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Correlating pore size and shape to local disorder in microporous carbon: A combined small angle neutron and X-ray scattering study

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ABSTRACT

We present a model free analysis of the structure of a microporous carbon (Kynol fiber cloth) with neutrons (SANS) and X-rays (SAXS). SANS with contrast matching is used to analyze the accessible pores. It is shown that the SAXS- and the SANS-intensities agree after correction of the SANS specific background. Moreover, we analyze the scattering contribution due to the finite size and the bending of the carbon sheets. This contribution that scales with q^{-2} at high q-values (q: magnitude of scattering vector) is subtracted and the remaining intensity that exhibits a q^{-4} final slope gives the specific inner surface (1090 m^2/g) and the porosity (29%) with excellent precision. The spatial distribution of the pores is analyzed in terms of the chord length distribution $g(r)$. This distribution has its maximum below 1 nm and a finite intercept $g(0)$ that indicates pores with sharp edges. The analysis gives furthermore the number and weight-average chord length. Finally, a parameter characterizing the degree of disorder of the carbonaceous structure introduced by Ruland was determined. Its value (25%) indicates a rather disordered structure that is visualized in terms of a detailed model. The entire analysis shows the power of small-angle scattering for a detailed analysis of microporous structures.

1. Introduction

Porous carbon materials have found widespread applications in electrochemical systems as e.g. as electrodes for supercapacitors [1–5] and lithium-sulfur batteries [6–9]. Here the good conductivity of these materials and their enormous internal surface, mainly originating from the micropores are used to drive electrochemical reactions in aqueous or organic media. Evidently, a comprehensive characterization of the pores and their surface is central for the understanding and the design of these materials. In particular, only pores that are accessible for a given solvent provide an electrochemically active surface and a meaningful characterization of carbonaceous materials must put special emphasis on this question.

Small angle scattering (SAS) as small angle neutron scattering (SANS) and small angle X-ray scattering (SAXS) have been used intensively for characterization of porous carbons [1,3,4,10–17]. In particular, SANS has become a much applied method inasmuch as suitable deuterated liquids can match the scattering length density of carbon to a great extent. Hence, pores filled by such a liquid become virtually invisible for SANS. Moreover, a partial filling by controlling the vapor pressure of the liquid can discern between pores of different size [18]. Hence, SANS has become the main method to determine the accessibility of pores by solvents as e.g. D_2O or deuterated organic solvents [1,4,11,18–24]. The resolution of SANS, however, is limited by the incoherent background which originates from hydrogen atoms in the solvent or in the material. Thus, an analysis of the structure of micropores which contribute mainly at high scattering angles to the measured intensity may be hampered by these incoherent contributions. SAXS, on the other hand, has a much higher resolution due to the absence of incoherent scattering and thus allows us to obtain measurements up to the highest scattering angles. Matching of the scattering length density of carbon, however, is only achieved with special materials as e.g. sulfur. Thus, SAXS has recently been used to study the impregnation of porous carbons by sulfur [8,25]. Evidently, the combination of both SANS and SAXS would be very helpful to arrive

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at a full characterization of porous carbon materials. To the authors' best knowledge, this combination has only been applied to carbonaceous materials by Hoinkis and coworkers so far [21].

Here we use SANS together with SAXS to analyze an activated carbon fiber cloth purchased from Kynol®. This material has been chosen because of its widespread use in electrochemical storage applications [1,4,5,26]. The present study aims at a full evaluation of scattering data up to the highest scattering angles possible. In order to achieve this goal, we pay special attention to the scattering contribution originating from the imperfections inside the carbon layers due to finite size and bending of the carbon sheets. In a series of pioneering papers, Ruland and coworkers have been the first to point out that this feature is inherent to carbon materials [27–31] and leads an additional contribution to the measured intensity that decays with q^{-2} (q: magnitude of scattering vector). Together with the characteristic q^{-4}-Porod-term this term may lead to a decay of the total scattering intensity as q^{-3}. However, an interpretation in terms of a fractal structure would be erroneous in this case [30]. Recent modelling results corroborates that porous carbon materials exhibit slit-like pores made of wrinkled carbon layers that illustrate this feature discerned by Ruland many decades ago [32–36]. With proper subtraction of the scattering contribution that is due to this correlation, the analysis leads to an accurate value of the total accessible surface of all pores.

As in our previous work [8,18] we analyze the size and the shape of the pores in terms of the chord length distribution [37] which proceeds without prior assumptions. Moreover, this analysis allows us to see whether pores have a sharp or a round edge. The presented analytical technique is not restricted to any particular microporous carbon but can also be used for carbide derived carbons [38], carbons made from organic material (coconut shell) [39] or synthesized by hard-templating [8].

2. Experimental

The carbon cloth-like material made from activated fibers is sourced from Kynol® with commercial number ACN-157-15. The SEM micrograph in Fig. 1a shows the felt like structure of the material by randomly intertwined carbon fibers. This isotropic structure ensures that the small angle scattering experiments probe all fiber orientations equally. The information from the supplier related to the material is the following: (i) 100% carbon fiber content, (ii) areal density of 90 g/m^2, (iii) specific surface area of 1500 m^2/g and (iv) a tensile strength of 0.3 kg/50 mm. For all SANS measurements a circular piece, with a diameter of 1.2 cm giving a geometrical area of 1.131 cm^2, was cut from the of ACN cloth with an approximate thickness of 1 mm.

The skeletal density ρ_{Sk} of the ACN material was determined by helium pycnometry using a Micro-Ultrapyc 1200e (Quantachrome) to be 2.0 ± 0.1 g/cm^3. Nitrogen physisorption isotherms were recorded on a Quantachrome Autosorb-1MP (see Fig. S1). The specific surface area was determined using the Brunauer-Emmett-Teller (BET) model giving a value of 1522 m^2/g. However, it is known that the BET evaluation method may yield too large values for the specific surface of microporous carbons [40]. The quenched solid density functional theory (QSDFT) method [41] was used for the calculation of pore size distribution as shown in Fig. 1b. The pore size distribution shows that the majority of pores is smaller than 1nm indicating a purely microporous carbon.

2.1. SANS

SANS measurements were performed at the small angle scattering instruments V4 and V16 of which both are placed in the cold neutron guide of Helmholtz-Zentrum Berlin (HZB). The magnitude of the scattering vector is defined as $q = (4\pi/\lambda)(\sin\theta)$ with λ being the wavelength and 2θ the scattering angle.

The ACN carbon was placed in a quartz cuvette with an inner spacing of 0.1 cm and placed in the beam for measurement. A Cd aperture of 1 cm was used. The 2D scattering data was reduced to a scattering curve ($\frac{d\Sigma}{d\Omega}(q)$ vs. q) by means of the BerSANS software. The raw data is then corrected for transmission, the quartz cell background scattering subtracted and converted to absolute units i.e. cm^{-1} taking into account the scattering from water [42].

V4: The measured neutron flux is ~10^6 cm^{-2}s^{-1} for the two wavelengths used, λ = 4.5 Å and 6.0 Å [43]. The scattering data was obtained at two sample detector distances (SDs) of 1.0 m and 4.0 m, which yielded a total momentum transfer range of 0.1 nm^{-1} < q < 7 nm^{-1}. The shorter wavelength of 4.5 Å was used during the 1.0 m SD measurement in order to extend the q-range. Further information regarding the V4 instrument and its resolution the reader is referred to references [43,44].

V16: The measured neutron flux is ~10^6 cm^{-2}s^{-1}. The scattering data was obtained at SDs of 1.7 m and 6.2 m, which yielded a total momentum transfer range of 0.1 nm^{-1} < q < 7 nm^{-1}. Further information regarding the V16 instrument and its resolution the reader is referred to reference [45].

Both the V16 and the V4-instrument lead to identical scattering curves within the momentum transfer region of 0.1 < q < 7 nm^{-1}. Fig. S2 shows that the two scattering curves $I(q)$ vs. q measured for a

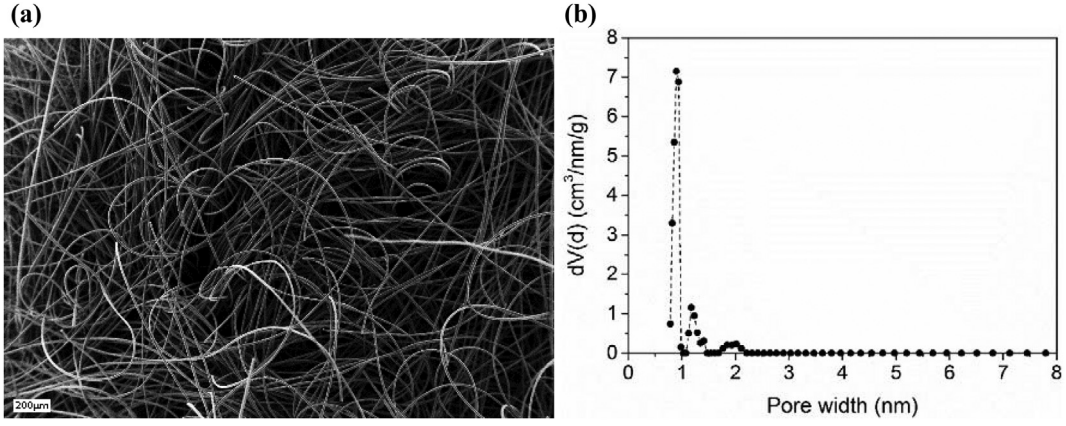

Fig. 1. (a) The SEM image showing the carbon fibers of the ACN-157-15. The scale bar represents 200 µm. The diameter of the individual fibers are approx. 8 µm. (b) Pore size distribution derived from the physisorption isotherm by DFT calculations.