



## 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://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

### Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

#### Experiment Report supporting a new proposal (“relevant report”)

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a “*preliminary report*”),
- even for experiments whose scientific area is different from the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as “relevant report(s)” in the new application form for beam time.

### Deadlines for submitting a report supporting a new proposal

- 1<sup>st</sup> March Proposal Round - **5<sup>th</sup> March**
- 10<sup>th</sup> September Proposal Round - **13<sup>th</sup> September**

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.

### Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number 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.



	<b>Experiment title:</b> Recording strain and ion redistribution in working supercapacitor electrodes with in situ ASAXS	<b>Experiment number:</b> SC-4752
<b>Beamline:</b>	<b>Date of experiment:</b> from:20.07.2018 to:23.07.2018	<b>Date of report:</b> 08.01.2020
<b>Shifts:</b>	<b>Local contact(s):</b> Peter Boesecke	<i>Received at ESRF:</i>

**Names and affiliations of applicants** (\* indicates experimentalists):

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### **Report:**

The development of future high performance supercapacitors demands for a detailed understanding of the double-layer formation in confined systems. In recent years, in situ small angle X-ray scattering (SAXS) and in situ X-ray transmission (XRT) measurements have been emerged as suitable methods to analyze global and local ion rearrangement.[1, 2] In addition, the use of specially designed hierarchically ordered mesoporous carbon materials combined with in situ SAXS allows to track electrode expansion and contraction on the nanometer length-scale [3] Although XRT and SAXS allow us to study structural and concentration changes, these techniques suffer from a major drawback: because of the lack of element sensitivity additional data (e.g. the overall charge) is needed to distinguish between the individual ions. Therefore, we proposed in situ anomalous small-angle X-ray scattering (ASXS) as a possible technique to overcome this issue.

We performed an in situ ASAXS experiment at ID02 during which a working supercapacitor cell was charged and discharged. The changes of the scattering intensity during charging and discharging are rather small (in the percent range) and lead to very small ASAXS effects. Therefore, the aim of this experiment was to demonstrate the principal applicability of ASAXS to provide both, element sensitivity and structural sensitivity without the need of additional (e.g. electrochemical) data. The cell used for this experiment had a specially designed housing optimized for in situ SAXS experiments. The cell itself contained electrodes made of a nanocast hierarchically ordered mesoporous carbon material, consisting of carbon nanorods on a hexagonal lattice, and a 1M RbBr aqueous electrolyte. The RbBr electrolyte was chosen according to the accessible energy range of ID02, allowing to perform ASAXS experiments at the absorption K-edges of both, Br and Rb ions. A fluorescence (XRF) detector was mounted behind the supercapacitor cell to track the change of the fluorescence signal during charging and discharging of the supercapacitor.

Two different electrochemical experiments were performed (cyclic voltammetry and chronoamperometry) while measuring SAXS intensity at four selected energies below the absorption K-edge of Br and Rb. During the chronoamperometry (Figure 1), the supercapacitor cell was charged to  $\pm 0.6$  V. After a 2000 s equilibration, the SAXS measurements at the 8 different photon energies were performed. Additionally, 1.5 cyclic voltammetry periods were measured at a constant photon energy, before switching to the next energy.

As a result, the time resolution was not limited by the change of photon energy. However, this procedure requires a good stability of the in situ cell over time, which was not perfectly the case. Therefore, only the chronoamperometry data could be evaluated quantitatively.

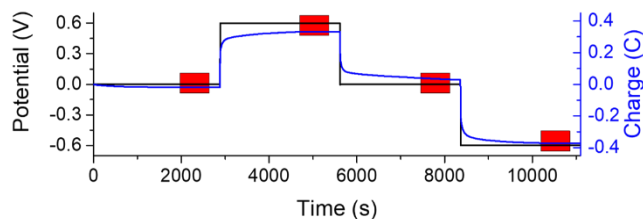


Figure 1: Chronoamperometry measurements (black line) with the red boxes indicating the time period needed to perform the ASAXS measurements at 8 different energies. The blue line shows the accumulated charge measured by a potentiostat.

By analyzing the ASAXS data carefully, we were able to track ion specific concentration changes for positive and negative applied potentials. Additionally, we have shown that it is also possible to see structural changes (due to local ion rearrangement) with a single experiment without the need of additional electrochemical data. The results of this experiment have already been published in ACS Applied Materials and Interfaces. [4] It turned out, that fluorescence contributions from Br when measuring at the Rb edge significantly influence the measurements. Since both, fluorescence and ion concentration changes lead to an approximately constant intensity contribution at large  $q$  in ASAXS, their separation is usually not straight forward. Here, the independent detection of the fluorescence signal can be very helpful. Unfortunately, the fluorescence detector was not synchronized with the SAXS detector. Therefore, it was not possible to evaluate the fluorescence contribution of the SAXS data in this experiment, but will be taken care for in future work. Nevertheless, the intensity of the fluorescence radiation is proportional to the ion concentration in the whole irradiated volume. As a result, we have been able to track the concentration changes of Rb and Br during cyclic voltammetry without the need of additional (electrochemical) data (Figure 2).

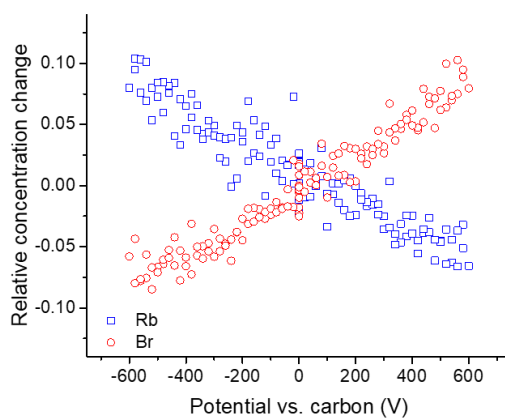


Figure 2: Calculated ion concentration change from XRF as a function of the applied potential.

In conclusion, this experiment represents a first proof-of-principle study showing that ASAXS is indeed capable of tracking structural changes for individual ion types at the nanometer level. In a next step, chronoamperometry measurements at different potentials and the use of different electrolytes (e.g. RbCl, CsBr) would greatly help understanding the behavior of the individual ions in more detail. Additionally, the synchronization of the fluorescence detector and the SAXS detector would be beneficial.

#### References:

1. C. Prehal, C. Koczwara, N. Jäckel, H. Amenitsch, V. Presser, O. Paris, Phys. Chem. Chem. Phys. **19**, 15549 (2017).
2. C. Prehal, C. Koczwara, N. Jäckel, A. Schreiber, M. Burian, H. Amenitsch, M.A. Hartmann, V. Presser, O. Paris, Nat. Energy **2**, 16215 (2017).
3. C. Koczwara, S. Rumswinkel, C. Prehal, N. Jäckel, M.S. Elsässer, H. Amenitsch, V. Presser, N. Hüsing, O. Paris, ACS Appl. Mater. Interfaces **9**, 23319 (2017).
4. C. Koczwara, C. Prehal, S. Haas, P. Boesecke, N. Huesing, O. Paris, ACS Appl. Mater. Interfaces **11**, 42214 (2019).