X-ray eye is able to observe the edge of the electrode. (bottom left) Pouch cell mounted in beam path and connected to portable potentiostat

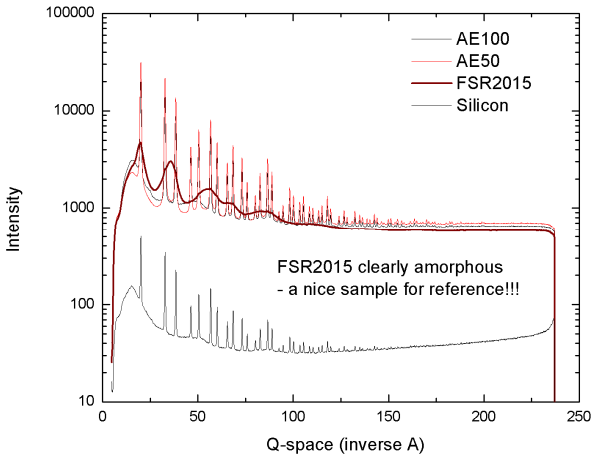

Figure 3. Reference data from *ex situ* capillary measurements.

In situ experiment #1 – through-thickness pouch cell

Our first *in situ* measurement used a simpler approach with measuring coin-cell sized electrodes in a pouch cell. The cell setup and results of the x-ray eye are shown in Figure 2. Because we had fabricated many of these cells before and it is planar in design, the cell cycled moderately while it was measured. However, because of the through-thickness scattering, the Si signal of interest is convoluted by the Cu current collector, Li metal, and polymer separator. Data analysis is in progress and is aimed at deconvoluting the signals.

In situ experiment #2 – pouch bar cell

In our second experiment, we attempted to measure the electrode in the edgewise direction instead of through-thickness. This approach was significantly challenging due to the thickness of the Si electrode being about 10 to 15 microns thick. However, with the aid of the x-ray eye, we were able to visualize each layer of the cell when viewed edgewise, as shown in Figure 4. After reducing the slits, although the counts were lower, we could measure the scattering from roughly each layer of interest.

However, we discovered a design flaw in all of the pouch bar cells, which is that Al was used as a current collector for the Li metal counter electrode instead of the more stable Cu. Although cells can still operate as observed in *in situ* experiment #1, the mechanical stress of flexing the pouch bar cell and/or the pooling of the electrolyte solution away from the electrode disabled the battery cell from cycling. Although we could observe different layers of the cell edgewise, we were not able to make *in situ* measurements of the cell as it cycled.

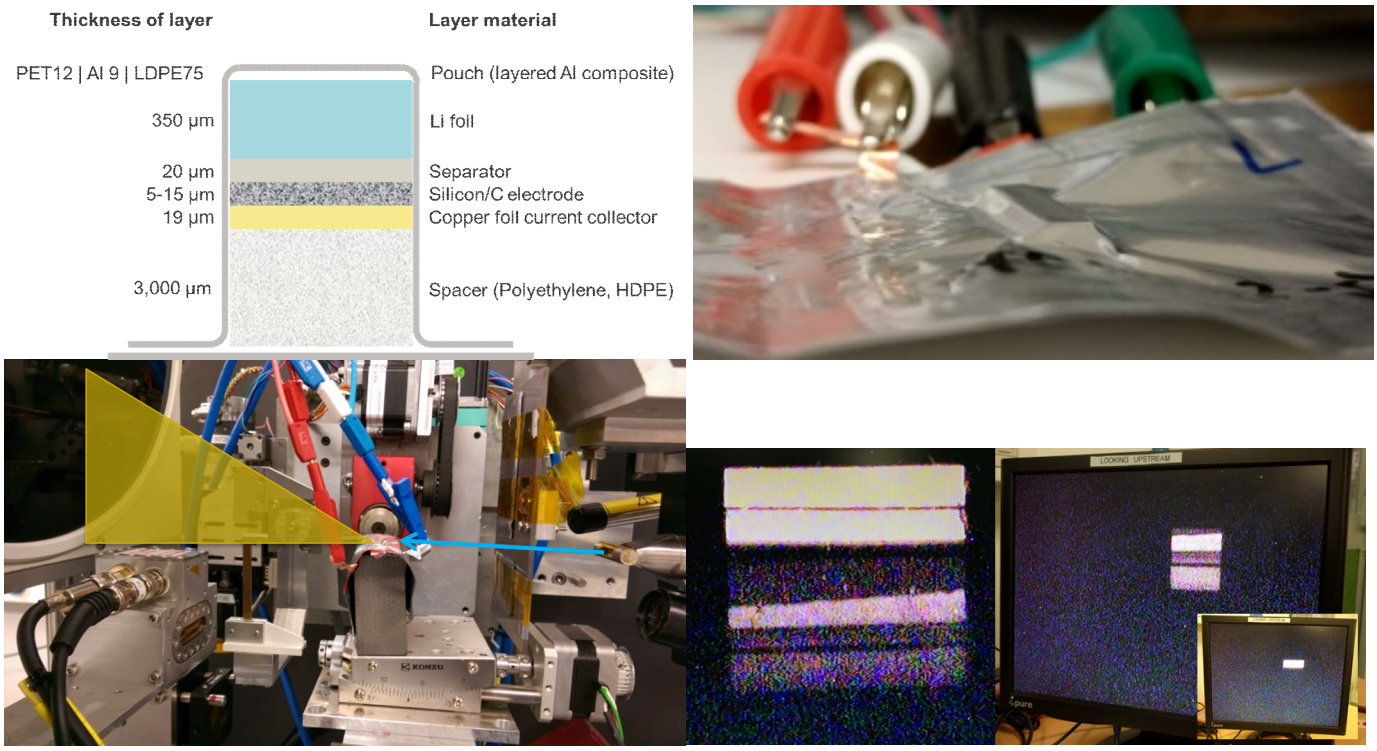

Figure 4. (top right) Sealed, prpeared pouch bar cell as viewed at a glancing angle. (top left) Cross-sectional diagram of the pouch bar cell. (bottom left) Pouch bar cell as mounted on a metal block on a Huber stage with arrows and triangle depicting incident x-ray beam and scatter beam paths, respectively. (bottom middle, right) Real-time X-ray eye video feed of the bar cell layers. (bottom right, inset) X-ray eye view after slits are reduced the beam to a layer of interest.

In situ experiment #3 – pouch bar cell, silicon nitride

Our third *in situ* experiment was a repeat of experiment #2 but with silicon nitride. Silicon nitride also has good performance as a Li-ion battery anode with some interesting phenomena that occur in the first lithiation cycle. We aimed to use the evolution of the local structure of Si to help explain its performance, but encountered the same issues as in experiment #2 because of the common design. Some electrochemical activity was recorded since the silicon nitride operates differently chemically from pristine Si but it was less than ideal.

Secondary experiments

If our main *in situ* experiments had completely failed, we prepared a lower priority "Plan B" experiment to support other researchers at IFE. These experiments were intended for utilizing idle beamtime during more complex sample and equipment preparation and when the team, particularly when the battery testing specialists (Samson and Asbjørn), needed rest. The samples were simple *ex situ* measurements of capillaries of titanium-manganese bimetallic alloys for hydrogen storage. During our delayed transport of the *in situ* battery pouch cells, we used the time to measure these samples.

Conclusions

We were partly successful in conducting different types of *in situ* x-ray scattering experiments for Li-ion battery cells based on Si anodes. The degree of success also depends on how easily we can deconvolute the scattering signal and the eliminate or reduce the contributions from foreign parts of the pouch cell. The pouch bar cell design demonstrated its feasibility in large

part thanks to the x-ray eye equipment, which was surprising given that beam alignment to the layer of interest was considered the most challenging part of the experiment. However, it faltered unexpectedly because of logistical transport issues and during the electrochemical tests.

Improvements for future experiments

There are several points of improvement, both scientific and logistical.

1) Shipping of batteries was a significantly larger challenge than expected. Although we researched the requirements and regulations, ultimately our approach faltered because we did not know the expected delivery time of the batteries (on the order of weeks instead of days) by cargo plane.
2) Although our through-thickness pouch cells were previously tested many times, our pouch bar cell was less robust and did not perform as expected. It also contained a design flaw that we suspect was fatal. Although the same design flaw is present in the through-thickness pouch cells, it was not severe because of the larger size of the cell and less stringent mechanical stress, thus, we did not anticipate the issues with the pouch bar cell. However, we are certain the solution is to replace the Al current collector with Cu, which is also thicker and stronger. These improvements can take place immediately.
3) At the same time of this improvement in cell design, we are augmenting the pouch cell to incorporate Kapton windows for increased x-ray transparency, reduction of noise, and minimizing the signal contribution to the pouch cell material. We will push the boundary of this design principle as far as possible, including modifying the internal electrode cell separator with a Kapton window.
4) Further, sample alignment and motor control consumed a significant amount of time. Besides improving the pouch cell, we plan to devise our own sample holder that would provide more reliable control with less influence on the cell’s performance.