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SAXS on Glassy Carbon with Variable Scattering Contrast

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Introduction

Small Angle X-ray Scattering (SAXS) and adsorption measurements like the Brunauer-Emmett-Teller method (BET) are complementary tools to study such properties of porous materials as void fraction and internal surface area. With SAXS, all inhomogenities can be detected, while BET is sensitive to open pores only.

Information on the scattering contrast is necessary for the quantitative analysis of the SAXS data [1].

Glassy Carbon (GC) is often utilized as a reference material in Small Angle X-ray and Neutron Scattering. In our project, GC is also used as an electrode material for Electrochemical Double Layer Capacitors (EDLC) [2,3].

GC contains closed pores, which can be opened by thermal oxidation [4].

However, during oxidation, the GC undergoes structural changes [5] that affect the skeleton density and thus the scattering contrast of GC.

For the characterization of GC electrodes for EDLC, we take this effect into account.

Experimental

Thin GC sheet samples were thermally oxidized at 450°C for various times to provide samples of different film thickness having open pores. Thicknesses were determined (Fig. 1) with Scanning Electron Microscopy (SEM). The scattering contrast (Fig. 2) of oxidized GC was investigated with X-ray Diffraction (XRD). The internal surface area was determined using SAXS (Porod-plot) and BET nitrogen adsorption isotherms (Fig. 3).

Particular problem: Separating the bulk and film contributions.

Solution: Linear approximation of the scattered intensity I_{SAXS} of the sample (thickness $D \approx 55$ µm) and of the film (thickness $d \approx 16$ µm), because the absorption µ is small

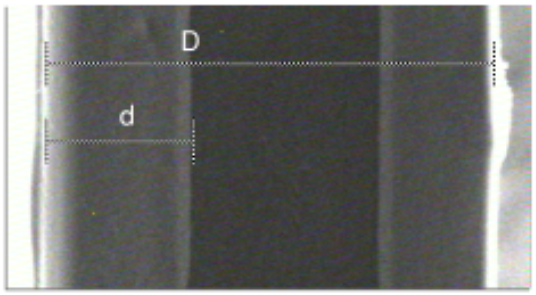

Fig. 1: SEM micrograph of an oxidized GC sample. The film (gray) on the left and right side envelopes the bulk GC (black).

Results

Depending on oxidation time, the (002)-peak of the GC samples shift to larger diffraction angles (Fig. 2), indicating that graphene sheets in GC move closer to each other, which can be explained by the recently proposed *falling cards model* for hard carbons [6]. Thus the x-ray density ρ_X, which is in principal the scattering contrast $\Delta\eta_f$, increases with activation time:

- ρ_X of non activated GC 2.11 g/cm³
- ρ_X of 3 hrs. activated GC 2.21 g/cm³
- ρ_X of graphite 2.26 g/cm³ (Reference value)

The increase of ρ_X is approximately linear with oxidation time and causes an overestimation of internal surface area of about 10% after 3 hours, if it is not

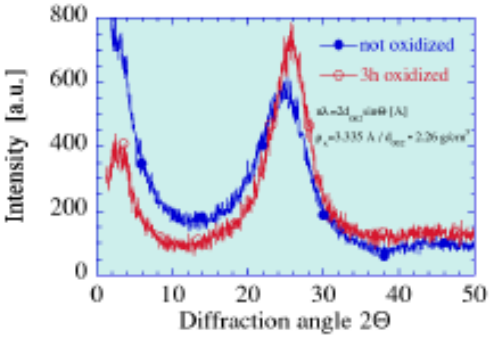

Fig. 2: Shift of XRD (002)-peaks of GC samples during oxidation.

For oxidation times between 30 and 180 minutes (Fig. 3), the SAXS surface area decreases linear from 1800 to 1170 m²/cm³.

However, after correction for the scattering contrast, the final value after 3h oxidation yields 1070 m²/cm³.

As a preliminary and qualitative reference, the BET surface area is displayed in the plot as well. Some differences between surface areas as characterized by SAXS and BET are not unexpected because of differences in the quantities characterized in these two different methods.

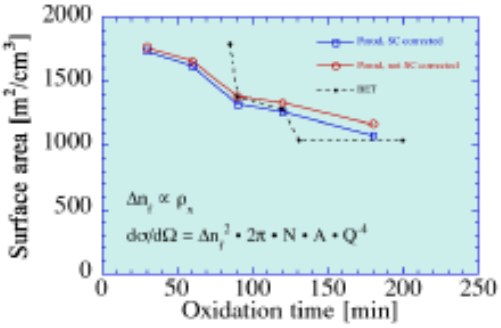

Fig. 3: Internal surface area of GC as obtained from SAXS and BET.

Conclusions

In the system under investigation, we found a change of the x-ray scattering contrast during oxidation of around 10%. Thus, for a very accurate quantitative analysis of SAXS data (pore volume, surface area), the precise determination of the scattering contrast is indispensable.

Particular attention must be paid when structural changes occur in the sample and alter the scattering contrast.

Acknowledgment

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References

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