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INDUCED DEFECTS IN CARBONACEOUS MATERIALS FOR HYDROGEN STORAGE

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Introduction

The use of hydrogen as an energy carrier will require a means to transport and store hydrogen, yet no existing technology meets the performance requirements established by the U.S. Department of Energy. Carbon nanomaterials (SWNT, MWNT, GNF) have several properties favorable for adsorption—surface area, pore size, and electrical conductivity—and these properties can be tuned by judicious selection of the conditions by which the carbons are prepared. However, hydrogen storage claims in these carbon nanomaterials have been highly scattered, ranging from 0.4%-67%. The discrepancies in these reports are thought to be due to experimental artifacts, impurities, carbon properties, and assessment techniques.

There has been a recent resurgence in hydrogen storage claims for graphite nanofibers (GNF) and multi-wall nanotubes (MWNT), and the results have been reported by a number of research groups: 3.8% at 69 bar,[1] 6.5% at 120 bar for GNF[2]; and 1.97% at 40 bar[3] to 6.3% at 148 bar[4] for MWNT. These recent claims discuss how: (a) the nanotube structure and defects relate to hydrogen uptake,[1] (b) these defects can be formed during synthesis or subsequent pretreatment[1]; (c) terminal carbon groups act to dissociate hydrogen,[1, 2]; and (d) the carbon structure may become expanded after exposing the carbon to hydrogen.[5] The ball-milling of graphite has been used to obtain a total hydrogen capacity of 7.4% with neutron diffraction evidence of chemisorbed hydrogen.[6] Ball-milling of carbon nanotubes has also shown promise, as long as the graphitic nature of the nanotubes is partially retained.[7] Additionally, graphitic carbon has shown a synergistic effect when ball-milled with magnesium.[8] These reports suggest that defects within the graphitic structure lead to enhanced hydrogen storage and that this effect can be magnified through synthesis, pretreatment, and processing.

The goal of this project was to induce defects in carbonaceous materials through both ball-milling and/or carbon exfoliation; here, we report initial exfoliation results. This study serves to test the emerging hypothesis in the literature: carbon defects chemisorb hydrogen, with possible expansion of the graphite lattice. If the advantageous effect of carbon defects is confirmed and better understood, controlled introduction of defect may increase hydrogen storage by introducing new hydrogen storage sites.

Methods

Materials. Ultra-high purity hydrogen (99.999%) was used in adsorption experiments, and ultra high purity helium (99.999%) was used to determine the bulk density of the adsorbents for buoyancy corrections, both gases were pretreated with an in-line 3A molecular sieve zeolite column to eliminate possible moisture contamination. Graphite nanofibers were purchased from Catalytic Materials, Ltd. A powdered graphite sample was obtained from Carbone and used as received.

Introduction of Defects. Carbon exfoliation served as one means to impart defects and increase interlayer spacing between graphene sheets. Methods to exfoliate graphite are well known and were extended here to other graphitic carbons. The primary exfoliation method used in this study was a mixture of nitric and sulfuric acids followed by thermal shocking at 700 °C.[9]

Materials were treated *in situ* on the IGA prior to adsorption measurements. The thermal treatments were chosen based on previous studies[1] and the thermal stability of the fibers.

Characterization. Standard physisorption methods, including surface area and pore size distribution, were determined in situ on the Hiden IGA-003 after thermal degassing and prior to adsorption measurements. Electron microscopy, including TEM and SEM (Philips XL20), was used to determine the morphology and diameter of the material, before and after treatments. The bulk density of the carbon materials was determined by helium isotherms on the IGA. Carbon materials were thermally decomposed on the IGA in 100 ml/min helium with a ramp rate of 4 °C/min. These thermal decomposition studies were used to determine applicable degas temperatures and to give an indication of the thermal stability of the fibers after the treatments.

Hydrogen Uptake. A high-pressure TGA (Hiden Isochema IGA-003) was used to evaluate hydrogen uptake at pressures up to 20 bar. The IGA provided a high sensitive measurement with precise temperature and pressure control for automated measurements of adsorption and desorption isotherms. In addition, the IGA enabled *in situ* treatment and characterization prior to hydrogen measurements; typical pretreatments consisted of inert thermal treatments with or without partial thermal degradation. All hydrogen uptake measurements are normalized to sample mass after pretreatment, with buoyancy corrections determined from bulk density measurements with helium.

Results and Discussion

Introduction of Defects and Exfoliation of Graphite Lattice. The relatively mild sulfuric/nitric acid treatment successfully exfoliated graphite (Figure 1), in agreement with previous results.[9] Preliminary results of GNF exfoliation with the same method illustrate definite differences in SEM micrographs (Figure 2): exfoliated GNF had ragged edges when compared to the untreated GNF. TEM analysis is underway to better analyze the effect of exfoliation and quantify the GNF diameter before and after exfoliation. There was some indication that a milder exfoliation method may be needed for GNF, as SEM indicated that some regions of the sample lost the fiber structure after exfoliation (data not shown). The bulk density of the GNF, as measured by helium buoyancy on the IGA, changed from 1.86 g/cc to 1.31 g/cc upon exfoliation.
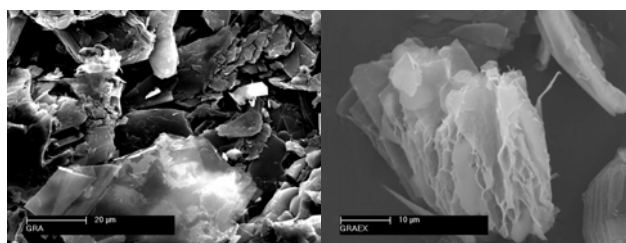

Figure 1. Exfoliation of powdered graphite in a mixture of nitric/sulfuric acid with thermal shocking at 700 °C (a) before exfoliation; (b) after exfoliation.

Thermal decomposition of the GNF before and after sulfuric/nitric acid exfoliation indicated a clear loss of thermal stability. Prior to exfoliation, the GNF showed no significant degradation in helium at temperatures up to 1000 °C; however, the onset of thermal degradation of the sulfuric/nitric acid exfoliated

GNF was at 100 °C with a maximum rate of mass loss at 120 °C (Figure 3). This thermal reactivity is an initial indication of both the increased reactivity and the decreased graphicity of the GNF samples upon exfoliation. Comparison of the 70% mass loss to SEM visualization suggests that the increased reactivity occurs in both amorphitized GNF and exfoliated GNF, however further quantification of this is clearly needed.
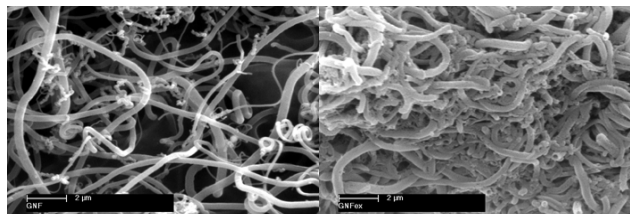

Figure 2. Exfoliation of GNF in a mixture of nitric/sulfuric acid with thermal shocking at 700 °C (a) before exfoliation; (b) after exfoliation.
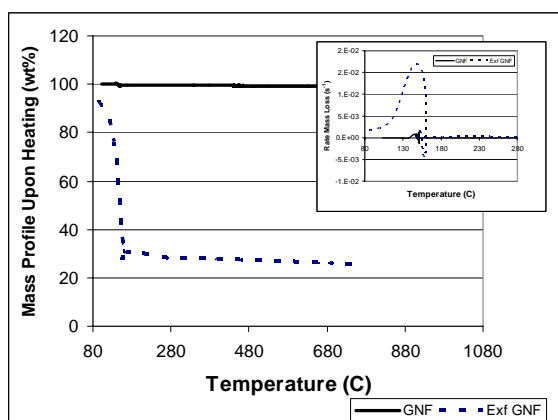

Figure 3. Exfoliation of the GNF in a mixture of nitric/sulfuric acid resulted in a loss of thermal stability of the materials, indicating a higher overall reactivity of the fibers caused by loss of graphitic structure and/or chemical defects. The inset shows the rate of mass loss for the fibers; the rate of thermal degradation was greatest at 120 °C.

Hydrogen Uptake. Prior to exfoliation, the GNF had 0.02% hydrogen uptake, with apparent saturation at 10 bar (Figure 4). Exfoliation of the GNF led to a slight increase in hydrogen uptake: 0.046 % after outgassing at 80 °C and 0.099% after outgassing at 100 °C. The two temperatures were chosen based on the thermal degradation discussion, with mass loss at 80 °C corresponding outgasing but little or no thermal degradation and 100 °C corresponding to partial gasification of the exfoliated GNF (Figure 3). It is expected that the amorphous carbon is more reactive than GNF, and decomposes before the GNF. Thus, the higher pretreatment temperature is intended to preferentially remove amorphous carbon leaving a higher purity of exfoliated GNF. Future studies will include characterization of the materials to quantify the GNF content.

Conclusions

GNF exfoliation enhanced the hydrogen uptake by a factor of five compared to the untreated GNF. Further studies will explore additional exfoliation methods and further characterize the sample to better quantify the degree of exfoliation. The nitric/sulfuric exfoliation method may have been too severe for GNF as evidenced by the high thermal reactivity; our next attempt will be the milder nitric/formic acid exfoliation method, as described previously.[10, 11] However, the overall degree of hydrogen uptake was low; we will explore additional carbon samples and verify the extent of exfoliation before addressing the expanded graphite lattice and/or defect hypothesis.
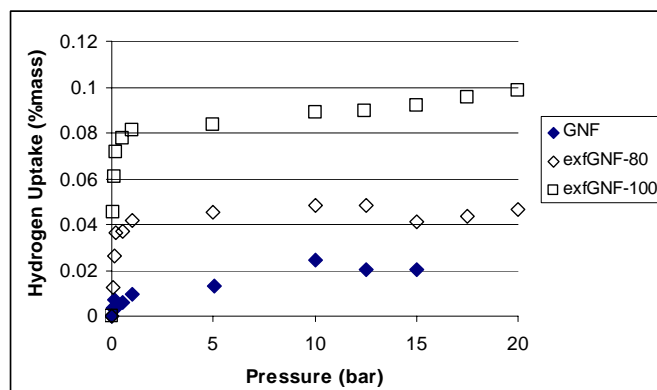
Figure 4. Hydrogen uptake of the GNF before (a) and after (b) exfoliation, followed by different degrees of thermal degradation. Hydrogen uptake is normalized per mass of carbon remaining after each pretreatment.

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