Doped Carbon Nanotubes for Hydrogen Storage

Ragaiy Zidan (Primary Contact), Apparao M. Rao, Ming Au

Hydrogen Technology Laboratory
Savannah River Technology Center (SRTC)
773-41A/ 247
Savannah River Site
Aiken, SC 29808
Phone: (803) 725-1726; Fax: (803) 725-4129; E-mail: ragaiy.zidan@srs.gov

DOE Technology Development Manager: Sunita Satyapal
Phone: (202) 586-2336; Fax: (202) 586-9811; E-mail: Sunita.Satyapal@ee.doe.gov

Objectives

Develop reversible high-capacity hydrogen storage material to meet the DOE goals for a hydrogen storage system:

- Hydrogen capacity greater than 6 wt.%
- Favorable thermodynamic and kinetics suitable for transportation applications
- Stable with hydriding/dehydriding cycling

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- M. Hydrogen Capacity and Reversibility
- N. Lack of Understanding of Hydrogen Physisorption and Chemisorption
- O. Test Protocols and Evaluation Facilities
- P. Dispensing Technology

Approach

- Produce large quantities of consistent structure carbon nanotube material
- Attempt to create a weak covalent hydrogen bond, dihydrogen
- Dope carbon nanotubes with transition metals and alloys
- Dope carbon nanotubes with other elements and metal clusters
- Tune material for hydrogen sorption to occur at desired temperature and pressure

Accomplishments

- Synthesis of material was achieved with:
  - Different dopants
  - Different quantities of dopants
  - Different diameters and configurations
- Thermodynamic and material characterization were conducted by:
  - Setting up a high pressure thermovolumetric (TVA) system

- Measuring the hydriding and dehydriding of material
- Examining nanotubes with cycling
- Spectroscopic analysis of product was performed

Future Directions

- Continue production of nanotubes with different dopants
- Determine thermodynamic characteristics of hydrogen uptake and release
- Identify the type and size of nanotubes and clusters that result in a reversible, high hydrogen capacity material
- Tune conditions to result in a high yield of material possessing favorable characteristics
- Utilize theoretical modeling to guide the experiment

Introduction

The absence of a practical means for hydrogen storage has been a major obstacle in the transition to a hydrogen economy. Developing a solid-state hydrogen storage system that meets the DOE objectives has been the goal of researchers for years. Unfortunately, the extensive work in the area of conventional metal and intermetallic hydrides did not result in materials suitable for on-board hydrogen storage. Carbon nanotube technology represents a new direction for solid-state hydrogen storage, especially if these materials can be altered to store large amounts of hydrogen at room temperature. Persistent research activities, worldwide, have been exploring the use of carbon nanotubes for hydrogen storage [1-5].

This research is taking into account the barriers that face the development of a hydrogen storage system in general as well as taking into account problems that are inherent to carbon nanotube technology. This research is focused on modifying carbon nanotube systems in an attempt to enhance and tune the hydrogen storage capabilities of the nanotubes. The objective of this research has been to introduce transition metals and hydrogen bonding clusters into the nanotubes. The intent is aimed at producing consistent size dopants and structures of carbon nanotubes to avoid inconsistency in measurements. The success of making doped carbon nanotubes with transition metals and alloys can allow for a weak covalent bond similar to cases of dihydrogen bond that is not restricted to pure physisorption or chemisorption bond [6,7]. Controlling the type and size of tubes and dopant is expected to tune the product for hydrogen sorption to occur at desired temperature and pressure.

Approach

Our research is focused on modifying carbon nanotubes by doping them with different atoms and encapsulating metal clusters inside the tubes to make them suitable for hydrogen storage. Relying on physisorption alone will lead to a bond that is too weak, and chemisorption will lead to a bond that is too strong. Therefore, our objective is to establish a weak covalent bond where the electron donation from the (s) orbital of hydrogen to the doped tubes weakens but does not break the hydrogen-hydrogen bond.

The method of producing doped carbon nanotubes with controlled characteristics is a method developed at SRTC and is in the process of being patented. Thermodynamic characterization of hydrogen uptake and release will be conducted. Different spectroscopic methods are applied to identify the type and size of nanotubes and clusters that could result in a reversible high hydrogen-capacity material. Collaboration with academia and other government laboratories has been established.

Results

The synthesis of different doped carbon nanotubes has been achieved using SRTC technique that allowed for controlling the type and amount of dopants in the tubes. It was possible to produce large quantities of consistent structure carbon nanotube systems (see Figures 1 and 2). Preliminary results of hydrogen sorption showed 1% by weight hydrogen uptake and release. A thermogravimetric (TGA) system capable of operating at a wide range of temperatures was used to measure hydrogen uptake and release. Nitrogen doped carbon nanotubes, with average nitrogen content of about 5 wt. %, were also synthesized (see Figure 3).

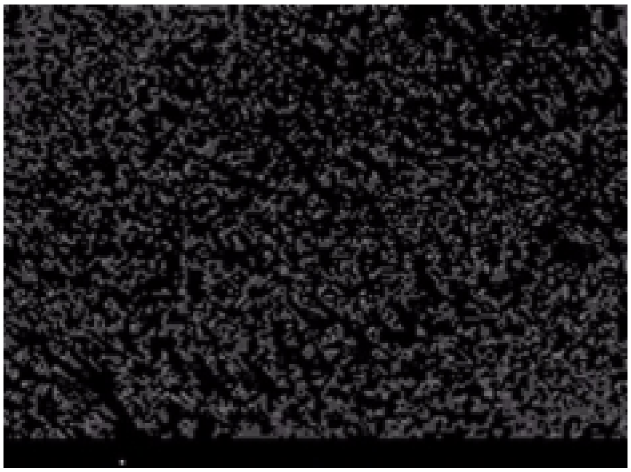

Figure 1. Consistent Structure Doped Carbon Nanotubes

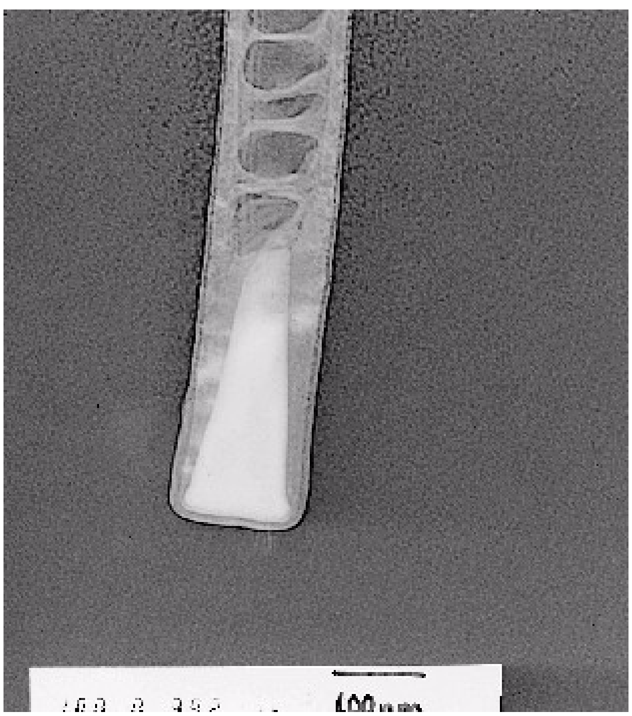

Figure 2. Tip of a Nanotube with Encapsulated Metal Particle

Conclusions

Although more investigation is needed to identify the type of hydrogen bond with the carbon nanotubes, the preliminary results look encouraging. One of our goals has been to synthesize nanotubes containing other elements such as boron or nitrogen, largely due to the possibility of fabricating nanotube materials with tailored electrical and mechanical properties. This goal was achieved as nitrogen doped carbon nanotubes were synthesized [8].

References

1. A. C. Dillon, K. M. Jones, T. A. Bekkedahl, C.H. Kiang, D. S. Bethune and M.J. Heben Nature, 386 (1997). 377.

2. Y. Ye, C.C. Ahn, C. Witham, B. Fultz, J. Liu, A.G. Rinzler, D. Colbert, K.A. Smith, and R.E. Smalley, Applied Physics Letters 74, 2307 (1999).

3. C. Liu, Y.Y.Fan., M. Liu, H.T. Cong, H.M. Cheng, and M. Dresselhaus, Science 286, 1127 (1999).

4. P.,Chen, X. Wu, J. Lin, and K.L. Tan, Science 285, 91 (1999).

5. R. Chahine and P. Bénard, IEA Task 12: Metal Hydrides and Carbon for Hydrogen Storage 2001.

6. G.J Kubas, R.R. Ryan B. I. Swanson, P.J. Vergamini, and .J. Wasserman, J. Am. Chem. Soc. 106, 451 (1984).

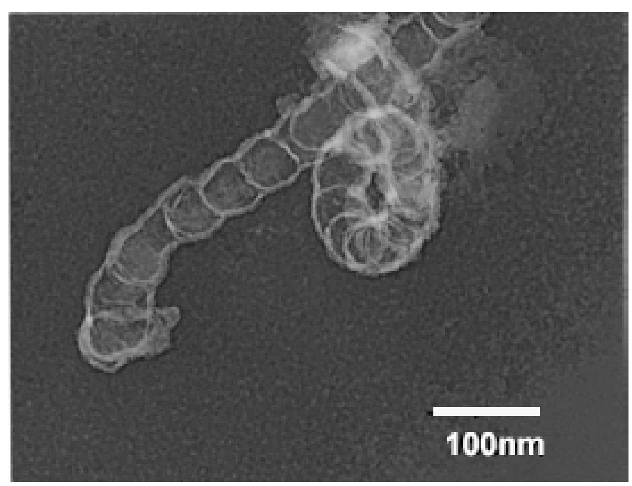

Figure 3. Nitrogen-doped Carbon Nanotube

7. G.J. Kubas, Acc. Chem. Res. 21, 120 (1988).

8. B.Sadanadan a, T. Savage a, S. Bhattacharya a, T. Tritt a, Alan Cassell b, M. Meyyappan b, Z.R. Dai c, Z. L. Wang c, R. Zidan d and A. M. Rao a, J. nanoscience and nanotechnology, 3 99 (2003).

FY 2003 Publications/Presentations

1. "Synthesis and Thermoelectric Power of Nitrogen Doped Carbon Nanotubes"
2. B.Sadanadan a, T. Savage a, S. Bhattacharya a, T. Tritt a, Alan Cassell b, M. Meyyappan b, Z.R. Dai c, Z. L. Wang c, R. Zidan d and A. M. Rao a, J. nanoscience and nanotechnology, Volume: 3 Number: 1, 99 - 103 (2003).

Special Recognitions & Awards/Patents Issued

1. Patent disclosure has been submitted, on producing and controlling the characteristics of doped carbon nanotubes