

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

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th 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.



	Experiment title: Drying of Nanoporous Supercapacitors: An Anomalous X-Ray Scattering Study on Liquid and Ion Rearrangement in Pore Space	Experiment number: SC-5240
Beamline: ID02	Date of experiment: from: 08.07.2022 to: 11.07.2022	Date of report: 17.10.2022
Shifts: 6	Local contact(s): Michael Sztucki <sztucki@esrf.fr>	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Manuel Brinker, Laura Gallardo-Dominguez, Yannick Tetzner, Lars Damman and Prof. Dr. Patrick Huber; Hamburg University of Technology Benjamin Rudolph and Prof. Dr. Michael Fröba; University of Hamburg Dr. Sujeet Dutta; Institut Lumiere Matiere Université Claude Bernard Lyon 1 Dr. Sylvio Haas, Dr. Milena Lippmann; DESY Department of Photon Science		

Report:

We conducted a synchrotron-based anomalous (ASAXS) with conventional small angle X-ray scattering (SAXS/WAXS) experiment to study the liquid and ion rearrangement upon drying and wetting of aqueous electrolyte-filled nanoporous carbon. The aim of the study is to provide fundamental mechanistic insights in the drying processes, in terms of the coupling of thermodynamics and transport processes in the porous medium. Thus, it potentially allows for an appropriate design of electrodes to be used in wetting-drying energy harvesting applications.

The samples are prepared by using a nanoporous, CMK-8 carbon powder with a cubic pore symmetry. The powder is rolled in a hotpress together with 15 wt% PTFE to form 350 μ m thick thin-films with a lateral size of approximately 1.5cm x 2.5cm. These films are fixated on a frame, which is attached to a sample holder. The whole sample is installed in an in situ measurement cell. The cell has two nalophan-foil windows on front and backside, where the incidence and scattered X-ray beam passes through. It is filled at the bottom with a 1M RbBr electrolyte solution. The sample is only in contact with the solution at its very bottom. A humidifier with

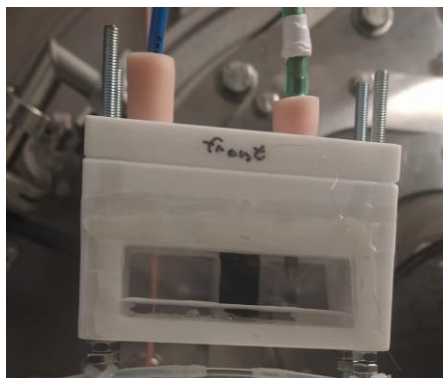


Figure: 1 In situ measurement cell.

a humidity sensor is connected at the top of the cell. Hence, it is possible to influence the humidity inside the measurement cell. Figure 1 shows a picture of the measurement setup.

For a typical measurement the sample is stored in a glass beaker with 1M RbBr solution for at least three hours so that the electrolyte solution fully fills the sample. The sample is then installed in the cell and the humidity is set to >95%RH. Hence, the evaporation of the solution from the sample is negligible. First of all, it is checked, if the sample behaves as desired in an electrochemical cyclic voltammetry measurement. All samples investigated, showed a clear capacitive behaviour. Bromide anions are stored in the electric double layer that forms on the surface of the nanoporous carbon. More charge is stored when the potential is increased and anions are expelled from the double layer when the potential is decreased. Without an applied potential the positive surface charge of the carbon surface should preferentially attract the bromide anions.

After the electrochemical check, a first SAXS measurement is conducted. The result can be seen in Figure 2 in comparison to a completely unfilled sample in a dry, inert atmosphere. The measurements are already

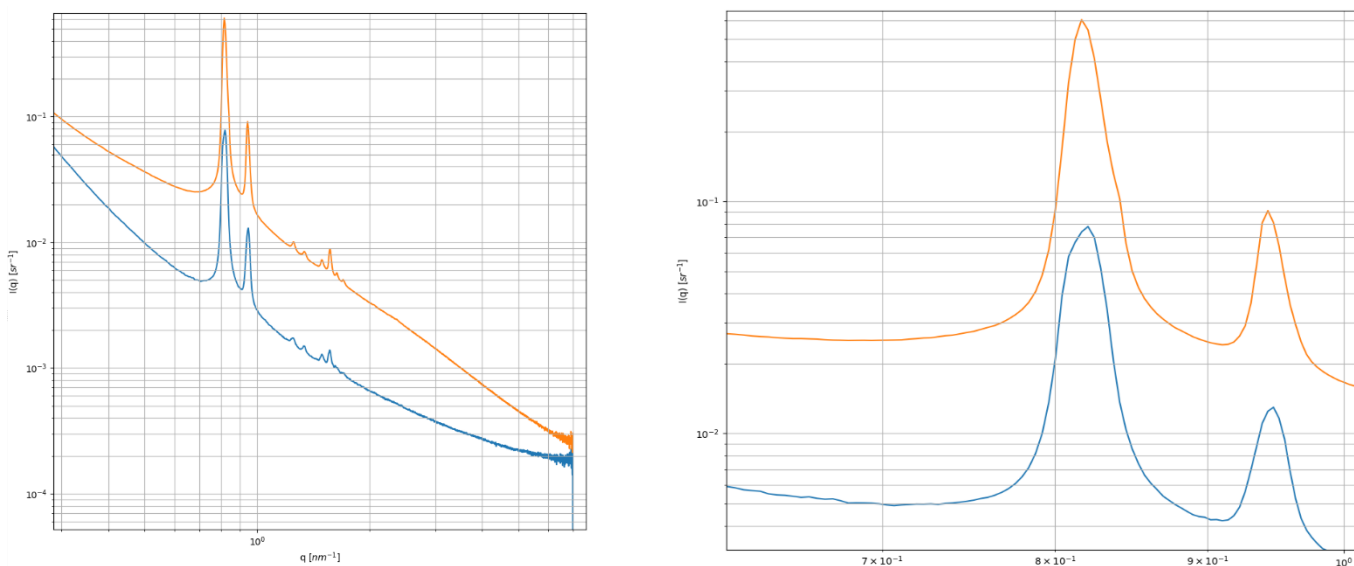


Figure 2: SAXS measurement on CMK-8 nanoporous carbon with an empty pore space (orange) and filled by electrolyte solution (blue).

normalized to the intensity of a SAXS measurement on a water capillary and to the intensity influenced by the cell, i.e. the cell-windows and the humid atmosphere inside the cell. It is plotted versus the wave vector transfer q . The SAXS measurement shows the clear pattern of a cubic symmetry. It can be seen that the overall intensity is lower due to the absorption through the liquid.

Then an ASAXS measurement is performed. Therefore SAXS measurements with an exposure time of 1s are conducted at different beam energies. Five beam energies are chosen below the absorption K-edge of Bromine, which is determined by a XANES measurement as 13.477keV. One SAXS measurement is conducted directly at the edge and two measurements have beam energies above the edge. In total the energy values chosen are:

- 13227 eV (-250eV below edge(=13.477keV)),
- 13377 eV (-100 eV),
- 13427 eV (-50 eV),
- 13457 eV (-20 eV),
- 13467 eV (-10 eV),
- 13477 eV (0 eV),
- 13497 eV (+20 eV)
- 13527 eV (+50 eV)

Through this beam energy dependent set of measurements it should be possible to detect if the bromide-anions are preferentially assembled at the carbon interface. Thus, an energy dependent intensity shift below and above the absorption edge should be detectable, as already shown in literatur.[1,2] However, at the beamtime

we were not able to see any energy dependence of the scattering curves. Different spots on the sample were tried as well as higher electrolyte concentrations. Even a high applied potential of 1.2 V, which assembled significantly more anions in the electric double layer on the carbon surface, did not lead to the desired outcome. An ASAXS measurement has also been performed on the absorption edge of the rubidium cation at 15200 eV. A energy dependence of the SAXS intensity could also not be determined.

ASAXS measurements were meant to monitor the arrangement of bromide anions on the carbon surface during the drying and wetting process of the nanoporous carbon. For the drying process, the relative humidity is set to 65%. Thus, the liquid in the nanoporous carbon that is not in contact with the bulk electrolyte solution evaporates from the pores of the material. But since the sample is still in contact with the bulk electrolyte solution, a capillary force still enables the imbibition of liquid into the sample. Lab studies suggest that the two effects are equilibrating so that a front within the samples form until which the liquid rises. However, depending on the conditions, i.e. relative humidity, the immersion depth of the sample into the bulk electrolyte solution and the porosity-induced capillary forces, it is also possible that the evaporation leads to so called streaming currents. Thereby, the liquid imbibes into the whole sample so that it never fully dries.

During the measurements it was found, that SAXS measurements at one beam energy show a large dependence on the wetting state. Figure 3a shows a fully wetted sample where the relative humidity has been

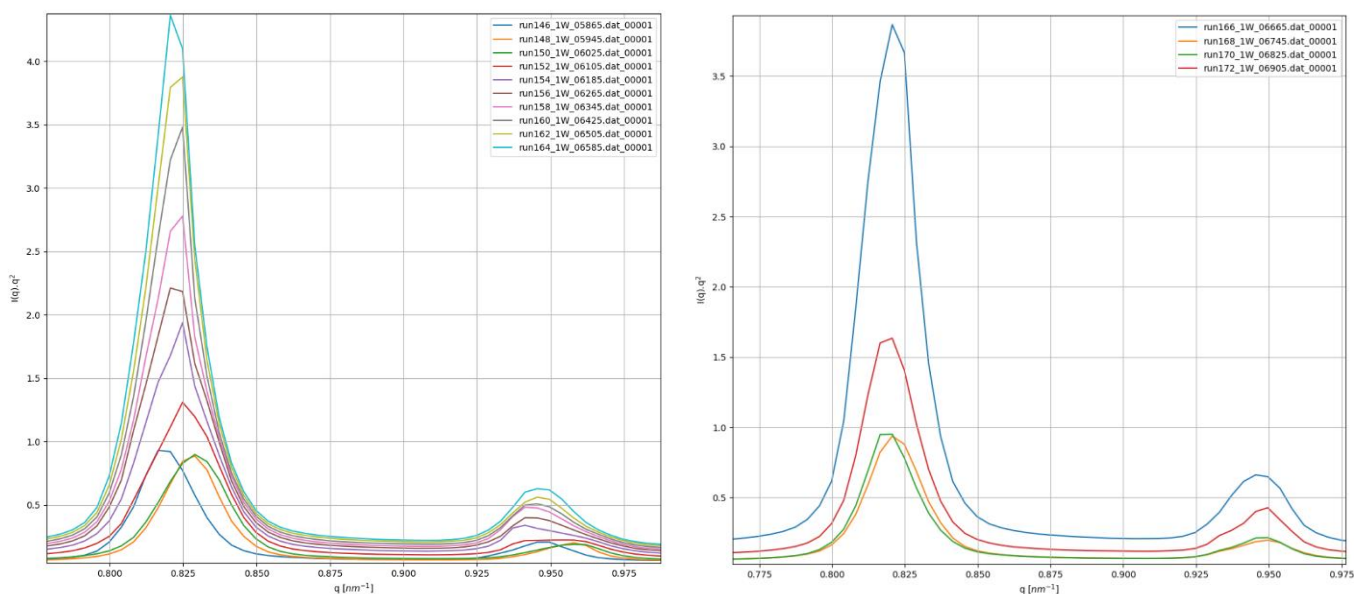


Figure 3: a) SAXS measurements during drying of nanoporous carbon with increasing peak intensity and b) during wetting of sample with decreasing peak intensity.

successively reduced to 65%. During the measurement the flow of charge is measured with a potentiostat. Hence, it can be determined how the anions are assembling on the surface. The consecutive SAXS measurements depicted in Figure 3a show that the peak position first shifts and then the intensity of both peaks significantly increases while it slightly shifts back. The electron density of the carbon material with respect to the pore filling, either the ambient atmosphere, when the porous material dries, or the electrolyte solution, changes the scattering and thus the peak intensity. When changing the humidity back to 100%, the trend is reversed, as displayed in Figure 3b. However, the last (red) curve is increasing again. This is likely caused by the crystallisation of ions in the pores.

Overall, the experiment could gather valuable information about the overall drying and wetting behavior. The support by beamline scientist Michael Sztucki was excellent. To improve the experiment an X-ray fluorescence detector would be helpful so that it is possible to determine the concentration of ions at the specific site of the sample in dependence of its overall wetting/drying state. Thus it can be determined if, for example, streaming currents lead to an accumulation of ions. Furthermore, parallel WAXS measurements could monitor if crystallisation occurs.

[1] Prehal, Christian, et al. "Quantification of ion confinement and desolvation in nanoporous carbon supercapacitors with modelling and in situ X-ray scattering." *Nature Energy* 2.3 (2017): 1-8.

[2] Haas, Sylvio, et al. "Analysis of nanostructure and nanochemistry by ASAXS: Accessing phase composition of oxyfluoride glass ceramics doped with Er ³⁺/Yb ³⁺." *Physical Review B* 81.18 (2010): 184207.

