

## Experimental Report SC-4491 ID02

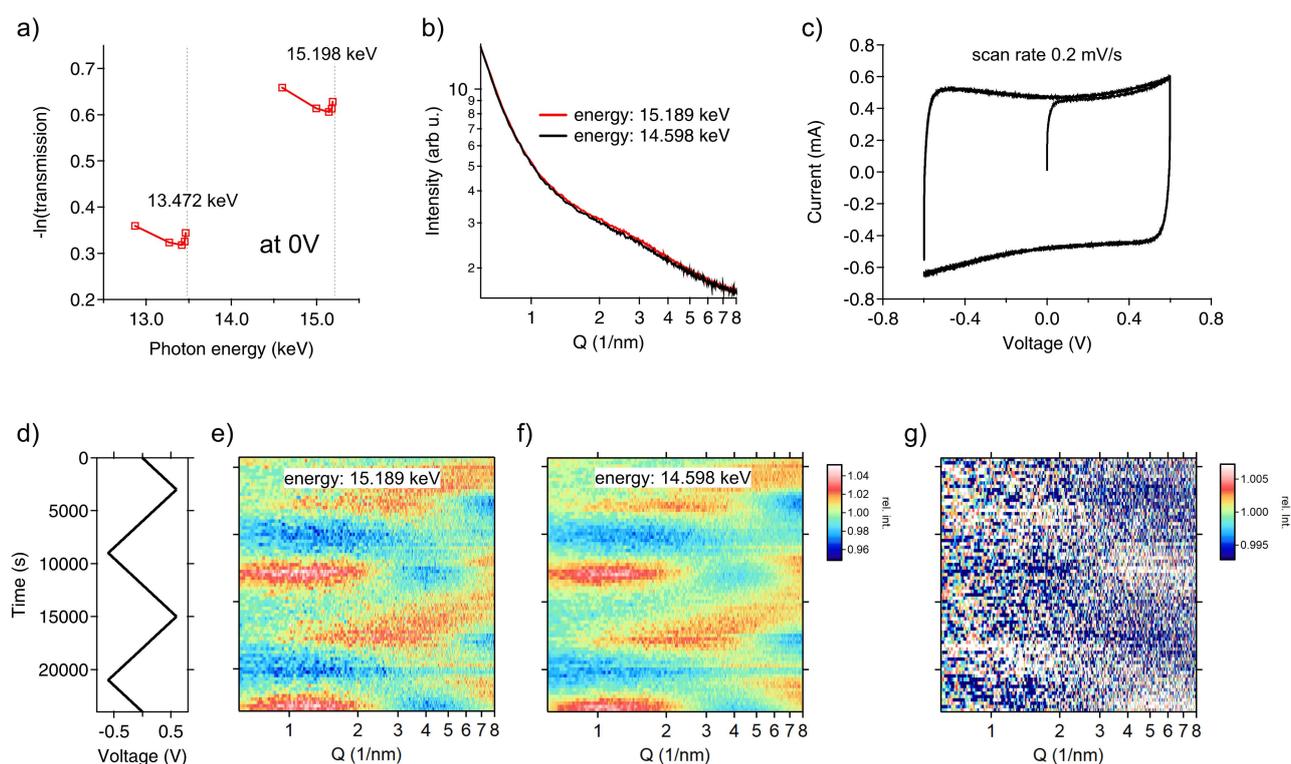
In situ SAXS is a suitable method to study concentration and structural changes of ions in nanoporous carbon supercapacitor electrodes during charging and discharging. In a recent work we developed a method combining atomistic Monte Carlo simulations with in situ scattering experiments to obtain structural details about ion confinement and partial desolvation as a function of the applied cell voltage.<sup>1</sup> Although important correlations between local ion rearrangement and the macroscopic performance of the supercapacitor cell could be retrieved, some important aspects of the multiphase system remained hidden. Therefore, we proposed to apply anomalous small angle X-ray scattering (ASAXS) as contrast variation approach, which would allow the separation of scattering contributions from cations and anions respectively. In addition, information about the voltage dependent change of the solvent structure and the electrosorption induced swelling of the carbon pore structure may also be deduced indirectly from such data.

For this reason we performed an in situ ASAXS experiment at ID02 during charging and discharging of a supercapacitor cell, using a disordered nanoporous activated carbon electrode and a 1M aqueous RbBr solution as electrolyte. Since the voltage dependent changes of the SAXS intensity are rather small (in the order of a few percent), and the expected ASAXS effects are in the same order of magnitude, the aim here was to fundamentally demonstrate the applicability of ASAXS in this pioneering proof-of-principle experiment. The particular cell design and in situ experimental setup were established in previous in situ SAXS experiments at ELETTRA.<sup>2</sup> Here, in addition, the X-ray energies were varied. The SAXS intensity was measured at five photon energies on the lower E-side of the absorption K-edges of both, Br and Rb (Fig. 1a) in a row, before starting with the next sequence of photon energies. In-between each sample measurement at a certain photon energy, the cell was moved out of the beam and a glassy carbon standard sample was measured. Measuring the sample plus glassy carbon at ten photon energies takes in total 300 s. At the same time the supercapacitor was charged and discharged applying slow Cyclic Voltammetry (CV) between  $\pm 0.6$  V and a scan rate of 0.2 mV/s (Fig. 1c, 1d), i.e. one period takes 12000 s. Besides time- and Q-dependent scattering intensity changes caused by ion electrosorption in the carbon nanopores, a small, yet clearly detectable dependence on the photon energy (anomalous effect) was observed (Fig. 1b).

A first data full data set could be measured for an activated carbon electrode having an average pore size of 0.9 nm and a surface area of 1707 m<sup>2</sup>/g. In Fig. 1a the negative logarithm of the transmission signal is given for the ten photon energies at zero applied cell voltage. The background and transmission corrected SAXS intensity as a function of the scattering vector length Q reveals a small, yet distinct anomalous effect at the hump around 2-3 nm<sup>-1</sup> (shown in Fig. 1b for two energies at the Rb edge). The position and shape of this hump is related to the structure of carbon nanopores filled with ions and water molecules. The in situ experiments were carried out as described previously.<sup>1-3</sup> The cyclic voltammogram (Fig. 1c) reveals pure electrical double-layer behavior, with negligible faradaic contributions. The relative SAXS intensity (i.e. the SAXS intensity normalized to the average SAXS intensity over the whole CV cycle, see “heat plots” in Fig. 1e-f) is changing as a function of time (or the cell voltage, Fig. 1d) and the scattering vector length Q. Both, local ion rearrangement into pore sites with different “degree of confinement” and global ion concentration changes are responsible for these voltage dependent intensity changes.<sup>1-3</sup> A simple

division of the  $E=14.598$  keV in situ SAXS data by the  $E=15.189$  keV data clearly shows the presence of time and voltage dependent anomalous effects (Fig. 1g). This result therefore confirms the principle ability of time dependent ASAXS to record (and separate) structural and concentration changes of two sorts of ions, independently from each other.

The detailed data analysis, including the separation of resonant and non-resonant scattering terms is currently under work. We expect, that the combination of such data with our recently developed data analysis tool<sup>1,3</sup> should allow a direct verification and detailed interpretation of the anomalous in situ SAXS signals towards a deeper understanding of ion electrosorption in complex nanopore networks.



Apart from measurements where the full ASAXS experiment was performed within a period of 300 s during continuous CV cycling, two entire cyclic voltammetry periods were measured at a constant photon energy, before switching to the next energy. This enabled higher time resolutions but requires a good stability of the in situ cell over the time of all ten cyclic voltammetry measurements (each CV measurement at a different photon energy).

## References:

- 1 Prehal, C. *et al.* Quantification of ion confinement and desolvation in nanoporous carbon supercapacitors with modelling and in situ X-ray scattering. *Nat. Energy* **2**, 16215 (2017).
- 2 Prehal, C. *et al.* Tracking the structural arrangement of ions in carbon supercapacitor nanopores using in situ small-angle X-ray scattering. *Energy Environ. Sci.* **8**, 1725-1735 (2015).
- 3 Prehal, C. *et al.* A carbon nanopore model to quantify structure and kinetics of ion electrosorption with in situ small angle X-ray scattering. *Phys. Chem. Chem. Phys.* **19**, 15549 (2017).