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Technical Evaluation Report

on
Hydrogen Storage in Carbon Nanofibers

as being studied by

Northeastern University

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Background:

On December 10, 1996, I met with Drs. Terry Baker and Nellie Rodriguez at Northeastern University in Boston, MA. This was part of the technical evaluation of carbon-based hydrogen storage projects being performed by Energetics. Dr. Baker's team had recently relocated to Northeastern (from Penn State) and were working on the manufacture of graphitic carbon nanostructures and their subsequent use as a storage medium for large quantities of hydrogen. In an initial proposal to DOE, Dr. Baker's team claimed (while they were at Penn State) that theoretically, their platelet graphitic material was capable of chemisorbing a monolayer of hydrogen on all carbon surfaces. This, they claimed, (apparently assuming planar graphite and hydrogen at the molecular level) could result in a total monolayer presence of over ten liters of hydrogen per gram of carbon. At the time, however, they were able to show only the higher retentive abilities of the fibers as compared to active carbon at liquid nitrogen temperatures. The overall reported chemisorption by the fibers at that time was only about 20 cc per gram of carbon -- almost two orders of magnitude lower than their theoretical claim. When they moved to Northeastern, they resubmitted their proposal and included some additional data. The most significant addition was their claim to have chemisorbed and retained 5.8 liters of hydrogen on one gram of carbon. This amounts to about 1/2 gram of hydrogen on every gram of carbon at STP, a truly remarkable claim!

As part of the current Energetics technical evaluation effort, I was tasked with going to Northeastern, interviewing Dr. Baker and his team, seeing a demonstration of the storage process, and making an assessment of the validity of the claim and the soundness of the research.

Summary Findings:

Dr. Baker and his group have a process that, if proven to work, could be the breakthrough that is needed in the area of on-board hydrogen storage. One of the biggest problems may be the fact that the results look so good, that even if they are real, they will be viewed with skepticism by many. The chemisorption value of 5.8 liters of hydrogen per gram of carbon that Dr. Baker claimed at the time of his proposal has now been surpassed many times. Dr. Baker has reported reproducible hydrogen take-up levels as high as 30 liters per gram, depending on fiber structure. The fibers are loaded with hydrogen at ambient temperature using a pressurized feed at levels of about 600-900 psi. The hydrogen will be retained at pressure, but can apparently be essentially totally recovered upon pressure release.

I believe that the Northeastern group should perform a proof-of-concept study. There is no need, at this time to optimize the nanofibers or catalyst past the point that has already been

done. Reproducible results of 5 or 10 liters hydrogen per gram of carbon, would certainly be enough to work with at this point. What Dr. Baker could do is:

- Pick one of his "good" fiber configurations and characterize it as to cyclic sorbency and release of hydrogen. Demonstrate the reproducibility; show that the fibers are robust.
- Show that he can make fibers in reasonable quantity (say 100 grams) that exhibit the same ability to chemisorb hydrogen.
- Run a demonstration in which they can show a small prototype system (maybe a vessel 50-100 cc in volume.) The hydrogen would be loaded, the vessel disconnected from the source, a value for increased weight of the system obtained directly, the vessel stored off line for a predetermined time, maybe a day, and then the hydrogen is released. The purity and quantity of the hydrogen can then be measured independently.

If Dr. Baker is able to show that he has a viable system, then he can look at optimization at a later time. The important thing to see is: can he indeed store previously unheard of quantities of hydrogen in this manner, and are the fibers sufficiently robust for recycling without decay of capacity.

The rate of hydrogen take-up is slow at the present time and Dr. Baker plans to try some runs at elevated temperatures (maybe raising 100-200° C) to increase the diffusion rate. This is not viewed as necessarily critical, however, if, for instance, the total hydrogen capacity can be made high enough to provide thousands of miles of range rather than hundreds. In such a case, the fuel tanks might be able to be made of a modular design with take-up rate not being a critical issue.

Trip Details

I met with Dr. Baker and his associate, Dr. Nelly Rodriguez, for several hours on December 10, 1996. During that time, the two Northeastern researchers made a more-or-less formal slide presentation (a hard copy of the presentation was requested, but never provided), ran a demonstration of a hydrogen chemisorption run, and spent several hours discussing their project. I had previously sent Dr. Baker a list of several questions, and these formed the basis for part of the discussion.

Presentation

Originally, the researchers, being catalysis experts, were trying to learn what they could about the mechanism for the formation of carbon structures, to prevent unwanted coking of catalysts. Thus, they learned how these structures grow, and from this, began to grow them intentionally. The hydrogen sorption properties were also found by accident, when during a calcining operation involving the nanofibers, the researchers found an unexpected rise in temperature, which they

later determined was due to adsorbed hydrogen. The catalysts are proprietary, but are generally either nickel- or iron-based. They are structured to provide a large amount of "edge sites" for deposition of graphitic carbon. Another feature is the presence of an additional "add-an-atom", a proprietary modification to the catalytic surface that electronically enhances the adsorption surface for graphite deposition. The fibers are formed by passing a hydrocarbon such as ethylene, possibly with some hydrogen or some CO added, over the catalytic surface at a predetermined temperature (in the 600° C range). In this way, the catalyst acts more or less like a mold for the forming carbon material. The fibers take on a graphitic platelet-like structure with a spacing between the platelets of about 0.34 nanometers (nm). The spacing is thus selective for the insertion of hydrogen molecules (which have a kinetic diameter of 0.29 nm), while being too small for other molecules. The catalyst is then later removed by acid washing.

The fibers are generally somewhere between 10 and 100 microns in length and have an average diameter of about 5 nm, but the largest can have a diameter of about 100 nm. While the fiber packing density varies, being dependent on various preparation properties, a measurement on a sample was performed at METC, and was found to be about 0.8 grams/ cubic centimeter.

Dr. Baker feels the main advantage that his nanofibers have over nanotubes is that there are fewer access points for hydrogen to get into the nanotube when compared with the fibers, which have openings between platelets at each edge.

Two independent cost analyses have been performed, one by Exxon and one by Hyperion Catalysis. They both concluded that in mass-production, the nanofibers would cost about \$1.50 per pound, and certainly less than \$2 per pound.

Demonstration

The demonstration, performed by a postdoctoral student, was very straightforward. About 0.1 grams of the nanofibers had been pre-placed into a small chamber attached to but valved off from a gas-handling system. The system, which could be monitored by a pressure transducer, had been evacuated. A tank of hydrogen was opened to the gas-handling system, resulting in a pressure of a little over 1500 psi. The hydrogen tank was shut off, and the pressure allowed to stabilize within the gas-handling system. The valve to the fiber chamber was opened, resulting in an instantaneous drop to about 1490 psi (due to the additional exposed volume). From this point on, the pressure in this closed-off, constant-volume system dropped steadily. At the end of about three hours, it was down to about 900 psi. The only place the hydrogen could go was into the fibers. The post doc indicated that based on the rate of pressure drop, this particular run would result in a hydrogen sorption of about 30 liters per gram of carbon fiber.

The research group has performed several other runs on various fiber structures as well as on some non-nanofiber material such as active carbon and alumina. A plot of some runs for various nanofiber structures as well as active carbon and alumina is attached. The two things that we need to see is that 1) there is obvious hydrogen sorption with the nanofibers, but not with the other materials, and 2) the hydrogen take-up takes a long time. These items are addressed in the discussion.

Questions and Additional Discussion

The questions sent to Dr. Baker together with their answers are presented here. These questions were based on my reading the technical portions of the two proposals to DOE.

1. The claimed theoretical monolayer storage capacity for hydrogen of 10.368 liters per gram of carbon is based on a 100x100-ring model of graphite containing 44,100 carbon atoms. A diagram in the proposal shows hexagonal rings in which each carbon atom is shared by three rings. Thus, there are $6/3 = 2$ carbon atoms per ring, and a 100x100 array of rings would only contain about 20,000 carbon atoms.

Dr. Rodriguez indicated that her initial calculation was incorrect, and the 100X100 array would contain close to 20,000 carbon atoms rather than 44,100. Therefore, the theoretical monolayer capacity for hydrogen would be closer to 6.5 liters per gram of carbon. (This was close to the number that I had calculated independently, assuming Dr. Bakers assertion of planar graphite and hydrogen at the molecular level.)

Comment: The 6.5 liters per gram is interesting in that it assumes that both carbon and hydrogen are planar on a molecular level, and that the coverage is total. Calculations using more likely packing densities for hydrogen under these conditions would result in much lower coverage – perhaps about 0.7 liters per gram of carbon. Of course, the fact that the researchers have apparently found far more than monolayer capabilities makes the point somewhat moot. The researchers do not yet understand why their results are so good. They speculate that the hydrogen molecules must be reorienting into a more favorable form (and potentially condensing) within the platelet structure. Capillary action (similar to nanotubes) may also be a factor.

2. If the inter layer spacing of 0.34 nm between platelets is ideal for selective hydrogen sorption, what is the rationale for developing larger spacings in multiples of 0.34 nm?

Selectivity may not be as much as an issue as overall loading. The wider spacing may increase the hydrogen loading as well as the diffusion rate.

3. How structurally sound are the nanofibers to begin with, and how much is their ability to sorb hydrogen bound to their structural integrity?

The researchers believe their fibers to be “very sound” structurally. They have run at least two cycles with some fibers and found no breakdown in take-up properties or in structure.

4. A figure was presented showing comparative sorption/desorption properties for the nanofibers and activated carbon at -196° C. While the percentage retention capabilities for the nanofibers are obviously superior, the curves also show that the activated carbon will sorb more hydrogen at high pressures, and that both materials appear to have the same absolute retention abilities at ambient pressure (about 20 cc/ g carbon). Is there any data similar to the sorption/desorption curves at the sorption levels now being obtained at room temperature (5.8 liters of hydrogen/ g carbon)?

When active carbon was used, there was virtually no hydrogen take-up in the system at room temperature. Curves were provided, and are attached here.

5. Why would spiral fiber structures produce higher hydrogen loadings?

The researchers believe that the slightly irregular structure that one would get from a spiral fiber (different spacings at the edges and centers of the platelets) will lead to higher loadings. They have seen that non-uniform spacing of their standard fibers leads to higher loading.

Comment: While this may be true, it is probably a non-essential optimization process, and should not be a part of a near-term proof of concept study.

6. What are the variables in fiber structure determination (temperature, catalyst, etc.)?

Temperature, catalyst, the “add-an-atom” portion of the catalyst, and hydrocarbon gas mixture all are important variables.

7. Do any volumetric packing data for the nanofibers exist?

As mentioned above, METC data shows an average of about 0.8 grams of fiber per cc.

Other discussion topics yielded the following:

- One of the keys to the high take-up levels is the fact that the carbon is graphitic. It's probably the π electron interaction on the graphitic structure that allows interaction with the hydrogen electron cloud. Dr. Baker referred to the unsuccessful Syracuse University carbon storage process as one that used amorphous carbon.
- The researchers have not yet identified the threshold pressure for sorption and desorption. They would like to build an apparatus to determine this.
- Dr. Baker raised another possibility: if they used a feed gas consisting of methane and CO₂, they may be able to simultaneously make nanofibers and hydrogen.

Comment: This is an interesting thought, but probably not of short-term importance.

- When they make fibers, it's “100% fibers,” and they have a homogeneous structure.

Comment: This was said so as to compare it to the carbon nanotubes being researched at NREL. At the time of the visit to Northeastern, NREL was having trouble producing nanotubes in anything more than a fraction of a percent conversion.

- The highest hydrogen loading attained was 3.32 grams hydrogen (37.2 liters) per gram of

carbon (76.9% by weight). They can "routinely" get 1.5 grams (17 liters) per gram of carbon (60%).

- Drs. Baker and Rodriguez have formed a small business, Catalytic Materials, Limited. They are looking for partners in this potential business venture, perhaps one company to produce the catalysts in mass quantity and another to make the fibers.

Some Additional Comments (written at the time of the visit).

The levels of hydrogen loading being claimed here are almost too good to be true, and are therefore naturally looked at with understandable skepticism. As a first round "sanity check", the visit to Northeastern could provide no obvious answer as to the manner in which the researchers could have obtained erroneous results. There was nothing in the experimental work that looked either incorrectly performed or measured. It should be mentioned that we are talking only about the ability of the fibers to take-up hydrogen. No demonstration was provided at that time on fiber production, hydrogen desorption, or recycling capabilities. No leaks were observed, pressure decrease was readily monitored, and data was provided showing that these results were unique to nanofibers. Activated carbon demonstrated no take-up.

If these high loadings are indeed real, the possibility exists for a totally different route toward on-board storage, and refueling: modular "quick-connect" fuel tanks. Fibers are packed into a tank capable of withstanding, say 1000 psi pressure. Hydrogen is loaded into the system at a refueling depot. The driver picks up the filled tank, and drops off an empty one, much as one would a propane tank. Depending on how robust the fibers are, the tank can be filled and emptied several times. Depending on the hydrogen loading, the driving range may be measured in thousands of miles instead of hundreds.

To put these levels of hydrogen loading into perspective, let's take an "intermediate" case of 10 liters per gram (and one well below the 17 liters the researchers claim they can routinely obtain):

At STP, 10 liters of hydrogen is equivalent to 0.89 grams of hydrogen.

$(10 \text{ liters}) \div (22.4 \text{ moles/liter}) \times (2 \text{ gram H}_2 \text{ per mole}) = 0.89 \text{ grams H}_2 \text{ per gram of carbon.}$
On a percentage basis, this is $0.89 \div (1 + 0.89) = 47$ percent by weight hydrogen. (The nanotube project researchers claim that they can get 6.5% hydrogen by weight in a system, and that is in a system where all the carbon is in nanotube form.)

Independent measurements at METC performed on the nanofibers have shown average carbon packing densities to be about 0.8 grams/ cubic centimeter. Thus, the hydrogen concentration is:

$$(0.89 \text{ grams H}_2 \text{ per gram of carbon}) \times 0.8 \text{ grams carbon per cubic centimeter} \\ = 0.72 \text{ gram H}_2 \text{ per cc}$$

If we use Gene Berry's number of a 300 mile range fuel-cell powered vehicle requiring a tank

containing 3.75 kg of hydrogen, a tank of hydrogen stored in the Baker system, would only be 5.2 liters (1.37 gallons) in volume. A 10 gallon-sized tank of hydrogen would have a range of over 2100 miles!

Depending on hydrogen loading, fiber strength, and tank parameters, the options for the mode of fueling are numerous.

The important thing is to keep the project focused on a rapid proof-of concept. The researchers need to affirm their hydrogen loading, demonstrate the recycling parameters, show reproducibility, and if it still appears to be real, scale it up into a fuel cell vehicle demonstration.

Additional Comments Added at the Time of Submission of this Report

This project has become the subject of much disagreement and controversy over the past few months:

- The researchers were interviewed by the *New Scientist* in December 1996, and their claims were disputed by others in the same article.
- The Northeastern claims were featured as the lead article in an issue of *The Hydrogen and Fuel Cell Letter* in February 1997.
- During the 1997 National Hydrogen Association meeting, the Northeastern research was mentioned several times, including a presentation in which its authenticity was questioned.
- Representatives from industry have visited Northeastern, seen a demonstration, and have reportedly more-or-less mixed opinions.
- Drs. Baker and Rodriguez have reportedly been offered support from a "German Company."
- The project has recently received funding from the DOE Hydrogen Program.

Among some of the questions raised concerning the experimental procedure being used by the Northeastern group, were comments that hydrogen take-up was overestimated. This was due to the fact that the metal vessel was being pacified by hydrogen and/or that there was a leak in the system caused by a piece of filter paper protruding through a joint in the vessel. Pacification is an unlikely explanation, as it would have resulted in false take-up readings into activated carbon as well as into the nanofibers. The accompanying figure shows that this did not happen. The filter paper issue is a harder one to rebut, as the paper was reportedly only present when the nanofibers were being used. It was apparently used in conjunction with the preparation of the nanofibers, but was not used in the case of activated carbon. Nevertheless, I observed no filter paper protrusion during my visit. Further, it is unlikely that the problem would occur with every run involving nanofibers.

Regardless, a proof of concept study, at a somewhat larger scale would end the matter. If an error is present, it will be found. If the claims are valid, the overall way in which we view hydrogen on-board storage will change.