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Pressure-Induced Insertion of Liquid Alcohols into Graphite Oxide Structure

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Abstract: Graphite oxide (GO) immersed in an excess of methanol and ethanol media is found to undergo a phase transformation at about 0.2−0.8 GPa, with an expansion of the unit cell volume by $\sim$40%, due to pressure-induced insertion of solvent into interlayer space. The pressure at which the structural expansion occurs does not correlate with the solidification pressure of the alcohol, in contrast to the graphite oxide/water system. The expanded high-pressure phase of GO/ethanol could be quenched back to ambient pressure. Compression of graphite oxide with a 2:1 water/methanol medium revealed a complex anomaly with two steps attributed to insertion of methanol and water at different pressure points.

Introduction

Several nanoporous materials (e.g., some zeolites and pyrochlores) are known to exhibit the rare property of structural expansion due to pressure-induced insertion of a liquid medium into nanopores.[1−6] In most cases the pressure medium that hitherto has been observed to cause such structural expansion is water, but other solvents (e.g., methanol) were also observed in similar phase transformations.[7] Recently we discovered that the graphite oxide (GO) structure shows colossal expansion due to pressure-induced insertion of liquid water, with a maximum in the cell volume at around 1.4−1.5 GPa.[8] Experiments reported in this study show that liquid media other than water could also be inserted into the GO structure under high pressure.

Graphite oxide is a nonstoichiometric material obtained by strong oxidation of graphite.[9−13] It keeps the layered structure of pristine graphite but the interlayer distance is increased up to $\sim$7 Å due to functionalization with oxygen and OH groups. The structure is strongly disordered and it is believed that GO sheets are buckled, deviating from the ideal planar shape at the points of functional group attachment. Recent interest in structural studies of graphite oxide was heated up by the synthesis of various graphene-related and composite materials with GO as a precursor.[14−25]

A unique property of graphite oxide is its ability to incorporate polar solvents into interlayer space under ambient conditions. This results in further expansion of the GO structure up to $\sim$12 Å.[10–13] Recently we showed that the unit-cell volume of graphite oxide pressurized in the presence of water continuously increases

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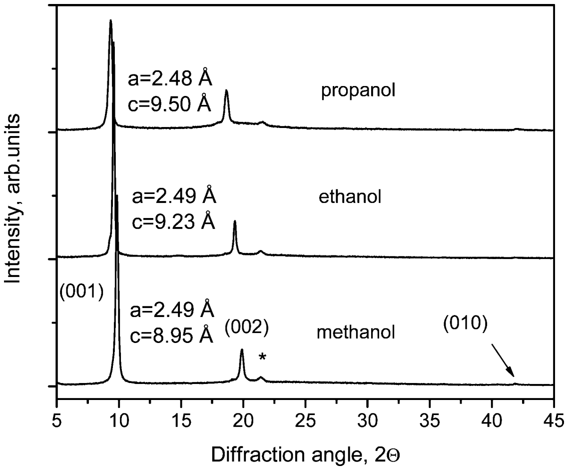

Figure 1. XRD patterns of graphite oxide powder immersed in excess amounts of methanol ethanol, and propanol ($\lambda = 1.5418$ Å). Reflection from plastic foil (used to seal solution from evaporation during data recording) is marked by an asterisk.

(by 28−30%), reaching a maximum at 1.3−1.5 GPa. A sharp downturn in the pressure dependence of the unit-cell volume of the graphite oxide correlates with solidification of liquid water. The effect is reversible, resulting in a unique breathing of the structure upon pressure variation.[7]

In this study we show that graphite oxide immersed in methanol- or ethanol-based media undergoes a steplike expansion of the structure at 0.2−0.8 GPa due to insertion of an additional amount of liquid into interlayer space.

Experimental Section

The GO sample was prepared by Brodie's method.[8] The X-ray diffraction (XRD) pattern recorded for the pristine sample of GO at ambient conditions was indexed by a turbostratic graphite-like hexagonal structure with cell parameters $a = 2.48$ Å and $c = 6.60$ Å.[7]

A high-pressure study of GO/alcohol systems was performed by synchrotron radiation X-ray diffraction in a diamond anvil cell (DAC). High-pressure experiments were performed using a diamond anvil cell (DAC) with 0.4−0.6 mm flat culets. The samples were loaded into a 0.2−0.3 mm hole in the steel gaskets together with a ruby chip used for pressure calibration. The pressure was increased gradually in steps of 0.1−0.2 GPa, and XRD patterns were recorded on every step during compression and decompression.

XRD patterns were recorded from graphite oxide samples by use of synchrotron radiation Swiss−Norwegian Beamlines (BM1A) at wavelength $\lambda = 0.7092$ Å with a MAR345 image plate detector. The two-dimensional XRD patterns were integrated by use of Fit2D software. Initial experiments were performed at ambient pressure in glass capillaries. Experiments were performed with GO powder loaded with excess methanol, ethanol, and water/methanol mixtures as pressure media.

Results and Discussion

Immersion of GO sample in excess amounts of alcohols at ambient conditions results in solvent insertion into the interlayer space and a significant expansion of the structure. The interlayer distance (001) in the solvated GO structure was measured under ambient conditions in methanol as $d = 8.85$ Å, ethanol $d = 9.23$ Å, and propanol $d = 9.50$ Å; see Figure 1 (see also Figure 1S in Supporting Information). It increases, correlating with the size of the alcohol molecule, by ∼2.2−2.6 Å compared to the "dry" state, which corresponds approximately to insertion of one monolayer of solvent molecules.

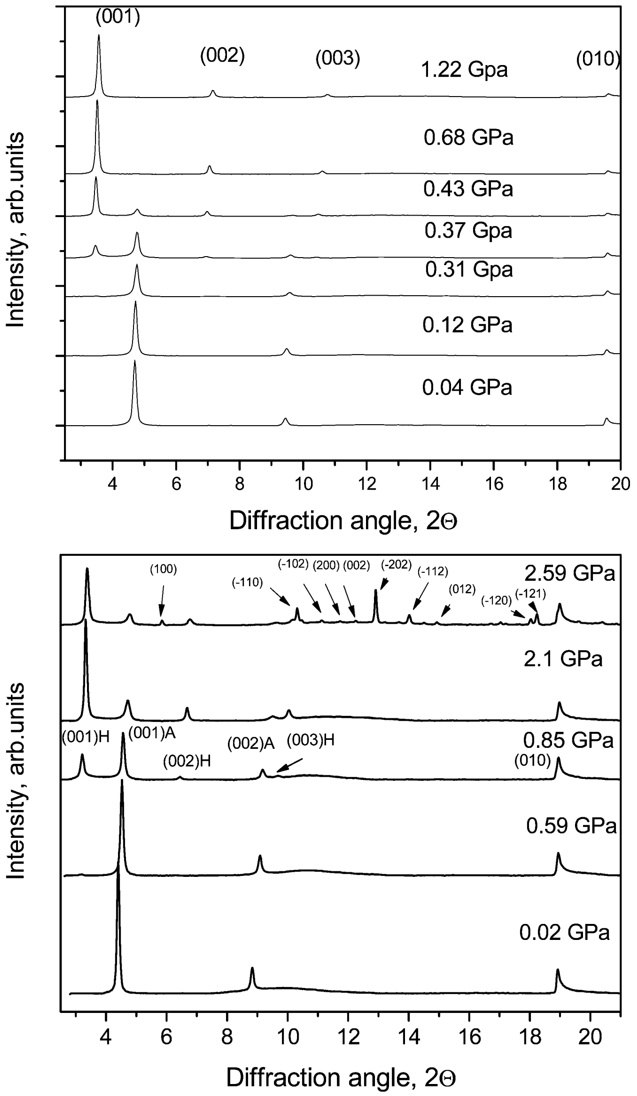

Figure 2. XRD patterns ($\lambda = 0.7092$ Å) recorded upon compression from a GO/methanol sample (top panel) and a GO/ethanol sample (bottom panel). Indexing for the GO/ethanol phases is given on the 0.85 GPa pattern: A, ambient-pressure phase; H, high-pressure phase. A solid ethanol phase is indexed on the 2.59 GPa pattern by a $P2_1/C$ structure with $a = 7.543$ Å, $b = 4.738$ Å, $c = 7.1904$ Å, and $\beta = 114.48°$, in agreement with literature data.[26]

As shown in Figures 2 (top) and 3, compression of the GO/methanol sample resulted in a sharp phase transformation that starts at 0.37 GPa. The interlayer distance of the graphite oxide structure increases stepwise by approximately 2.5 Å. The patterns recorded at 0.37 and 0.43 GPa showed coexistence of the high- and low-pressure phases, while from 0.68 GPa and above the low-pressure phase has disappeared. This anomaly is explained by insertion of additional methanol between graphite oxide layers. The layers themselves remained unchanged as evidenced by a monotonous pressure dependence of the (010) peak *d*-spacing (see Figure 4).

A very similar phase transformation was also observed for the GO/ethanol system above 0.59 GPa; see Figure 2b (in a separate pressure run starting from 0.4 GPa). However, the high-pressure phase of GO/ethanol could not be obtained in pure

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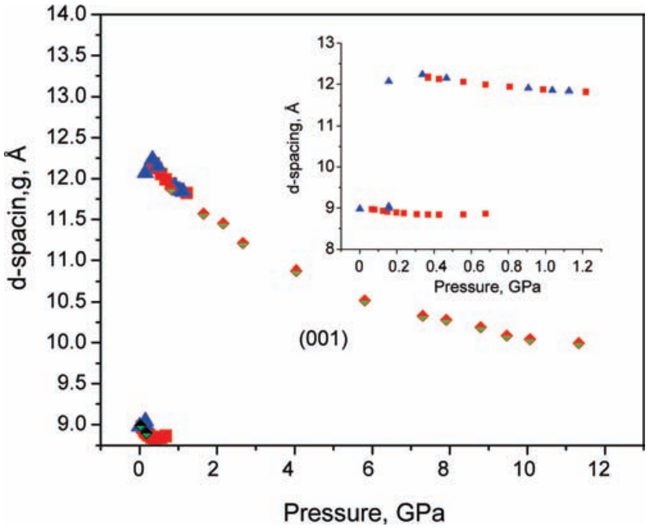

Figure 3. Pressure dependence of (001) *d*-spacing for a methanol/GO sample for two experiments (red squares, diamonds). Points recorded for decompression are shown by blue triangles. (Inset) Pressure region of the phase transformation: red squares, compression; blue triangles, decompression.

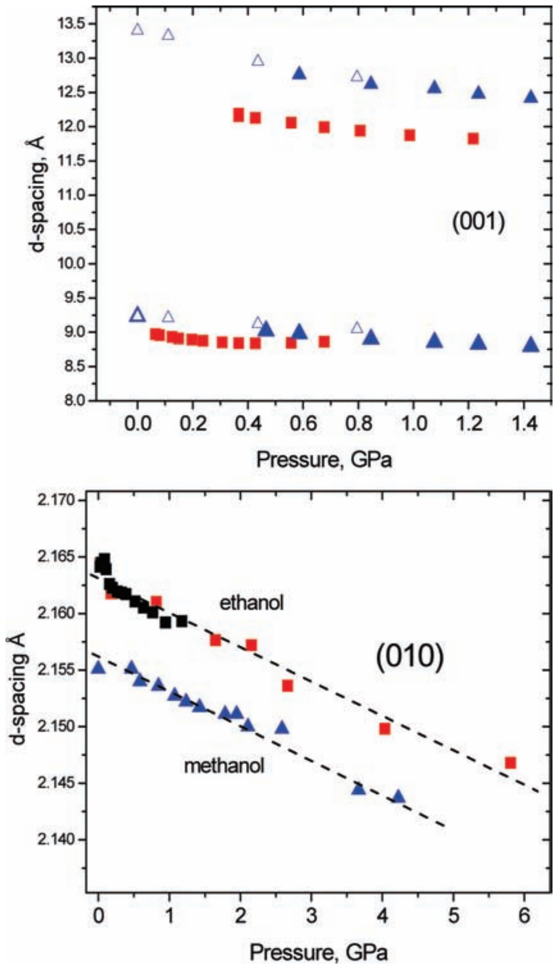

Figure 4. Pressure dependence of (001) and (010) *d*-spacings for GO/methanol during compression (red and black squares represent two separate experiments) and for GO/ethanol with compression (solid blue triangles) and decompression (open blue triangles).

form even at pressures above 4 GPa. Coexistence of the low- and high-pressure phases up to 3.6 GPa was observed also in an additional experiment with a stronger excess of ethanol, approximately half the amount of powder for the same sample volume. No difference in phase transformation pressure or in the relative intensity of reflections was observed in this experiment.

The pressure dependence of the *d*-spacings calculated from (001) and (010) reflections of the GO/methanol and GO/ethanol systems is shown in Figures 3 and 4. Decompression results in a reverse steplike transformation back to the low-pressure phase for the GO/methanol system, but in the case of GO/ethanol the high-pressure phase was observed to be unchanged even after full release of pressure (irreversible). At ambient pressure the interlayer spacing of the high-pressure GO/ethanol phase reached the value of 13.4 Å, which is about 1 Å higher than its value at the pressure where this phase appeared during compression.

The structural expansion of GO occurs in a very similar way in both methanol- and ethanol-based media, with approximately the same magnitude of about 2.5 Å, which corresponds approximately to one monolayer of solvent. The single-step pressure insertion of alcohols into the GO structure (with a pressure region where two distinct phases coexist) is remarkably different compared to the water insertion previously studied,[8] which occurs with a gradual expansion of the GO lattice and with only a single phase observed at any pressure point. Alcohol molecules are likely to be very weakly bound to GO layers, since we could not detect any heat effect when performing differential thermal analysis (DTA) measurements on GO/methanol samples in the pressure range 0−2.0 GPa.

Despite the structural expansion of GO, the total density of the graphite oxide/solvent sample should increase according to Le Chatelier's principle. Therefore, methanol and ethanol in the interlayer space of graphite oxide should have a higher density than the bulk liquid. A similar phenomenon is known, for example, for water incorporated into the interlayer space of montmorillonite[27] and for nanoconfined water in general.[28] Graphite oxide behaves like a weak acid when immersed in most polar solvents due to dissociation of OH groups.[17] Pressure is also known to affect proton transfer from weak acids to ethanol.[29] Stronger dissociation at high pressure is likely to result in a higher surface charge of the GO planes, which could possibly contribute to a stronger interaction with water molecules.

In contrast to the GO/H_2O system, no anomalies were observed in GO/methanol and GO/ethanol systems upon further increase of pressure near the solidification points of methanol and ethanol. Ethanol crystallization was observed at 2.6 GPa, while for methanol, formation of a solid amorphous glass phase occurs around 3.6−7.0 GPa[30,31] (however, it is not possible to detect this phase in our XRD experiment). In general, the shape of the high-pressure anomaly for GO/alcohols is surprisingly different from that for the GO/H_2O system. Graphite oxide in water medium was found to exhibit a "breathing" effect upon compression and decompression: the interlayer spacing changed continuously upon pressure variation with only one phase observed at each pressure point.

The point of water solidification was also correlated with a sharp downturn in the pressure dependence of cell parameter *c* of the GO structure.

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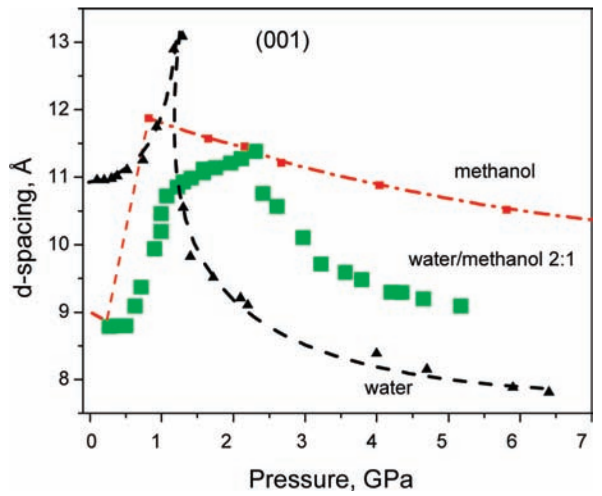

Figure 5. Interlayer *d*-spacing of GO compressed in a 2:1 water/methanol medium (green squares) compared to compression in pure methanol (red squares) and water (black triangles).

In the case of methanol and ethanol, solidification of the media did not influenced the distance between graphite oxide layers. The expansion of the GO lattice occurs while alcohols are in the liquid state with the following characteristic features: there are two phases with different cell parameters; there is a point of transition and a short range of pressures where both phases coexist. Phase transformations in GO/alcohol media are very similar also to phase transformations observed previously in some zeolites and pyrochlores: there is a steplike increase of cell volume due to insertion of liquid medium into nanopores. The difference is only in the magnitude of the structural expansion, which is much higher for graphite oxide and reaches about 40% for the GO/ethanol system compared to a maximum of 5−7% in other materials.[1–6] Another difference is that *only water* was selectively inserted into the zeolite structures even if the pressure medium was a mixture of water with methanol and/or ethanol in various proportions.[5]

To test whether GO is chemically selective in the same way as zeolites, mixtures of methanol and water were loaded as pressure media for the next experiments. The first experiment was performed with 10% water and 90% methanol. However, for this pressure medium the high-pressure dependence of the graphite oxide cell parameters remained exactly the same as for pure methanol (see Supporting Information). An experiment with water/methanol in the proportions 2:1 revealed a pressure dependence remarkably different: see Figure 5. It should be noted that the freezing point of pure methanol at ambient conditions is 200 K; the same freezing point is found if 10% methanol is added. However for 35% methanol the freezing point is known to be higher (247 K). In correlation with the freezing points discussed above, the solidification pressure for GO/methanol/water mixture was found to be higher (∼2.4 GPa) than that for GO/pure water (∼1.3 GPa[7]).

Analysis of Figure 5 shows that GO in a 2:1 water/methanol medium shows two anomalies, the first of them likely related to methanol and the second to water. The resulting curve for the pressure dependence of the (001) *d*-spacing of GO in water/methanol is in intermediate position between curves found for pure water and pure methanol. Unlike GO in pure methanol, compression in the 2:1 water/methanol mixture shows a *continuous* change of structure ("breathing"), and an absence of a sharp transition between the high- and low-pressure phases. The general shape of the anomaly found with the 2:1 water/methanol medium is more similar to the one found for pure water: there is a maximum in the pressure dependence of the interlayer spacing which correlates with the solidification point of the medium. However, a *continuous* but rather steep increase of the interlayer distance was observed at around 1.0 GPa, most likely due to incorporation of methanol into the GO structure.

Comparing the shape of the anomalies for pure water and for the 2:1 water/methanol mixture gives an interesting observation: the decrease of the (001) *d*-spacing above the solidification point is remarkably different for the three tested media. Analysis of Figure 5 allows us to suggest that the high-pressure phase of GO/methanol keeps its composition upon further compression above the phase transition point, while GO in pure water shows a "breathing" effect: some water is pressed out of the GO structure above the point of maximum. This could happen only if water inside the interlayer space of GO remains in a liquidlike state at pressures where the bulk water forming the pressure medium is solid. In the case of the 2:1 water/methanol medium, the pressure dependence of (001) *d*-spacing can be interpreted to show that part of the water is squeezed out of the GO structure above the point of maximum, while most of the methanol remains inside.

Summarizing all available data, it is possible to propose the following models for the high-pressure anomalies in the GO/water and GO/alcohol systems. According to recent NMR data, the graphite oxide hydrated to saturation (interlayer distance above 10 Å) contains part of water with translational motion between GO layers. This water could be considered as "liquid-like".[12]

Additional water inserted into the GO structure under compression could also be considered as being in a nanoconfined liquidlike state. It is known that water confined in nanosized pores has different properties compared to bulk water. Therefore, it is likely that nanoconfined water in GO slit pores remains liquid even at pressures above the solidification point of bulk water and can be squeezed out of the structure. The GO structure saturated with methanol or ethanol shows much smaller expansion under ambient conditions (∼9 Å compared to ∼12 Å for water), and solvent molecules are probably fixed in the structure. The high-pressure phase with increased interlayer spacing keeps its composition upon further pressure increase (see Figure 2). It can be noted that the pressure dependences of the (001) *d*-spacing for GO/water and GO/methanol become almost parallel above ∼3.0−4.0 GPa, which could be explained by suggesting that excess water is squeezed out of the GO/water structure in the 1.4−3.0 GPa pressure region, above which the composition of the material remains unchanged.

In the case of water/methanol mixtures, the shape of the observed anomaly can be explained if only water keeps its translational motion inside the interlayer space of GO, while methanol is mostly fixed in the structure. Above the solidification point of the medium, water is gradually squeezed out of the GO structure, which explains the much smaller decrease in the (001) *d*-spacing of 2:1 GO with water/methanol compared to GO compressed with a pure water medium. Note that, for example, at 5.0 GPa the interlayer distance of GO is above 9 Å for water/methanol mixtures, while for pure water it is about 1.5 Å smaller.

Pressure-induced insertion of alcohol molecules into GO occurs at relatively low pressures, which broadens possibilities for functionalization of GO. Solution-based functionalization of graphite oxide has attracted significant interest recently due to the possibility to convert GO into graphene-related materials.[18] The increased interlayer distance in high-pressure phases allows larger molecules to be inserted into the GO structure. Functionalization of GO in its expanded high-pressure phase could possibly be achieved on bulk samples by high-energy ball milling. Ball milling is known to produce kinetic pressures on the level of 1−2 GPa,[33] sufficient for pressure-induced insertion of alcohols into the GO structure. Functionalized GO materials could later be converted into graphene-related composites by heat treatment. Recently we proved that exfoliation of graphite oxide occurs at 5.0 GPa in the same temperature interval as at ambient conditions.[32]

In conclusion, graphite oxide immersed in an excess of liquid methanol or ethanol undergoes a sharp phase transition at ∼0.3−0.8 GPa with an expansion of the lattice by an extraordinarily high value of ∼40%. The structural expansion is explained by pressure-induced insertion of a solvent monolayer. In the case of a 2:1 water/methanol mixture the high-pressure anomaly shows features typical for both GO/water and GO/methanol systems. Graphite oxide is thus one of very few materials that exhibits pressure-induced expansion of its structure due to insertion of not only water but also other solvents.

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Supporting Information Available: Detailed description of GO synthesis procedure and four figures showing XRD patterns of GO and GO/ethanol samples at ambient conditions, pressure dependence of (001) reflection of GO/ethanol in a broader pressure interval, pressure dependence of (001) reflection for samples of GO loaded with mixture of water and 10% of methanol, linear compressibility in c-direction for pristine “dry” GO and for high pressure phase of GO/ethanol. This material is available free of charge via the Internet at http://pubs.acs.org/.

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