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Optimization of Single-Wall Nanotube Synthesis For Hydrogen Storage

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Abstract

Carbon single-wall nanotubes (SWNTs) are capable of adsorbing hydrogen quickly, to high density, at ambient temperatures and pressures. Last year, we showed that hydrogen storage densities on SWNTs made by laser vaporization ranged from 3.5 to 4.5 wt% after a cutting procedure was performed. We present details of the cutting procedure here and show that, when optimized, hydrogen storage densities up to 7 wt% can be achieved. Infrared absorption spectroscopy measurements on pristine and H₂-charged samples indicate that no C-H bonds are formed in the process. These experiments are in agreement with an earlier temperature programmed desorption analysis that showed that hydrogen molecules are not dissociated when bound to the SWNT surfaces. All in all, we find that the interaction between H₂ and single-wall nanotubes is mid-way between conventional van der Waals adsorption and chemical bond formation. A detailed understanding of the mechanism coupled with a high degree of control during synthesis should allow useful hydrogen adsorbents to be designed and constructed.

Currently Available Hydrogen Storage Technologies

Hydrogen can be made available on-board vehicles in containers of compressed or liquefied H₂, in metal hydrides, or by gas-on-solid adsorption. Hydrogen can also be generated on-board by reaction or decomposition of a hydrogen-containing molecular species [1]. Although each method possesses desirable characteristics, no approach satisfies all of the efficiency, size, weight, cost and safety requirements for transportation or utility use. The U.S. Department of Energy energy density goals for vehicular hydrogen storage call for systems with 6.5 wt % H₂ and 62 kg H₂/m³.

Gas-on-solid adsorption is an inherently safe and potentially high energy density hydrogen storage method that should be more energy efficient than either chemical or metal hydrides, and compressed gas storage. Consequently, the hydrogen storage properties of high surface area "activated" carbons have been extensively studied [2-4]. However, activated carbons are ineffective in hydrogen storage systems because only a small fraction of the pores in the typically wide pore-size distribution are small enough to interact strongly with gas phase hydrogen molecules.

The first measurements of hydrogen adsorption on carbon single-wall nanotubes (SWNTs) were performed with highly impure samples. The room-temperature stabilization that was demonstrated at atmospheric pressures suggested the possibility of 5-10 wt % hydrogen storage in SWNT-based systems [5]. Contradictory results from purified SWNTs indicated that such high storage densities could only be achieved with cryogenic temperatures (80 K) and high pressures (158 atm) [6], consistent with theoretical consideration of van der Waals interactions between H₂ and SWNTs [7-9]. However, we showed last year that SWNTs can adsorb between 3.5 and 4.5 wt% at room temperature and room pressure when un-optimized preparation procedures were employed [10], and large-diameter SWNTs were recently shown to adsorb 4.2 wt % hydrogen at room temperature and ~100 atm. [11]. This year we show that hydrogen storage densities can be optimized to values as high as 7 wt%, and also present results from experiments designed to elucidate the mechanisms responsible for the unique hydrogen adsorption properties.

Motivation for and Explanation of IEA Activity

We have been working on the idea that aligned and self-assembled single wall carbon nanotubes could serve as ideal hydrogen adsorbents since 1993 [12]. The concept was motivated by theoretical calculations that suggested that adsorption forces for polarizable molecules within SWNTs would be stronger than for adsorption on ordinary, planar graphite [13]. Thus, we expected that high H₂ storage capacities could be achieved on SWNTs at relatively high temperatures and low pressures as compared to adsorption on activated carbons.

The research group of Patrick Bernier at Universite de Montpellier II was the first to generate large quantities of SWNT materials with the arc-discharge technique. We were interested in investigating the hydrogen adsorption properties of their arc-discharge materials to afford a comparison to the lower quality arc-discharge materials that were being made at NREL during that time. We began to collaborate during 1997 and planned to continue future work together under the auspices of the IEA. This collaborative effort was included in Task 12 of the IEA Hydrogen Agreement at the end of 1997 and our participation began soon thereafter. Unfortunately, Bernier's portion of the effort was never approved for inclusion into the IEA, so our planned effort, as detailed in our Material Development Plan, could never be fully realized. These issues were further complicated by the fact that both of our efforts had gained interest from industrial sponsors and that the intellectual property created through these interactions was considered proprietary until patent protection could be obtained. Nevertheless, we did perform some temperature programmed desorption spectroscopy on materials obtained from Bernier that will be discussed later. We also continued to carry out a less formalized relationship with Bernier on the topics of carbon nanotube synthesis and hydrogen storage.

In addition to our activities with Bernier, we have interacted with others in IEA Task 12 by exchanging information and/or insight regarding technical issues of the specific research projects. In particular, it has been valuable for us to be exposed to the different experimental techniques and viewpoints offered by a group that has been historically dominated by a metal hydride perspective. On the other hand, we hope that our presence in Task 12 has provided some of the stimulation for the expansion of carbon related activities that has occurred in the past few years. Finally, our participation in Task 12 has led to a new interaction with Richard Chahine that promises to be very fruitful going forward into the new Task 17.

Technical Progress

Last year we improved our laser-based method so that material containing between 20-30 wt% SWNTs could be generated at a rate of ~ 150 mg/hr or ~ 1.5 g/day. A simple 3-step purification technique was developed that resulted in single walled carbon nanotubes of greater than 98 wt% purity [14]. A thermal gravimetric analysis (TGA) method was also developed to allow the accurate determination of nanotube wt% contents in carbon soots. We also developed a process for reproducibly cutting purified laser-generated materials. This advance was necessary since laser-produced tubes were found to be unresponsive to the oxidation methods that successfully opened arc-generated tubes. TPD spectroscopy demonstrated that purified cut SWNTs adsorb between 3.5 – 4.5 wt% hydrogen under ambient conditions in several minutes and that the adsorbed hydrogen is effectively "capped" by CO₂ [15].

This year we present the details of the cutting procedure and show that, when optimized, hydrogen storage densities up to 7 wt% can be achieved. Infrared absorption spectroscopy measurements on pristine and H₂-charged samples indicate that no C-H bonds are formed in the process. These experiments are in agreement with an earlier temperature programmed desorption analysis that showed that hydrogen molecules are not dissociated when bound to the SWNT surfaces. Only a relatively brief discussion of our progress is given here because of space constraints. A more detailed discussion is available elsewhere [10].

Hydrogen Adsorption on Cut SWNTs

Figure 1 displays the H_2 TPD spectrum of a degassed sample following a brief room temperature H_2 exposure at 500 torr. The spectrum is characterized by two separate desorption signals peaked at ~ 375 and 600 K indicating at least two different types of sites for hydrogen adsorption. The peak desorption temperatures of these signals can be as much as 100 K lower depending on the SWNT sample and the specific cutting conditions. The hydrogen adsorption capacity, as measured by calibrated TPD, was ~ 6.5 wt% on a total sample weight basis after sonication for 16 hrs at 50 W/cm^2 and degassing to 825 K. A transmission electron microscope image of the SWNT sample after cutting is shown in Figure 2. This sample was found to contain ~ 15 wt% $TiAl_{0.1}V_{0.04}$ by combusting the carbon fraction in flowing air and accounting for the oxidation of the metals. In addition to being used in the construction of ultrasonic probes, $TiAl_{0.1}V_{0.04}$ is also employed in fusion reactor components. The latter application has led to numerous studies of the interactions between the alloy and hydrogen. A maximum of ~ 3 wt % hydrogen is observed [16-18], while virtually no absorption is seen for $T < 373$ K due to poor kinetics [18]. We generated $TiAl_{0.1}V_{0.04}$ samples with the ultrasonic probe for 16 hrs in 4M HNO_3 without the addition of SWNTs. The generated particles exhibited Xray patterns consistent with the alloy found in the SWNT samples. After a normal degas and H_2 exposure, the $TiAl_{0.1}V_{0.04}$ sample exhibited only ~ 2.5 wt% hydrogen adsorption as measured by both TPD and volumetric techniques. Assuming that the alloy in the SWNT sample behaves like the pure alloy sample, the hydrogen uptake on the SWNT fraction is ~ 7.2 wt%. Samples with higher alloy contents had reduced overall hydrogen capacities, but the value of ~ 7 wt% on the SWNT fraction was relatively constant. The total adsorption capacity of the cut samples varied between 27 wt% depending on the material, the sonication power, sonication time, the hydro-dynamics of the sonication vessel and the sample degas temperature. Adjustments in these parameters also affected the temperatures of the hydrogen desorption signals, but these results will be discussed in detail later [19]. The storage results were highly reproducible within 10-20% for a given set of experimental conditions. The samples are stable to cycling with no apparent degradation when the vacuum and the hydrogen are relatively clean and the sample temperature does not exceed ~ 825 K.

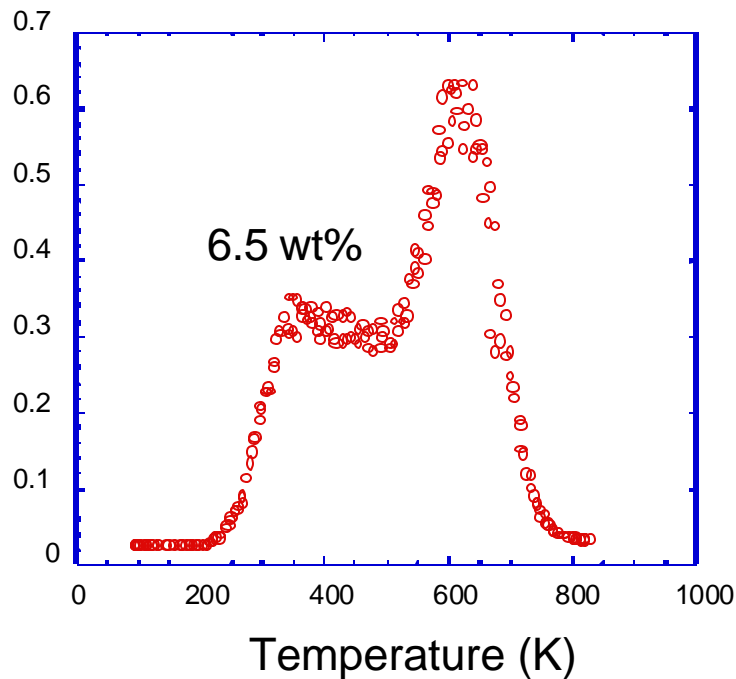


Figure 1 – Temperature programmed desorption of H_2 at 1 K/s from a SWNT sample containing 15 wt% $TiAl_{0.1}V_{0.04}$.

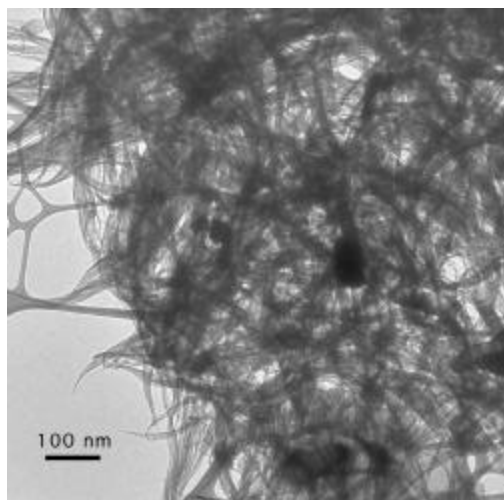


Figure 2 - Transmission electron microscope image of the SWNT sample after cutting (see text).

Mechanism of Hydrogen Adsorption

An understanding of the mechanism of hydrogen adsorption on SWNTs is critical to the growing community that seeks to utilize these materials - as well as other types of nanostructured carbons - for the storage of hydrogen. There is considerable debate over the issue in the scientific community, and it is important to obtain a deeper understanding so that (i) accurate theoretical models and predictions may be developed, (ii) specific SWNT diameters and chiralities may be targeted for synthesis and (iii) capacities and performance characteristics may be optimized. We have previously shown that hydrogen is not dissociated when adsorbed on arc-generated SWNTs even though the binding energy is 19.6 kJ/mol [5]. We recently presented infrared absorption data that shows that no C-H bonds are formed during absorption [10]. This conclusion is further supported by the first neutron scattering measurements that were performed through collaboration with researchers at NIST and the University of Pennsylvania [20]. Additional evidence pointing at the true nature of the stabilizing interaction cannot be discussed here as this work has been submitted for publication elsewhere. All in all, we find that the interaction between H₂ and single-wall nanotubes is mid-way between conventional van der Waals adsorption and chemical bond formation. A detailed understanding of the mechanism coupled with a high degree of control during synthesis should allow useful hydrogen adsorbents to be designed and constructed.

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