Available online at www.sciencedirect.com
SCIENCE DIRECT
Journal of Physics and Chemistry of Solids 67 (2006) 1106–1110
JOURNAL OF PHYSICS AND CHEMISTRY OF SOLIDS
www.elsevier.com/locate/jpcs

Hydration behavior and dynamics of water molecules in graphite oxide

A. Lerf [a,*], A. Buchsteiner [b], J. Pieper [b], S. Schöttl [c], I. Dekany [d], T. Szabo [d], H.P. Boehm [e]

[a] Walther-Meissner-Institut der Bayerischen Akademie der Wissenschaften, Walther-Meissner-Strasse 8, D-85748 Garching, Germany
[b] Hahn-Meitner-Institut, Glienicker Straße 100, D-14109 Berlin, Germany
[c] National Physical Laboratory, Teddington, Middlesex TW11 0LW, UK
[d] Department of Colloid Chemistry and Nanostructured Materials Research Group of the Hungarian Academy of Sciences, University of Szeged, Aradi v.t. 1, H-6720 Szeged, Hungary
[e] Institut für Anorganische Chemie der Ludwig-Maximilians-Universität, Butenandtstraße 5-13, D-81377 München-Großhadern, Germany

Abstract

In contrast to graphite intercalation compounds, graphite oxide (GO) is hydrophilic. However, the information about the mobility of the water molecules is still sparse. We show in this report that the degree of hydration and the kinetics of water uptake depend crucially on the preparation and aging conditions. The best sample we have ever got shows layer distances of 8, 9 and 11.5 Å at relative humidities of 45, 75 and 100%, respectively. With time-of-flight (TOF) neutron scattering (V3/NEAT spectrometer) diffusion processes for rotation and translation have been investigated in the temperature range 220–320 K with an energy resolution of 93 μeV. Quasi-elastic scattering was observed for all temperatures. Three types of motion can be sorted out. The first one is a translational motion of water molecules in pores between the GO particles for samples equilibrated at 100% relative humidity. Samples equilibrated at 45 and 75% relative humidity do not show this type of water. They exhibit two types of localized motions with different activation energies. We try to assign one type of these motions to confined water molecules encapsulated in the interlayer space between the functional groups attached to the carbon grid.

Keywords: A. Non-crystalline materials; C. Neutron scattering; C. X-ray diffraction; D. Lattice dynamics

1. Introduction

Graphite oxide (GO) has been known since the 19th century [1]. Recent interest grew due to proposed application as material for battery electrodes [2–4] or membrane models [5–7]. Depending on the conditions of oxidation, GO may contain variable amounts of oxygen. Because of the highly disordered state of GO, diffraction methods were of very restricted help in deciding which model is correct [8]. Solid-state NMR has ruled out models involving carboxyl groups in the bulk of the sample [9], and suggested a carbon grid with 1,3-ether and OH functions. However, the peak at 60 ppm assigned to 1,3-ethers by Mermoux is found only in 1,2-ethers [10]. As the presence of epoxide bonds cannot be established by NMR examination of GO alone, we have subjected GO to a variety of chemical modifications and studied the products using ^{13}C and ^{1}H NMR [11,12]. The ^{13}C spectra confirm the assignment of the 70 ppm line to C–OH groups and led us to a new structural model, which assigns the 60 ppm line to epoxide groups (1,2-ethers), and the 130 ppm line to aromatic entities and conjugated double bonds. GO contains aromatic regions with unoxidized benzene rings and regions with aliphatic 6-membered rings.

In contrast to graphite intercalation compounds, GO is hydrophilic. It is very hard to remove the water completely out of the sample [8,13]. Thus layer distances between 5.9 and 6.7 Å have been reported for the dry samples [8]. For the fully hydrated sample values up to 12 Å can be found in literature [8,13–16]. In slightly basic solutions, the GO can swell to infinity forming a colloidal solution [13,14]. The most thorough study of water uptake from the gas phase has been carried out by de Boer and van Doorn [15]. However, the information about the mobility of the water molecules is sparse. In order to get the information about the water dynamics, we carried out quasi-elastic neutron scattering experiments. In preparing the samples for these studies, we found to our surprise that the degree of hydration and the kinetics of water uptake depend crucially on the preparation and aging conditions. Thus, we report first on the new (XRD) results on the hydration behavior of GO, and then in the second part on our findings with respect to water dynamics.

* Corresponding author. Tel.: +49 89 289 14225; fax: +49 89 289 14206.
E-mail address: anton.lerf@wmi.badw.de (A. Lerf).

0022-3697/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jpcs.2006.01.031

2. Experimental

2.1. Hydration experiments

Four substances have been studied concerning their hydration behavior. Two of them have been prepared by the method of Staudenmaier in Boehm's working group (samples 'schmid&boehm' and 'wagner&boehm') in the 1960s. The other two samples have been prepared in Szeged by the Brodie method (samples 'imre' and 'imre2'; the preparation methods are discussed comparatively in Ref. [17]).

To adjust the hydration level and to get a homogeneous water distribution, the samples were first saturated with water and then they were stored in humid environments generated by saturated salt solutions: NaCl for 75% and K_2CO_3 for 44% relative humidity. The highest hydration level was reached by using pure water resulting in a relative humidity of 100%. The 10% humidity level was reached by using the GO as provided by the preparation process. As the hydration process depends strongly on the purity of the materials, we used Millipore water for preparing the salt solutions. In case of the in- situ XRD study, a small vessel with water was placed in the sample chamber of the spectrometer near to the sample.

The layer expansion due to the change of hydration level has been measured with XRD on powder samples (AXS-Brucker D8 Advance diffractometer) using Ni-filtered Cu-Kα radiation. This investigation was also performed in dependence on time, thus to determine the necessary equilibration times for the samples. In some cases, the dehydration was followed by in-situ XRD in normal laboratory atmosphere.

2.2. Quasi-elastic neutron scattering experiments

The motions of the water molecules and the functional groups of the GO were investigated by means of quasi-elastic neutron scattering. These measurements were done at the time-of-flight spectrometer NEAT at the Hahn-Meitner-Institut in Berlin [18].

The samples with different humidities were enclosed in slab-shaped aluminium sample containers. The experimental resolution (FWHM of the resolution function) was 93 μeV ($\lambda =$ 5.1 Å). The measured raw data were corrected for the contribution of the empty container and the different detector efficiencies.

A standard vanadium slab of 1 mm thickness was measured to determine the experimental resolution function, which is an almost perfect Gaussian function for NEAT at reasonable resolution values. To get a good statistics the data were grouped into 10 angular groups before the transformation to the energy scale was done. As the transmission values of the samples were relatively large with $T > 0.9$ (except the samples with highest humidity), it was not necessary to correct the data for multiple scattering. All corrections and data fits were done with the program package FITMO [19], which provides standard routines for the data treatment and fitting.

For the investigation of the temperature dependencies, the temperature was varied in the range between 220 and 320 K, which should cover the most interesting region where possible freezing and melting processes of the water take place.

2.3. Quasi-elastic neutron scattering experiments: basic principles

We restrict ourselves to the discussion of incoherent scattering as protons scatter mainly incoherently and we can neglect the small coherent contributions. The incoherent double-differential cross-section

$$\frac{\delta^2\sigma}{\delta\Omega\delta\omega} = \frac{1}{4\pi}\frac{\vec{k}_\mathrm{f}}{\vec{k}_\mathrm{i}}\left[b_\mathrm{inc}^2 \cdot S_\mathrm{inc}(\vec{Q},\omega)\right] \tag{1}$$

describes the number of neutrons scattered into a certain angle element $\delta\Omega$ and energy transfer element $\delta\omega$, where $\vec{k}_i$ and $\vec{k}_f$ are the wave vectors of the incident and scattered neutrons, respectively, $\vec{Q} = \vec{k}_\mathrm{i} - \vec{k}_\mathrm{f}$ is the momentum transfer, and b_inc the incoherent scattering length.

Using the Van Hove formalism [20], the incoherent scattering function gives information about the dynamics of individual (hydrogen) atoms. We analyze the dynamics using the general theoretical incoherent scattering function [21]:

$$S_\mathrm{theo}(\vec{Q},\omega) = \mathrm{e}^{-\langle u^2\rangle Q^2}\left[A_0(\vec{Q})\cdot\delta(\omega) + \sum_n A_n(\vec{Q})\cdot L_n(\Gamma_n,\omega)\right] \tag{2}$$

The scattered intensity is separated into an elastic δ-shaped component and a number of quasi-elastic Lorentzian-shaped contributions parametrized by the width $\Gamma_n = 1/\tau_n$ and the quasi-elastic incoherent structure factors A_n (QISF). The amplitude of the elastic component is given by the elastic incoherent structure factor (EISF) A_0. The Debye–Waller factor $\mathrm{e}^{-\langle u^2\rangle Q^2}$ describes the vibrational contributions, where $\langle u^2\rangle$ gives the global averaged mean square displacement of the vibrational motions.

The theoretical scattering function $S_\mathrm{theo}(\vec{Q},\omega)$ has to be convoluted with the resolution function $S_\mathrm{resol}(\vec{Q},\omega)$ to get a function, which can be used for fitting the measured scattering data

$$S_\mathrm{measured}(\vec{Q},\omega) = F\cdot\mathrm{e}^{(-\hbar\omega)/2k_BT}[S_\mathrm{theo}(\vec{Q},\omega)\otimes S_\mathrm{resol}(\vec{Q},\omega)] \tag{3}$$

where $\mathrm{e}^{(-\hbar\omega/2k_\mathrm{B}T)}$ is the detailed balance factor and F a normalization factor.

In GO we expect possible motions of confined water molecules (jumps between certain places, rotational motions), of functional OH-groups and bulk water molecules. All of them can be described phenomenologically by a sum of Lorentzian contributions and an elastic contribution as given above. We use the formula in isotropic approximation without taking into account special motions of certain atoms.