DOE/GO/10170--T8

Technical Evaluation Report

on

Carbon Nanotubes for Hydrogen Storage

as being studied by

The National Renewable Energy Laboratory

Prepared by:

Edward G. Skolnik
Energetics, Incorporated

Prepared for:

Sentech, Incorporated
Under
Subcontract Number 96DE-GFO01-EN1003
Prime Contract Number DE-FC36-96GO10170

August, 1997

DISCLAIMER

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Technical Evaluation Report
on
Carbon Nanotubes for Hydrogen Storage
as being studied by
The National Renewable Energy Laboratory

Background:

On June 17-18, I met with Dr. Mike Heben of the National Renewable Energy Laboratory (NREL) to discuss his research on the development of carbon nanotubes to be used for the storage of hydrogen on-board a vehicle. Dr. Heben has been working for the past several years on a project that will develop single walled nanotubes (SWNTs) composed of carbon for storage of hydrogen. Dr. Heben has spent much time trying to develop a method by which he could produce SWNTs in sufficient quantity, and then demonstrate the adsorption and desorption of hydrogen from these nanotubes at room temperature. While Dr. Heben was able to show hydrogen adsorption levels of up to 10 percent on a SWNT basis, generation of SWNTs from an arc-discharge was only about 0.05 percent of the total soot formation. Therefore, increasing SWNT concentration was a key consideration.

Summary Findings:

Dr. Mike Heben's project has made significant progress over the past year in their ability to generate nanotubes. They have built on the work of Dr. Smalley's group at Rice University, developing a process by which their production capabilities for SWNT have increased by about three orders of magnitude! In contrast to the group's former arc-discharge production method, which produced a soot containing only about 0.05 percent SWNTs, their current laser vaporization process, modeled after Dr. Smalley's work, produces materials which are 60-90 percent SWNTs.

Aside from optimizing the parameters for this process, there is still much to be done. The most significant problem is that hydrogen adsorption in these nanotubes is essentially zero. The arc-discharge nanotubes exhibited 5-10 percent hydrogen adsorption on a nanotube basis. Dr. Heben suggested two explanations for the current problem. First, many of the tubes are still capped, thus blocking adsorption. Second, the tubes produced by the laser method are so long that hydrogen adsorption is limited by the tube length. It would seem that the first explanation is more likely. Since there is essentially no hydrogen being adsorbed, it would indicate that none of the tubes are open at all. Limitations on hydrogen adsorption due to tube length would likely provide yet another problem once the tubes are decapped. Much of Dr. Heben's current efforts involve methods that will both de-cap, and shorten the tubes. Dr. Heben's theory about the difficulties of cap removal seems reasonable; that is, that the caps on the laser based nanotubes are harder to remove because they form stable, fullerene-like, C_{240} structures, while the arc-discharge nanotubes form with unstable caps.

The laser method produces tubes that, due to vander Waal's forces, are aligned parallel to one another, forming bundles. In an eventual commercial scenario, these unidirectional bundles could lend themselves for easy wrapping and incorporating into a fuel tank. Bundle formation appeared to be much more difficult using the arc-discharge method.

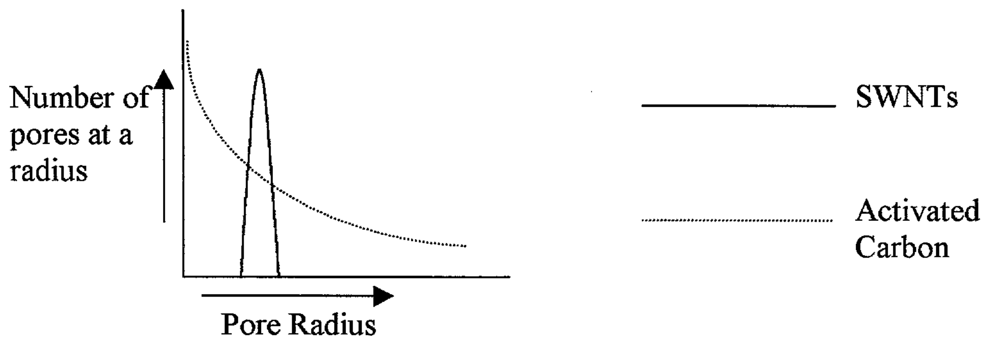
Carbon-based systems have the potential for being the lowest cost, lightweight, safe, practical approach to on-board hydrogen storage in automobiles. While Dr. Heben's claims do not approach that of the research group at Northeastern University (Northeastern claims have ranged up to 70% by weight hydrogen storage), he has demonstrated high nanotube production yields by the laser method, and reasonable hydrogen adsorption (on a nanotube basis) in nanotubes produced by arc-discharge. These results are much better documented at this time, than the Northeastern results, and they do address the DOE program storage goals.

Following the meeting, Dr. Heben spent some time in France in discussions with Dr. Bernier at the Universite de Montpellier. He later informed me that the French have discovered a high nanotube yield method using an arc-discharge method. Dr. Hebn believes that this holds promise and plans to investigate this further.

Meeting Details:

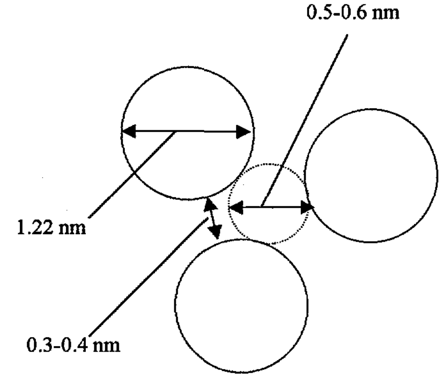
I met with Dr. Heben (and briefly with his associates Dr. Anne Dillon and Mr. Phil Parilla) on June 17-18 at his laboratory in the Solar Energy Research Facility at NREL. During that time, Dr. Heben and I discussed his project at length. He also answered several specific questions that I had prepared for him, and gave me a tour of his laboratories. I was also fortunate to be present at laser vaporization experiment on the evening of the 18^{th}, where I witnessed actual nanotube production.

The SWNT project is based on some early work performed by A.D. Little, who demonstrated the superior adsorption potential of nanotubes over activated carbon. By using heat to prepare the SWNTs to begin with, the tubes can be constructed to adsorb and hold hydrogen at room temperature. As opposed to activated carbon particles, SWNTs prepared by a particular method (e.g., arc-discharge, laser-vaporization) are uniform in pore diameters:



Pore diameter will vary according to the production method, but all SWNTs produced by a particular method under the same set of conditions will produce a single size of pore. For the arc discharge method, the tubes have a diameter of 12.2 Å; for the laser method under the current conditions, the diameter is 13.8 Å. Different experiments produce different sizes of tube. Theoretically, the larger diameter, and therefore, larger pore-volume tubes can adsorb more hydrogen, but Dr. Heben is not finding this to be true as yet. In fact, his laser-produced nanotubes are not yet adsorbing any hydrogen. Dr. Heben is attributing this in part to the fact that the laser-produced nanotubes are very long (up to hundreds of microns in length) and may be unable to effectively adsorb hydrogen up to that full length. In addition, the cap on the laser-generated nanotube may be harder to remove than its smaller counterpart. This is because a cap fitting on a 13.8 Å tube is a C_{240} molecule – a "perfect" fullerene, and therefore a stable structure. The cap fitting a 12.2 Å molecule is not as stable. Finally, vander Waal's energy between the hydrogen molecule and the nanotube will be smaller for the larger nanotubes, making them harder to fill. Dr. Heben believes that some over-pressurization during the fill step might help to overcome this third phenomenon. It will be necessary to remove the caps and shorten the tubes, however.

If one looks end-on at a nanotube bundle and considers the spacing between the tubes (being held in place by vander Waal's forces), the arrangement is somewhat like:



The laser vaporization system being used at NREL now, employs a Neodymium/ "YAG" (yttrium/aluminum/garnet) laser. The low-power (30-watt) laser produces a near-infrared (10640 Å) light beam that can operate either in pulsed or continuous mode. It impacts the target with a 50-micron spot that scans across the target. The target, a disc that is about one inch in diameter, is composed primarily of activated carbon impregnated with small amounts of nickel and cobalt catalytic material. (The activated carbon is supplied by Spectracorp, a potential partner in this activity). Another proprietary additive is used to control thermal conductivity within the target. The target is set on-end in a tube through which about 500 mm of argon gas is flowing. The laser generates a temperature of about 3500° K at the point of impact. If the thermal conductivity of the target is too high, the heat will too readily disperse throughout the target rather than remain concentrated – the necessary scenario for SWNT formation. As I witnessed the experimental procedure, I could easily see carbon "streamers" coming off the target as it was being impacted by the laser beam. Dr. Heben has analyzed the streamers via transmission electron microscopy, and has seen them to be composed largely of bundles of nanotubes. He believes that tube growth (length) is enhanced by the presence of the metal catalyst at the tube edges attracting more carbon deposition at that site. If necessary, an acid wash could be applied to the tube to remove catalysts after fabrication.

Dr. Heben sees a heat treatment step as a potential to both decap and activate the tubes. He has found that heating SWNTs to, say, 800 °K (527 °C) will result in desorption of CO, CO_2, and water. He believes, plausibly, that this is due to the decomposition of surface oxides from the cap material. In other words, the caps are being removed. The process also activates the inner surface of the tubes, making them more attractive to hydrogen adsorption.

Dr. Heben sees pressure/temperature profiles of hydrogen ad- and desorption by SWNTs as being dependent primarily on their diameter. He thus envisions several different methods of making nanotubes, each providing a different diameter tube. The tubes could then be tailored to meet the pressure/temperature needs of a particular application.

<u>Questions and Answers:</u>

Prior to the meeting, I had prepared a series of questions for Dr. Heben. These were discussed in detail:

1) *What are the differences in the methods and products for the arc-discharge Rice University laser vaporization and NREL laser vaporization methods of SWNT preparation? Compare by yield, energy use, estimated cost, SWNT size (length, hole diameter, thickness), crush and breakage properties.*

   Arc-discharge methods generally produce less than 1-2 percent SWNTs. A group in France (headed by Dr. Bernier at the Universite de Montpellier II) is reporting much higher yields (approaching laser values) using an arc-discharge approach. Dr. Heben was going to France the week after our meeting to meet with Dr. Bernier.
   Dr. Smalley at Rice University is now routinely making 80-90 percent nanotubes using a laser discharge method under certain controlled conditions, and is approaching 100 percent yield in some cases. Dr. Smalley uses a pulsed laser, and preheats his target to about 1200° C to change its thermal conductivity properties. Even so, this process requires periodic down time so that amorphous carbon can be physically scraped off the target.

   The NREL process, as previously mentioned, operates the laser in both pulsed and continuous mode. It controls thermal conductivity via a proprietary additive that creates porosity within the target. The system is at room temperature and is much less energy intensive. Yields are nominally at the 60 percent level, although yields as high as 90 percent have been reached.

NREL has also looked at tube preparation in their solar furnace, but they find that they have a problem with the thermal conductivity of the target with this approach.

All of the nanotubes discussed are single-walled tubes (that is, single molecule thickness) having the same thickness and nominally the same crush strength.

2) *What pressures are needed for the room temperature ad- and desorption of hydrogen?*

Currently, all hydrogen sorption work has been run at one atmosphere. The laser-generated tubes are not adsorbing hydrogen at the expected level yet. This is probably due to the tubes being too long, and/or not having had their caps adequately removed yet. Dr. Heben anticipates that the tube length problem might be overcome with pressure of a few hundred psi.

Comment: As pointed out earlier, the problem with hydrogen adsorption is more likely due to failure to remove caps rather than tube length. It is likely, however, that once the cap problem is solved, a tube length problem will manifest itself. Tube shortening may be a better solution than overpressurization.

3) *How are the problems of tube shortening, cap removal, and eventually packing the SWNTs into a tank being addressed?*

Decapping and shortening of the nanotubes is being addressed by two methods: high power sonification, and ultraviolet photooxidation. Early results are showing that both methods are "damaging" the tubes, especially the UV method. It is known that UV photons damage fullerenes, and the SWNT caps are fullerene-like. It is hoped that this damage can be converted to actual decapping and tube cutting. Some of the longer tubes are now hundreds of microns long. Dr. Heben would like to see much shorter tubes – perhaps one micron in length.

Dr. Heben envisions a bundle of nanotubes all lined up in a brick-like formation, held in place with a surfactant, and wrapped into a tank-like structure. He is also considering looking at an alternate technology in which a template material is created containing a system of holes. A metal catalyst film is placed on one side of the template, and carbon nanotube bundles are precipitated into the holes. The details of the concept of a macroscopic organization of nanotubes are considered proprietary.

4) *What are the proposed mechanism differences for hydrogen take-up and discharge between the arc-discharge SWNTs and the laser vaporization-formed nanotubes?*

There is probably not a mechanistic difference; degree of hydrogenation apparently depends on both tube diameter and length. (This has already been discussed earlier in this report.)

5) *How do the size of the nanotube caps compare to the length, and are there any cases where a significant portion of the tube length is in the cap?*

As mentioned earlier, even the shortest tubes are about a micron (1000 nanometers) long. The caps are of fullerene dimensions, 2-3 orders of magnitude smaller.

6) *One of the reports from NREL on nanotubes described an attempt at cap removal by a hydrogen-based reduction method involving high temperature and pressure. It appeared that the tubes became hydrogenated during the process. Was the decapping attempt successful as well?*

No. It appeared that the hydrogenation occurred on the outside walls of the SWNTs only, and that the caps were not removed during this process.

Comment: This could indicate the possibility of increased hydrogen loading, if hydrogen can be adsorbed onto the outside of the tube as well.

7) *Is there any information yet available on the effect of repeated recycling of the ad- and desorption process?*

There have not been many attempts yet at this aspect of the process. The low (one atmosphere) pressure runs did not appear to cause degradation of the tubes. The attempt to remove caps via the reduction method discussed above in Question 6 did not appear to cause any damage to the tubes either.

8) *Two of the items proposed as future work for this project involve arc discharge in the NREL solar furnace and looking at polyacrylonitrile decomposition. What are the goals of these studies?*

Both the present arc-discharge and laser vaporization methods are energy intensive. If the solar furnace can be used it would be significantly cheaper.

Polyacrylonitrile decomposition is a precursor to the formation of the template material addressed in Question 3.

9) *If effort is placed on shortening of nanotubes, doesn't this actually result in decapping as well?*

Yes, but cutting itself is a problem. In fact, Dr. Heben hopes to use the knowledge gained in cap removal to develop cutting techniques. The cap is less stable than the tube walls, and it therefore should be easier to decap than to cut.

Comment: And this may be fortuitous. Decapping seems to be the key.

10) If the laser (or another) process were deemed to be most effective at less than a total conversion to SWNTs (for instance, the 60 percent conversion that is currently indicated for laser vaporization) would the non-nanotube fraction be removed? How would it be done?

The amorphous carbon would be removed, most likely by a gentle oxidation process. Since the amorphous fraction is much less stable, this would be a low energy process. In addition, remnants of metal catalyst would be removed, if necessary, by a vapor transport method, or by acid washing.

11) Are the reported hydrogen take-up percentages based on hydrogen-to-carbon values only, or is the weight of a container also taken into account?

The estimates for hydrogen take-up are on an installed basis. Dr. Heben believes 5 percent hydrogen on an installed basis is possible. This works out to a density of about 50 kg hydrogen per cubic meter.

Comment: This works out to approximately a 16 gallon tank being able to hold about 3 kg of hydrogen – or about a 300 mile range for an advanced system. Not unreasonable.

12) A reviewer at the Annual Hydrogen Review suggested that cap removal might be possible by a ball milling process. Is this at all plausible?

It does not appear doable. The grinding medium is so much larger that the nanotubes, that it is unlikely that ball milling would have any effect. Dr. Heben feels that chemical methods such as cap oxidation are much more likely to succeed. He will make the attempt at ball milling, however.

Comment: Perhaps this may be doable after all. Grinding media are generally much larger than the material to be ground.

13) How would you envision a commercial product?

Dr. Heben sees bundles of aligned nanotubes of a pre-selected diameter being extruded into thin sheets. The sheets would then be stacked, forming a "box", maybe a cube. The stack would be enclosed in a lightweight material, maybe aluminum. The system would be installed on-board and filled with hydrogen from a pressurized source. Hydrogen would be removed using either a small electric heater, or simply its own head pressure. As hydrogen was removed, more would come out of the nanotubes to replace the head pressure. Nanotube diameters could be tailored for operation at or near ambient temperatures.

Comment: Once the nanotubes and their hydrogen take-up are perfected, this is going to be the next big challenge.

Final Thoughts following the Visit

I see the following as the biggest positives to the nanotube project:

- The nanotube yield has been dramatically increased.
- Dr. Heben and his staff are well versed in the multitude of disciplines needed to carry out this project.
- NREL has the proper production and diagnostic equipment to facilitate the project.
- Collaborations with other researchers, especially Dr. Smalley at Rice provides a large added value.
- Dr. Heben's projected 5 percent hydrogen of total storage-system weight with room temperature operation meets the DOE Hydrogen Program goals.
- Carbon nanotubes provide a lightweight, moderate pressure, room temperature method for storage of hydrogen in automobiles. It could be the best way to get there!

The following are areas that need to be watched closely:

- I consider the biggest short-term priority for the project to be the ability to decap the tubes. Closely aligned with this is the affirmation of the fact that the lack of hydrogen take-up is in fact due to caps rather than, say, an activity problem based on the method of nanotube production or catalyst form.
- Once hydrogen take-up has been regained, a prime objective should be pressure, temperature, and importantly, recycling data gathering on the system.
- Tube length may limit hydrogen adsorption levels, but I don't think this has been shown experimentally yet. At any rate, tubes probably do need to be shorter to make them more commercially viable.
- The use of the solar furnace and other different methods of producing nanotubes may be of interest, but it should not be a primary focus. It could detract from what I believe to be the main objective (the ability to repeatedly adsorb and desorb hydrogen by laser-generated nanotubes).

Additional Comments Added Later:

Following our visit to NREL, Dr. Heben flew to France to meet with Dr. Bernier at the Universite de Montpellier. He has indicated that Dr. Bernier's group has developed a method of arc-discharge production that yields SWNTs in the same quantity as the laser vaporization method (60-90 percent). In addition, it produces them at a rate that is an order of magnitude more rapid. "Several grams per hour" was mentioned. Dr. Heben is planning to collaborate with Dr. Bernier.

The French arc-discharge method would, I presume, (although not confirmed) provide the smaller diameter (12.2 Å) nanotubes that would be easier to decap due to the caps' less stable, non-fullerene structure. This would probably lead to better hydrogen adsorption.

The near-term affirmation of SWNTs that can both be produced in high yields, and can adsorb 5+ percent (total system weight) of hydrogen is critical to this project. It would therefore appear that the French method is worth considering. Decapping the laser-produced SWNTs remains a top priority in my view.