In our study, we investigate the electroless deposition of manganese oxide (MnO$_2$) on the backbone of a porous amorphous carbon (carbon xerogel). MnO$_2$ is known to increase the capacitance of electrochemical capacitors (also called “supercapacitors”) due to fast redox-reactions on the surface of the metal oxide [1, 2]. Deposition of the poorly conductive MnO$_2$ on the large inner surface area of carbon xerogels was aiming at providing a high surface area C-MnO$_2$ hybrid electrode [3]. By varying the carbon xerogel primary particle size and thereby the specific surface area of the carbon backbone, we were able to show that the MnO$_2$-deposition is likely to take place mainly on the envelope (external) surface area of the carbon skeleton [4]. To verify this hypothesis, we performed an ASAXS study on the C-MnO$_2$ composites.

To provide carbon xerogels with different particle sizes, we use the synthesis approach described in reference [5] to prepare suitable organic (resorcinol-formaldehyde) precursors. The precursors subsequently were pyrolized under argon atmosphere, yielding samples with small (S, about 20 nm), medium (M) and large (L, up to 5 µm) primary particles (see Figure 1). MnO$_2$ was introduced into the porous carbon using an infiltration process described in reference [3]; the amount of MnO$_2$ was varied via the duration of the deposition.

The ASAXS measurements were performed at the DORIS III beamline B1. The energy regime was chosen to be at the K$_\alpha$-edge of Mn. Four scattering curves at 6.461, 6.515, 6.536 and 6.544 keV
were measured (see Figure 2). In order to correct for a fluorescence background, a power law was fitted to the scattering curve measured at the lowest X-ray energy (considered free of background) in the q-range above 2 nm\(^{-1}\):

\[ I(q, E_1) = a \cdot q^b . \]  

(1)

The fit yields for the parameter \( b \) a value of -2.1. The other scattering curves then were fitted to yield the same power law, allowing for an additional constant background \( b_{g_i} \):

\[ I(q, E_i) = c \cdot q^b + b_{g_i}, \quad i = 2, 3, 4. \]  

(2)

Figure 3 a) shows the influence of the MnO\(_2\)-coating on a sample with large primary particles: The so-called “micropore shoulder” around 3 nm\(^{-1}\) in the SAXS scattering of the pure carbon xerogel (Carbon L) is superimposed by the scattering originating in the additional MnO\(_2\)-phase (see Hybrid L). With MnO\(_2\) present, a kink around 0.3 nm\(^{-1}\) appears. The red curve in Figure 3 a) shows \( \Delta I(E_1, E_2) \) for the C/MnO\(_2\) composite. A direct comparison (Figure 3 b)) of \( \Delta I(E_1, E_2) \) for the sample with small (C/MnO\(_2\) S) and large (C/MnO\(_2\) L) particles, respectively, both containing about 32 wt.% MnO\(_2\), reveals that the kink shifts with increasing particle size to higher q-values and therefore smaller MnO\(_2\) layer thickness. Currently, evaluation of the SAXS data by applying a hollow-sphere model to the data is under way.

Figure 3: Left: Normalized SAXS-scattering curves for a pure carbon xerogel with large particles and carbon-MnO\(_2\) hybrid and \( \Delta I(E_1, E_2) \) for the hybrid sample. Right: \( \Delta I(E_1, E_2) \) for samples with small and large particles containing about 32 wt% MnO\(_2\).

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References