



Letters to the Editor

## Hydrogen storage by alkali-doped carbon nanotubes—revisited

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Much excitement has arisen on recent reports of promising results on carbon nanotubes for hydrogen storage [1,2]. High hydrogen adsorption capacities were reported for various carbon nanotubes. Most recently, interesting results were reported for using alkali-doped carbon nanotubes for hydrogen storage [3]. It was reported that Li- and K-doped carbon nanotubes adsorbed, respectively, 20 wt.% and 14 wt.% of hydrogen at 1 atm and mild temperatures (200 to 400°C for Li-doped and near room temperature for K-doped nanotubes). Lower but still substantial amounts of hydrogen adsorption were also reported for alkali-doped graphite [3].

Gases supplied in cylinders can be contaminated with moisture. This is particularly the case for hydrogen. In our work on hydrogen-carbon reaction using ‘ultra-high purity grade’ hydrogen (>99.999%), copious amounts of water were removed by using a series of traps [4]. The cause for the contamination may have to do with the practical problem of cylinder filling (such as water condensate left in the cylinder prior to filling). Hence in all of our work using gas cylinders, special care is taken to eliminate any possible moisture contamination. The grade of H<sub>2</sub> used in the work of Chen et al. was not reported but a purity of ‘>99.99%’ was noted [3]. Separately, special caution needs to be taken in using TGA (thermogravimetric analysis) for measuring adsorption or reaction kinetics. Upon a change in temperature or gas composition/flow-rate, the accompanying change caused by changes in buoyancy and friction forces from the gas flow is usually of the same order of magnitude as the signal that is being measured (i.e., the actual weight change). Hence rigorous calibration must be done for all changes [5].

With the above consideration, and because of the

significance of the recent report [3], we decided to reexamine the experimental results. Our findings and conclusion are reported in this letter.

The same procedure [6] used by Chen et al. [3] for preparing carbon nanotubes was used in this work. The carbon nanotubes were prepared by catalytic decomposition of methane [6]. 11.6 g nickel (II) nitrate hexahydrate (99%, Aldrich), 15.4 g magnesium nitrate hexahydrate (99%, Aldrich) and 13.0 g citric acid (99.5+%, Aldrich) were mixed in 150 ml deionized water. After the mixture was evaporated, the solid sample was calcined at 700°C for 5 h in air and Ni<sub>0.4</sub>Mg<sub>0.6</sub>O was obtained.

0.3 g Ni<sub>0.4</sub>Mg<sub>0.6</sub>O was loaded into a quartz tube and heated in a flow of H<sub>2</sub> (50 ml/min) at 650°C for 15 min. Subsequently, CH<sub>4</sub> was passed over the reduced sample for 1 h with a flow rate of 50 ml/min at the same temperature. The obtained material was then mixed with 6 M nitric acid and stirred for 24 h to dissolve the catalyst particles. The mixture was filtered and then washed with deionized water 5 times. Finally, the solid was dried at 100°C for 12 h in air and then calcined at 400°C for 1 h in flowing He. TEM showed that the obtained material was mainly composed of carbon nanotubes. The BET surface area (measured with a Micromeritics ASAP 2010 micro-pore size analyzer) was 148 m<sup>2</sup>/g. This surface area was slightly higher than that obtained by Chen et al., 130 m<sup>2</sup>/g [3]. The Li/nanotube (Li/C=1/15) and K/nanotube (K/C=1/15) were prepared by incipient wetness impregnation. This atomic ratio (1/15) was the same dopant/carbon ratio used by Chen et al. [3].

H<sub>2</sub> adsorption/desorption experiments were carried out with a thermogravimetric analyzer (Cahn, TG-121). In each experiment, 10 mg sample was loaded on a quartz sample holder and then heated at 550°C for 1 h in flowing H<sub>2</sub> (100 ml/min, ultra high purity grade, 99.999%, with moisture trap) or H<sub>2</sub> with added water. After the sample was cooled to 20°C, the temperature was again increased to 500°C at a heating rate of 5°C/min and then decreased to

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20°C in flowing H<sub>2</sub> or H<sub>2</sub>O/H<sub>2</sub> (when used). During the process, the weight change of the sample was recorded on the TGA. A moisture trap was used for the hydrogen for all runs. The trap was an adsorber bed of activated carbon maintained at 77 K. Calibration runs were made with 10 mg quartz under the same heating/cooling and flow conditions. All weight gains/losses reported here were after calibration and were hence true values.

Two sets of H<sub>2</sub> uptake measurements were performed, using dry and wet H<sub>2</sub>. The dry H<sub>2</sub> was obtained by using the trap, whereas the wet H<sub>2</sub> was made by addition of water vapor. Fig. 1 shows the adsorption/desorption loop for Li/nanotubes in dry H<sub>2</sub>. All qualitative features of the result of Chen et al. [3] are reproduced, i.e., a weight gain with increasing temperature followed by a peak at about 400°C and a subsequent, steep drop in weight, and a monotonic weight gain upon cooling. Similar to their experiment, the heating was at a constant rate of 5°C/min while the cooling rate was not programmed and was at slower rates. However, the total weight differential was only 2.5%, rather than 20% reported by Chen et al. This experiment was repeated by using wet H<sub>2</sub>, and the results are shown in Fig. 2. The total weight differential in wet H<sub>2</sub> was substantially greater, at 12%, compared to 2.5% in dry H<sub>2</sub>. The essential qualitative feature of the TGA profile was still maintained with moisture addition.

Fig. 3 shows the weight gain/loss TGA profile in dry H<sub>2</sub> for K-doped nanotubes. Again, the same conditions as those of Chen et al. [3] were used. The results also agreed

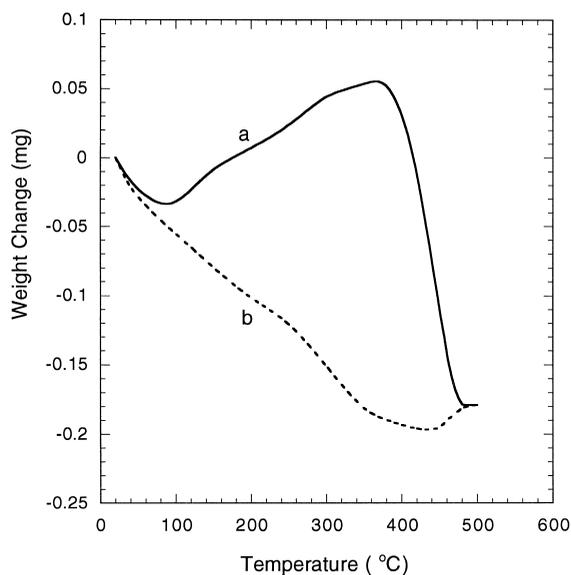


Fig. 1. TGA profile of Li-doped carbon nanotubes in 1 atm dry H<sub>2</sub>: (a) increasing temperature from 20 to 500°C at 5°C/min, and (b) cooling at slower rates. The total weight of Li/C was 10 mg. Ultrahigh purity H<sub>2</sub> (>99.999) with additional H<sub>2</sub>O trap was used.

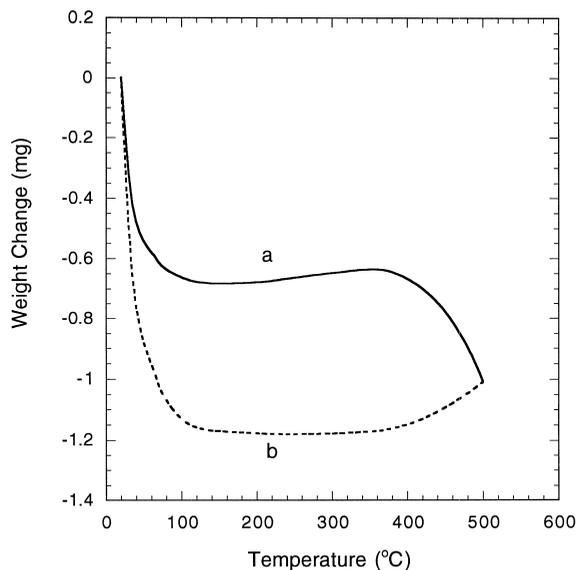


Fig. 2. TGA profile of Li-doped carbon nanotubes in 1 atm wet H<sub>2</sub>: (a) increasing temperature from 20 to 500°C at 5°C/min, and (b) cooling at slower rates. The total weight of Li/C was 10 mg. 2.3% (vol.) water vapor was added in H<sub>2</sub>.

qualitatively with those of Chen et al. However, the total weight differential was only 1.8%, compared to 14% of Chen et al. [3]. The TGA profile using wet H<sub>2</sub> is shown in

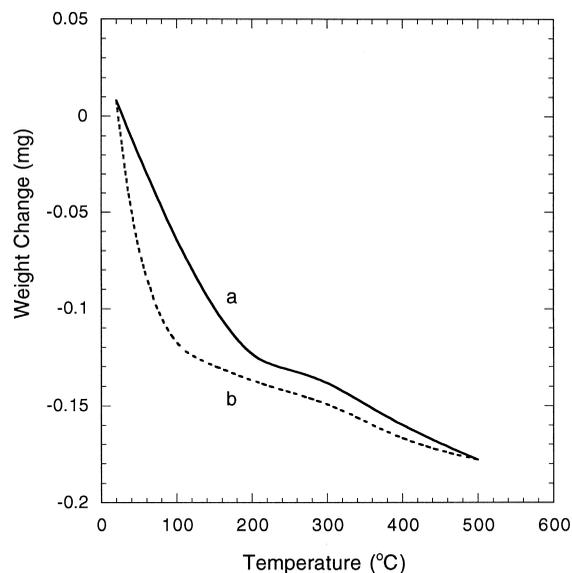


Fig. 3. TGA profile of K-doped carbon nanotubes in 1 atm dry H<sub>2</sub>: (a) increasing temperature from 20 to 500°C at 5°C/min, and (b) cooling at slower rates. The total weight of K/C was 10 mg. Ultrahigh purity H<sub>2</sub> (>99.999) with additional H<sub>2</sub>O trap was used.

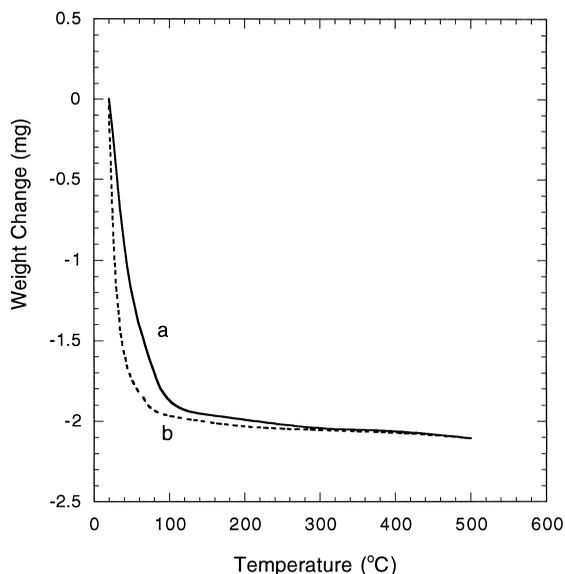


Fig. 4. TGA profile of K-doped carbon nanotubes in 1 atm wet  $H_2$ : (a) increasing temperature from 20 to 500°C at 5°C/min, and (b) cooling at slower rates. The total weight of K/C was 10 mg. 2.3% (vol.) water vapor was added in  $H_2$ .

Fig. 4. The moisture in  $H_2$  again drastically increased the total weight differential, from 1.8% to 21%. The value reported by Chen et al. [3] was 14%.

The alkali dopants in contact with carbon after the treatment in  $H_2$  at 550°C, as done in our experiments and those of Chen et al., were most likely in a reduced or metallic state. Reaction with moisture would produce alkali hydroxide, hence gain weight. Chen et al. also reported IR spectra of the Li/nanotube [3]. Their spectra showed two merged, strong bands at near  $1500\text{ cm}^{-1}$ , and a broad band near  $3000\text{ cm}^{-1}$  which grew with the time of exposure to the  $H_2$  flow. The IR spectrum of LiOH (with one hydrate) is shown in Fig. 5. A striking similarity exists between this spectrum and that of Chen et al. [3]. This result is a confirmation that alkali hydroxides were probably formed. Beside the formation of alkali hydroxide, additional hydrates could also be formed. For example, LiOH will bond one water molecule to form  $LiOH \cdot H_2O$ . The weight gains by forming hydroxides (plus hydrates) agreed well with the total weight gains reported by Chen et al. [3]. For example, the weight gain for Li/15C by forming  $LiOH \cdot H_2O$  should be 20% and the corresponding value for K/15C is 16%, compared with 20% for Li-doped nanotubes and 14% for K-doped nanotubes reported by Chen et al. [3]. KOH has no known hydrate forms, but is highly water soluble. Hence it can adsorb water at near room temperature. Other reactions involving other alkali species may also take place. It is likely that oxides such as semiquinones exist on the edge sites of the carbon nanotubes. Alkalis doped on these sites can exist in many

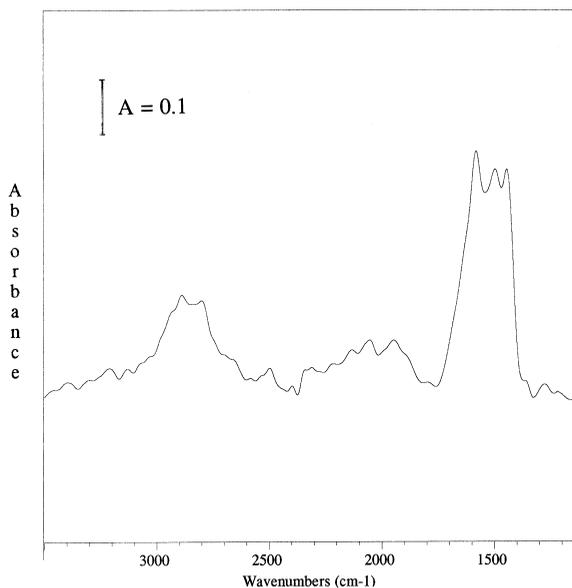


Fig. 5. IR spectrum of  $LiOH \cdot H_2O$  (in KBr pellet).

possible species, and a voluminous literature has been devoted to this subject [7]. One of the best proven species is phenolate,  $-C-O-K$  and  $-C-O-Li$  [7]. It is possible that these species may not be completely reduced to metallic states by hydrogen at 550°C. Interactions (adsorption/reaction) of water with these alkali species have not been studied.

We have also performed experiments with alkali-doped graphite, as well as using other flow conditions and other moisture concentrations. Similar results to nanotubes were obtained with alkali-doped graphite. The TGA profile also strongly depended on the flowrate, indicating a dependence on the rate of supply of moisture. In addition, the TGA results were strongly dependent on the concentration of moisture in the gas flow.

In conclusion, special caution needs to be taken to remove any moisture contamination from the hydrogen in measuring hydrogen storage in alkali-doped carbon nanotubes or graphite. Moisture drastically increased the weight gain by reactions with (or adsorption on) the alkali species on carbon. However, in dry hydrogen, it appears that alkali-doped carbon nanotubes can still adsorb nearly 2 wt.% hydrogen, and this is the novelty of the work of Chen et al. [3]. Further work is clearly needed to reach a better and definitive understanding of the  $H_2$ /alkali/nanotube system.

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## Direct synthesis of a polyaniline-intercalated graphite oxide nanocomposite

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Although conducting polymers such as doped polyacetylene can possess near metallic properties, ideal conducting polymers for use in electronic devices are not at present a reality because charge carriers mobilities are too low to be useful. Garnier and his coworkers [1] has prepared organized thin films of oligomers, but even for these the mobilities are around 4 orders of magnitude lower than those in crystalline silicon. For optimum carrier mobility, it appears to be necessary to produce a single crystal polymer, or at least a form that is largely crystalline. Based on these reason, research on electroactive polymers has recently focused on developing materials with a well-defined microstructure that is controllable at the nanometer level [2–7]. Toward this end, the Langmuir-Blodgett (L-B) techniques widely used for processing electrically conducting polymers into well-defined multilayered film structures with alternating conducting/insulating layers [8–10]. Another way to obtain orientation of polymer chains would be to grow them inside a structurally organized host framework. Among these systems, a intercalation of polymers into the interlayer space of two-dimensional inorganic systems has received a great deal of attention because the intercalation offers a means to simultaneously assemble thousands of layers by allowing guest molecules to diffuse in the van der Waals gaps provided by the layered lattice.

Intercalation of polyaniline into layered host materials has been extensively studied. More recently a polyaniline-intercalated graphite oxide (GO) nanocomposite, which was prepared via an exfoliation-adsorption process, has already been reported [11,12]. The existence of polyaniline between the layers enables the physiochemical properties

(electrical and thermal properties, etc) of graphite oxide to be greatly changed. But the X-ray diffraction analysis shows that this nanocomposite had a poor crystalline structure. Here a new approach was developed for the synthesis of polyaniline-intercalated GO nanocomposites. The result of X-ray diffraction shows that this compound has a higher crystallinity regularity than that of the previously prepared materials.

GO was prepared by the previously reported procedure [12]. 2 g of dried GO were put into 50 ml of aniline in a closed vessel, and this was stirred at ambient temperature for 24 hours and then centrifuged. The precipitate was washed with acetone three times and dried at 50°C for 24 hours and the aniline/GO intercalation complex was obtained.

Polyaniline/GO nanocomposite was prepared using the following procedure. 2 g of the aniline/GO intercalate was added in a closed vessel to 50 ml of a diethyl ether solution of anhydrous  $\text{FeCl}_3$  and the suspension was kept stirring at ambient temperature for 48 hours, then centrifuged, and the precipitate was washed with redistilled water until  $\text{FeCl}_3$  was removed completely. The solid was dried under vacuum at 50°C for 24 hours.

Fig. 1 shows the X-ray diffraction patterns of the polyaniline-GO nanocomposite together with that of aniline-GO intercalation compound and pristine graphite oxide. XRD analysis of the aniline-GO intercalation compound revealed a stacking height of 14.43 Å (Fig. 1b), an expansion of 6.6 Å relative to the pristine GO (7.82 Å), which is indicative of formation of the aniline-intercalated GO nanocomposite structure. When this compound is exposed to the diethyl ether solution of anhydrous  $\text{FeCl}_3$ , oxidative polymerization of aniline occurred and the polyaniline-GO nanocomposite was formed. The interlayer spacing increased to 15.28 Å (Fig. 1c), which is contrary to

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