

Pore Narrowing in Activated Carbon

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Introduction

Glassy carbon (GC) is a material with a very high specific surface area but inherently closed pores. The pores can be opened by an oxidation process (*activation*) so that the high internal surface area becomes accessible to liquids or gases. Recently, numerous fundamental and applied studies [1-9] have been made on the thermochemical gas-phase activation of GC, because such GC can be used as an electrode material for electrochemical double-layer capacitors (*supercapacitors*). We now demonstrate how the previously opened pores in activated GC can be narrowed or closed by post-treatment. The narrowing of the pores was monitored *ex situ* by using small-angle x-ray scattering (SAXS).

Methods and Materials

GC plates with a nominal thickness of 60- μm were thermochemically activated in a muffle furnace at 450°C for 1.5 and 3.5 h by using air as an oxidant. Some of the activated samples were then soaked with an organic solution (methanol) and laid on a hot plate for 30 s (*post-treatment*). The surface of the hot plate had a temperature of approximately 400°C. Those samples were subject to anomalous SAXS (ASAXS) at Beamline 12-ID at BESSRC-CAT. Scattering curves (SCs) at a photon energy of 6600 eV were recorded for scattering vectors ranging from 0.001 1/Å to 0.25 Å⁻¹.

Results

For the reader's better understanding of the present work and its motivation, we have to recall previously published results on GC activation. During oxidation, an active film with open pores is built on the surface of the GC, while the GC sample itself shrinks in thickness because of burn-off. After 1.5 h of activation, the total sample thickness is 50 μm , and the film thickness on each side is 10 μm . During activation, the interface between the active film and nonactivated core propagates into the sample interior until the interfaces from opposite sample faces meet and no nonactivated core is left. This stage is reached after 3.5 h of activation, with a total sample (*film*) thickness of 30 μm only.

Figure 1 displays the SC of nonactivated and activated GC. The nonactivated sample has the overall lowest scattering intensity. The enhanced scattered intensity of the two activated samples is indicative of the presence of a wide and extended pore network in GC. In particular, the activation creates two remarkable structural features (humps) in the range of $Q = 0.01$ 1/Å and $Q = 0.08$ 1/Å.

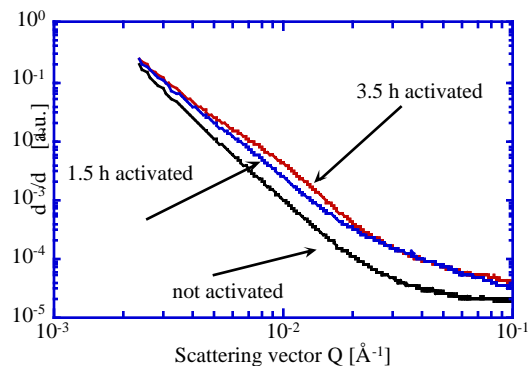


FIG. 1. SCs of nonactivated/activated GC.

Although considerably thinner, the activated samples are stronger scatterers than the nonactivated sample. Note that the sample activated for 1.5 h consists of an active film, which can be soaked with the organic liquid, and a nonactive bulk part, which is not accessible to the organic liquid [1].

Figure 2 displays the SC of the samples that were activated for 3.5 h and subsequently post-treated for pore closing. The SC of the nonactivated sample is shown for reference (black, lower curve). It is evident that the structural feature at $Q = 0.01$ Å⁻¹ of activated GC (green, upper curve) vanishes when the sample is post-treated (red, between other SC). However, further inspection of the SCs reveals that the intensity of the red SC is slightly higher, at $Q = 0.05$ 1/Å, than that of the green SC.

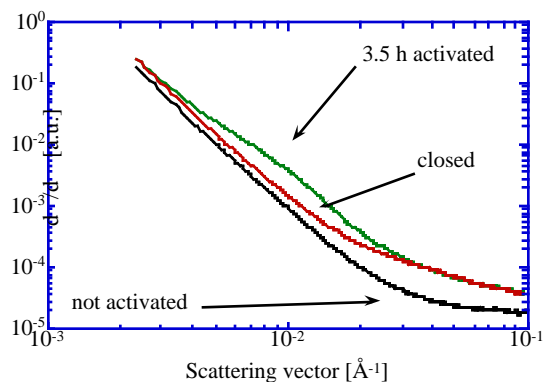


FIG. 2. SCs of nonactivated (black), activated (green), and closed (red) GC.

Figure 3 shows the SC of a similar couple of samples that were activated for only 1.5 h. The behavior of vanishing features upon post-treatment is recovered at the same Q value but to a lesser extent, because the active film thickness is smaller for 1.5 h of activation than for 3.5 h of activation. Also, the increase of intensity at $Q = 0.05 \text{ 1/\AA}$ is recovered for the post-treated sample.

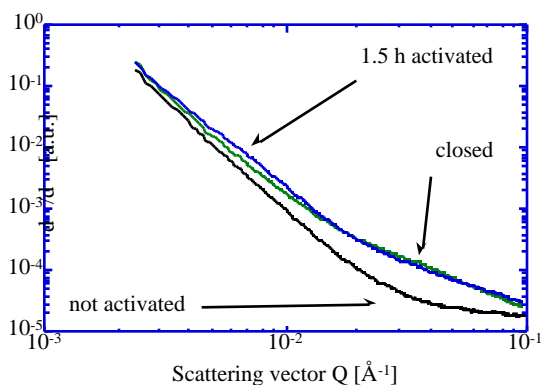


FIG. 3. SCs of nonactivated (black), activated (blue), and closed (green) GC.

Discussion

The curvature of the SC of activated GC reflects the presence of the closed and opened pores and the entire pore network. Nonactivated GC is known to have an at least bi-model pore size distribution, while activated GC has even more complex SCs. The humps at 0.01 1/\AA are caused by the activation and account for pores that connect the micropores, which finally are responsible for the huge internal surface area. When those activated GC samples are soaked with methanol and then heated on a hot plate, a possible scenario is that the methanol gets pyrolyzed and the inner pore walls get coated with carbon, which leads to a narrowing of the pore channels. Consequently, the signatures of those structures with a particular length of scale vanish. On the other hand, new structures of smaller-length scales are being created, and those appear in the SCs at larger Q values. Simply stated, the narrowing of pore diameters appears as a shift of humps in the SCs from smaller Q values toward larger Q values. Exactly the same thing happens in the reverse direction, when pores are being opened and enlarged as a result of the activation.

Acknowledgments

We are grateful to Dr. B. Schnyder (Paul Scherrer Institut, Villigen, Switzerland), who provided us with GC. This work was supported by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences (BES), under Contract No. W-31-109-ENG-38. Use of the APS was also supported by the DOE BES under Contract No. W-31-109-ENG-38 and by BESSRC-CAT.

References

- [1] A. Braun, M. Bärtsch, B. Schnyder, R. Kötz, O. Haas, H.-G. Haubold, and G. Goerigk, *J. Non-Cryst. Solids* **260**(1-2), 1-14 (1999).
- [2] A. Braun, B. Schnyder, M. Bärtsch, and R. Kötz, *Chem. Eng. Sci.* **55/22**, 5273-5282 (2000).
- [3] A. Braun, M. Bärtsch, B. Schnyder, R. Kötz, and A. Wokaun, *Carbon* **40**(3), 375-382 (2002).
- [4] A. Braun et al., *Mat. Res. Soc. Symp. Proc.* **575**, 369 (2000).
- [5] M. Bärtsch, A. Braun, B. Schnyder, R. Kötz, and O. Haas, *J. New Mat. Electrochem. Sys.* **2**, 273-277 (1999).
- [6] A. Braun, PhD thesis 13292, ETH Zürich (1999).
- [7] W. Gille and, A. Braun, "SAXS chord length distribution analysis and porosity estimation of activated and non-activated glassy carbon," *J. Non-Cryst. Solids* (under review).
- [8] A. Braun, M. Bärtsch, O. Merlo, B. Schaffner, B. Schnyder, R. Kötz, O. Haas, and A. Wokaun, "Evolution of electrochemical double layer capacitance in glassy carbon during thermal oxidation — crossover from exponential to logistic growth," *Carbon* (under review).
- [9] A. Braun, A. Wokaun, and H.-G. Hermanns, "Analytical solution to a growth problem with two moving boundaries," *Appl. Math. Model.* (in press).