

Deformation of porous carbons upon adsorption

C. Balzer and G. Reichenauer

Bavarian Center for Applied Energy Research, Division: Functional Materials for Energy Technology,
Am Hubland, 97074 Würzburg, Germany

The ad- and desorption of gas molecules on the surface of a porous solid is always connected to a macroscopic deformation of the solid. For the majority of porous solids the change of relative volume in the process of adsorption is below 1% and therefore mostly neglected both in practical applications as well as in theoretical considerations. Nevertheless, sorption-induced deformation can provide valuable additional information about the sample under study when measured with sufficient accuracy.

Figure 1 shows the results of dilatometric measurements performed in the course of nitrogen adsorption at 77 K for three porous synthetic carbons [1]. All samples were synthesized via a sol-gel process applying different synthesis parameters to provide pure carbons with different pore size distributions accessible to nitrogen: one sample exhibiting micropores (pore size below 2 nm) only, one sample exhibiting mesopores (pore size between 2 and 50 nm) only and one sample exhibiting both types of pores. The different stages of ad- and desorption visible within the sorption isotherms in Figure 1 are connected to different deformation characteristics. Each of these stages provides information about the material on a different length scale: micropore filling and deformation for relative pressures below 0.01, capillary condensation within the mesopores for high relative pressures (above 0.7 in case of the carbons investigated) and adsorption on the external surface in between.

For quantitative analysis of the length change isotherms a comprehensive knowledge of the sample material is necessary. Regarding density information SAXS-measurements provide more reliable results than sorption measurement since sorption measurements are limited to accessible porosity with pore sizes below about 100 nm and therefore may not be able to detect the complete pore volume. Therefore all samples were measured at the beamline B1 of HASYLAB in two detector-sample distances at an energy of the incident beam of 12 keV. The scattering curves are shown in Figure 2. They are given by the superposition of the scattering due to the microporous carbon skeleton and the scattering from the micropores within the backbone (shoulder at large q -values). From these data either the invariant Q_{sb} of the microporous backbone (red and blue curve) or the invariant Q_{pp} of a single primary particle (in case of the black curve) was calculated using the two-phase-model [2]. With the invariant the density ρ_s of the backbone was determined either by assuming a density of the nonporous carbon phase ρ_c of 2,2 g/cm³ or by using the macroscopic density of the porous carbon monolith ρ_m :

$$\rho_s = \rho_c - \frac{Q_{pp}}{2\pi^2 C^2}, \quad \text{or} \quad \rho_s = \rho_m + \frac{Q_{sb}}{2\pi^2 C^2},$$

with $C = 8,504 \cdot 10^{11}$ m/kg.

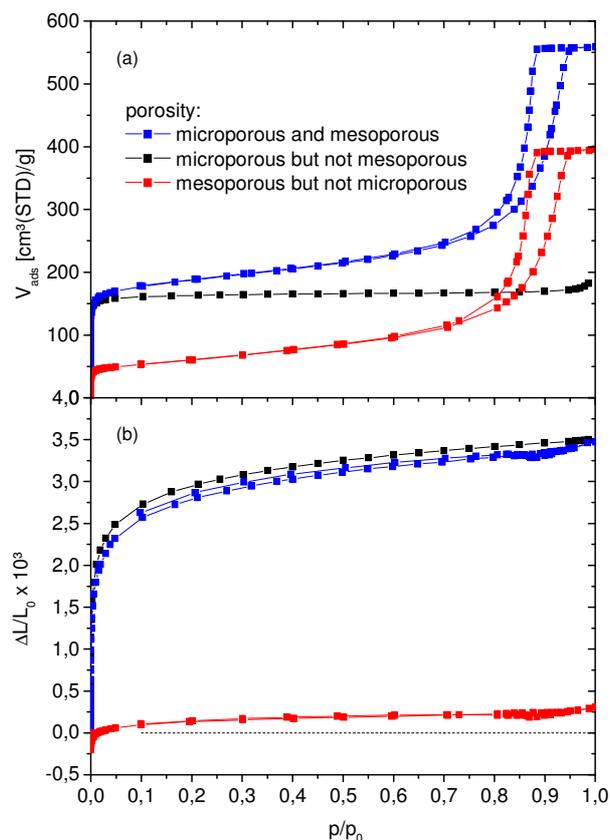


Figure 1: Nitrogen sorption isotherms taken at 77 K (a) for synthetic carbons with different pore size distributions and corresponding length change isotherms (b).

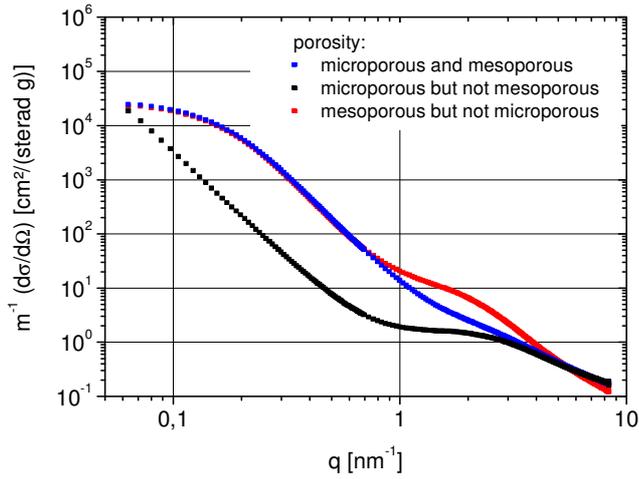


Figure 2: Scattering curves for the three synthetic carbons with different pore size distributions.

identical for both samples, while the porosity on length scale larger than the micropores is significantly different. The sample “without micropores” on the other hand yields an about twice as large value for E_S compared to the two “microporous” carbons although the density of the solid backbone is identical within the error bars for all samples. A more detailed analysis of the sorption and scattering data reveals that the sample “without micropores” actually contains micropores that are, however, not accessible to the probing gas upon sorption analysis. This explains the almost identical backbone density (Table 1). We assume that the high value of the backbone’s Young’s modulus for the “non microporous” sample is a consequence of the high temperature treatment the sample was subjected to. The treatment is known to result in a growth of the microcrystallites that form the microporous carbon backbone [5].

Table 1: Density ρ_S of the solid backbone (determined from SAXS), Young’s modulus E_S of the solid backbone (from dilatometry and SAXS) as well as macroscopic density ρ_m and Young’s modulus E_m (from sound velocity measurements) for all samples investigated.

sample	ρ_S [g/cm ³]	E_S [GPa]	ρ_m [g/cm ³]	E_m [GPa]
■ microporous and mesoporous	1.34	14.8	0,729	6.70
■ microporous but not mesoporous	1.28	13.6	0,288	0.084
■ mesoporous but not microporous	1.31	28.3	0,757	7.24

Acknowledgment

The authors would like to acknowledge the support of Dr. Ulla Vainio at the beamline B1 (JUSIFA) at the German synchrotron in Hamburg, Germany, and the assistance in evaluating the SAXS data by Dr. Christian Scherdel at the Bavarian Center for Applied Energy Research in Würzburg, Germany.

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With the density of the solid backbone ρ_S and the experimentally detected deformation the Young’s modulus of the solid backbone E_S can be determined using the theoretical models of Bangham [3] and Scherer [4]. Table 1 shows the density ρ_S and the Young’s modulus E_S of the solid backbone together with the macroscopic density and Young’s modulus E_m of the respective sample calculated from sound velocity measurements.

The results in Table 1 reveal that the mechanical properties on the macroscopic and microscopic scale are not directly connected. While the microporous samples largely differ in macroscopic Young’s moduli their solid backbones are very similar concerning mechanical properties. This was expected since the structure of the solid backbone is