Go/No-Go Decision:

Pure, Undoped Single Walled Carbon Nanotubes for Vehicular Hydrogen Storage

October 2006

United States Department of Energy

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Pure, Undoped Single Walled Carbon Nanotubes for Vehicular Hydrogen Storage
U.S. Department of Energy (DOE) Hydrogen Program

October 30, 2006

The following is the DOE Hydrogen Program's decision, arrived at from a review of input received through a Federal Register Notice[1], review of the open literature and information from technical and professional society public meetings, and technical feedback from both the FreedomCAR and Fuel Partnership Hydrogen Storage Technical Team[2] and the DOE Carbon-based Materials Center of Excellence[3].

> The DOE Hydrogen Program has decided to discontinue (a "No-Go" decision) future applied research and development (R&D) investment in *pure, undoped single walled carbon nanotubes (SWNTs)* for vehicular hydrogen storage applications. This decision is based on the previously established criterion that pure, undoped SWNTs have not met; achieving 6 weight percent hydrogen storage (on a materials basis) at close to room temperature. *However,* there are certain areas of carbon nanotube research, such as metal-doped hybrid materials, that may warrant additional R&D investment.

Criteria used to make decision

DOE reviewed the current status and results of carbon nanotube research activities and evaluated data against technical criteria, basing its SWNT go/no-go decision on an analysis of:

1. The technical progress to date on the demonstrated capacity for hydrogen storage in pure, undoped carbon SWNTs and whether SWNTs have met the criterion of 6 weight percent hydrogen storage (on a materials basis) at room temperature,
2. Whether a technically viable pathway exists to meet the original criterion of 6 weight percent at room temperature using either pure, undoped SWNTs or a "hybrid" approach (e.g., metal doped nanotubes).
3. Whether hydrogen adsorption on carbon nanotubes at low temperature (77K) should be considered at this early stage of the DOE Hydrogen Storage Program (although the original criterion of 6 weight percent was at room temperature), and

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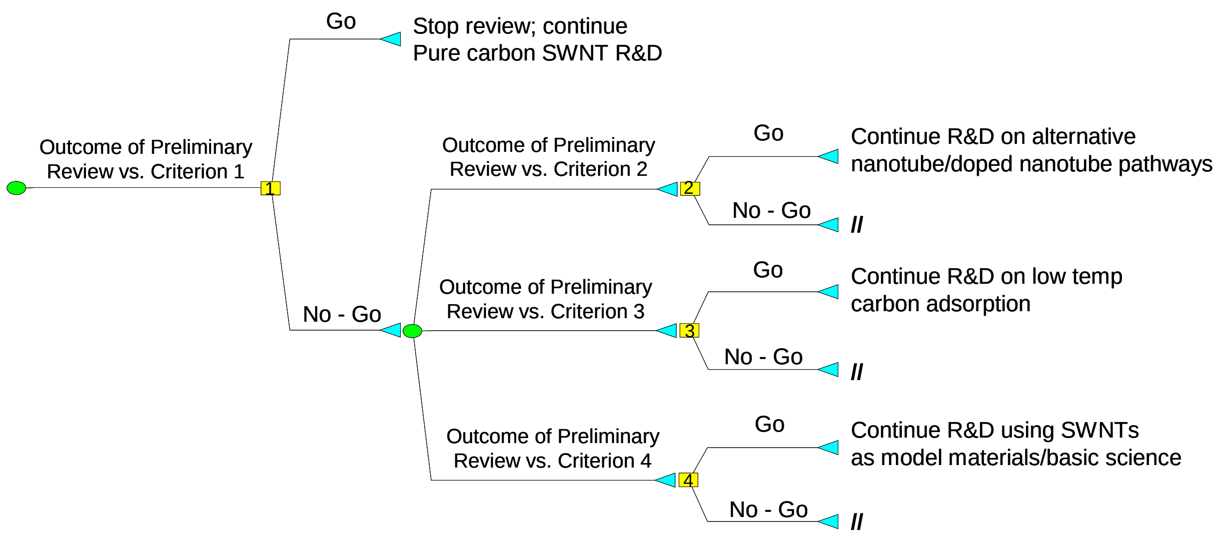
[1] Federal Register Notice, Vol. 71, No. 164, Thursday, August 24, 2006, page 50052.
[2] The FreedomCAR and Fuel Partnership Hydrogen Storage Technical Team has technical expert representatives from General Motors, Ford Motor Company, DaimlerChrysler, ConocoPhillips, Shell, Chevron, Argonne National Laboratory, Sandia National Laboratory-retired and DOE.
[3] The following institutions constitute the DOE Carbon-based Materials Center of Excellence: National Renewable Energy Laboratory, Air Products and Chemicals Inc., California Institute of Technology, Duke University, Lawrence Livermore National Laboratory, National Institute of Standards and Technology, Oak Ridge National Laboratory, Pennsylvania State University, Rice University, University of Michigan, University of North Carolina-Chapel Hill, and the University of Pennsylvania.

4. Whether SWNTs may be used as model materials for fundamental research, theoretical simulation and an improved understanding of nanoscale hydrogen storage mechanisms and the interplay between factors such as hydrogen charge/discharge efficiency, thermodynamics/kinetics considerations, and volumetric/gravimetric capacities.

In addition to the above criteria, DOE considered the following factors in making its "Go/No-Go" decision:

- Progress towards meeting FY 2007 system targets;
- Potential pathway leading to attaining FY 2010 and 2015 system targets; and
- Progress toward consistent synthesis of high capacity (greater than 6 percent by weight) nanotube material.

The decision tree used by the DOE Hydrogen Program is illustrated below:



Criterion 1	Go	☐	No-Go	X
Criterion 2	Go	X	No-Go	☐
Criterion 3	Go	X	No-Go	☐
Criterion 4	Go	X	No-Go	☐

Decision Rationale

The DOE Hydrogen Program initiated research at the National Renewable Energy Laboratory (NREL) to develop SWNTs as a storage medium for hydrogen in 1992. Investment in the level of research effort grew from one full-time equivalent (FTE) to at least 3 FTEs over thirteen years.

Initial hydrogen capacity measurements on nanotubes were promising, but the most promising results could not be repeated. Uncertainty in the performance of carbon nanotubes as a storage material grew as other research groups initiated their own efforts on this material. Published hydrogen capacity results ranged from ca. 0 to over 6 percent hydrogen stored in/on the nanotubes on a weight basis. Importantly, the differences in measured hydrogen capacity could not be correlated with specific carbon nanotube synthesis methods or with various properties of the carbon nanotube structure. Although the number of publications and the worldwide level of effort on carbon nanotube R&D have continued to grow in the last decade and important progress has been achieved, uncertainty remains concerning hydrogen storage capacity on pure, undoped samples.

The DOE Hydrogen, Fuel Cells and Infrastructure Technologies Program (HFCIT) used input obtained through a Federal Register Notice, the open peer-reviewed literature, and technical feedback from the FreedomCAR and Fuel Partnership and DOE researchers to make a "No-Go" decision on future investment in pure, undoped SWNTs for vehicular hydrogen storage applications. The following paragraphs provide the rationale for that decision according to the four technical criteria.

<u>Criterion 1: Pure, undoped carbon SWNTs achieving 6 wt.% hydrogen storage (on a materials basis) at room temperature. **No-Go**</u>

From a review of the source material[4], the DOE Hydrogen Program has determined that at room temperature, ca. 0.6 percent by weight excess capacity of hydrogen is the maximum achieved in pure, undoped single walled nanotubes. Compared to the criterion of 6 wt.% hydrogen storage at room temperature (on a materials basis), the pure, undoped materials cannot meet the target. At cryogenic temperatures (77K), NREL has measured a maximum of 3 wt.% hydrogen uptake at ~20 bar on pure, single-walled nanotubes.

Early literature results indicating a H/C ratio greater than 2 (i.e. more than 1 H_2 molecule per C atom, or ~14 wt.% H) have been found to be incorrect due to measurement errors and/or the presence of impurities. Literature results with high capacity on single walled carbon nanotubes were obtained on *metal doped samples* or at low temperature[5]. Current literature indicates (a) less than 1 wt.% sorption capacity for pure tubes except at low temperature and high pressure; (b) 3 to 6 wt.% at 77K and nominal pressure; or (c) significantly higher capacities at room temperature in metal hybrid materials.

<u>Criterion 2. Whether a technically viable pathway exists to meet the original criterion of 6 weight percent at room temperature using either pure, undoped SWNTs or a "hybrid" approach (e.g., metal doped nanotubes). **Go**</u>

The open peer reviewed literature has indicated that higher hydrogen uptake capacity can be achieved by increasing available surface area (e.g. number of adsorption sites) and increasing the binding energy to enable room temperature adsorption of hydrogen. A "Go" decision has been

[4] See the endnotes in the text and the bibliography in this document.
[5] Examples of pure nanotube experimental results: NREL internal result of 3 wt.% at 77K and 20 bar; Penn. State result of 6 wt.% at 77K, 2 bar, Pradhan, et al., JMR **17**, 2209 (2002); and Univ. of Quebec result of 4.6 wt% at 77 K, 1 bar, Poirer et al. APA 78, 961 (2004).

made for future investment in this area, emphasizing "hybrid" approaches incorporating metals supported and/or integrated with a carbon or a high surface area substrate.

There are recent examples of methodologies that show promise for designing materials that can store high hydrogen capacity at nominal pressure and close to room temperature. For example, NREL has reproducibly synthesized samples with 3 wt.% adsorption at room temperature on metal doped, single walled carbon nanotubes[6]. These samples contained between 60 to 80% metal content through the synthesis process. A capacity of 4 wt.% has been measured on samples containing metal function (not externally verified) but at 77K. R. Yang's group at the University of Michigan has published results on metal containing hybrid materials that showed four-fold enhancement in H_2 storage via a proposed "spillover" mechanism[7].

The DOE Hydrogen Program will continue funding for hybrid, high surface area materials using the following approaches with SWNTs as a "reactant" for incorporation into composite materials or for further chemical processing. The following examples are not considered an inclusive list:

- Small diameter (< 0.8 nm) SWNTs with enhanced heats of adsorption (greater than 12 kJ/mol)
- Components for building 3-D foams and appropriately expanded lattices for increasing available surface area
- Frameworks for incorporating active dopants such as boron or other light elements to increase heat of adsorption
- Hosts for modification, via, e.g., lithium incorporation, to increase available surface area and binding energy
- Sources of sp^2 bonded carbons as a substrate for complexing/isolating metals to increase capacity and binding energy
- Thermal management materials for metal and chemical hydrides

Criterion 3. Whether hydrogen adsorption in carbon nanotubes at low temperature (77K) should be considered (although the original criterion of 6 weight percent was at room temperature). **"Go"**

The research addressed in criterion 2 will advance progress under this category by allowing temperatures to be raised and pressures to be reduced. DOE has decided a "Go" in this area of research with a reassessment planned at the end of FY 2009. The current state-of-the-art storage capacity achieved at 77K is based on metal-organic framework (MOF) materials (~7 wt.%, >30

[6] "Background Information for Carbon Nanotube Go/No-Go Decision: Reproducibly demonstrate 6 wt% (materials-based storage capacity) in external laboratory (4Q FY 2006)", Management Report, 26 July 2006, National Renewable Energy Laboratory, M. Heben project leader. "Carbon Materials and Hydrogen Storage Capacity Development. Carry-out an external validation of a 4 wt% sample at room temperature and pressure at SwRI," September 2005 Milestone Report, National Renewable Energy Laboratory, M. Heben, project leader.

[7] Y. Li and R. T. Yang, J. Am. Chem. Soc., vol. 128, no. 5, 8136-8137 (2006).

g/L) developed by Yaghi et al. at UCLA[8]. The "Go" is accompanied with the caveat that room temperature operation is the primary goal for vehicular applications.

<u>Criterion 4. Whether SWNTs may be used as model materials for fundamental research, theoretical simulation and an improved understanding of nanoscale hydrogen storage mechanisms and the interplay between factors such as charge/discharge efficiency, thermodynamics/kinetics considerations, and volumetric/gravimetric capacities. **"Go"**</u>

Most of the work under this criterion will be basic research that more appropriately matches the mission of DOE Office of Science Basic Energy Science's portfolio. DOE Office of Energy Efficiency and Renewable Energy (EERE) will emphasize funding of applied research in this area if information to be obtained is essential to permit the advance and deployment of a technologically viable material or system. A reassessment by EERE is planned in FY 2011.

Path Forward

As discussed previously, the open literature indicates that higher hydrogen uptake capacity can be achieved by increasing available surface area and increasing the hydrogen binding energy (goal of ~ 10-20 kJ/mol) to enable near room temperature adsorption of hydrogen at nominal pressure. DOE may invest in materials research that could use SWNTs as a "reactant" in a material design "toolbox" to synthesize hybrid high surface area materials.

It must be emphasized that gravimetric capacity is only one attribute that is important to consider for vehicular storage of hydrogen. Volumetric capacity, hydrogen charge/discharge kinetics, material durability, hydrogen quality and system safety are also important attributes for the material designer to consider.

The materials under consideration for future investment include but are not limited to: MOFs, aerogels, polymers, fullerenes, aerogels, frameworks/supports, "propped" structures, doped structures, clathrates, and metal decorated and "catalyzed" carbons.

For use of SWNTs as an "ingredient" in composite, hybrid materials, the following issues have yet to be resolved: (a) No experiments have resolved the various sites (endo, exo, and interstitial) or observed expected changes with cutting and diameter variation. (b) Substantial surface area is "missing" and appears to be not available for binding of hydrogen. And (c) Experimental hydrogen capacity testing is needed on small diameter (less than 0.9 nm) SWNTs to confirm predictions of enhanced binding energy.

Bibliography

1. "Background Information for Carbon Nanotube Go/No-Go Decision: Reproducibly demonstrate 6 wt% (materials-based storage capacity) in external laboratory (4Q FY 2006)", Management Report, National Renewable Energy Laboratory, M. Heben project leader (2006).

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[8] A. G. Wong-Foy, A. J. Matzger and O. M. Yaghi, "Exceptional H_2 Saturation Uptake in Microporous Metal-Organic Frameworks," JACS 2006. and J. L. Rowsell and O. M. Yaghi. JACS 2006, 128, 1304-1315.

2. "Carbon Materials and Hydrogen Storage Capacity Development. Carry-out an external validation of a 4 wt% sample at room temperature and pressure at SwRI," Milestone Report, National Renewable Energy Laboratory, M. Heben, project leader (2005).
3. H. Cheng et al., "Molecular Dynamics Simulations on the Effects of Diameter and Chirality on Hydrogen Adsorption in Single Walled Carbon Nanotubes," J. Phys. Chem. B, 109, 3780-3786 (2005).
4. E. Poirier, R. Chahine, et al., "Storage of hydrogen on single-walled carbon nanotubes and other carbon structures," Appl. Phys. A 78, 961–967 (2004).
5. "Fundamental and Applied R&D on Carbon for Hydrogen Storage," Milestone Report, National Renewable Energy Laboratory, M. Heben, project leader (2004).
6. A. C. Dillon, M. J. Heben et al., "Assessing the Hydrogen Adsorption Capacity of Single-Wall Carbon Nanotube / Metal Composites," In "Hydrogen in Materials and Vacuum Systems" edited by G. R. Myneni and S. Chattopadhyay, American Institute of Physics Conference Proceedings no. 671: 77-89 (2003).
7. B. K. Pradhan et al., "Large cryogenic storage of hydrogen in carbon nanotubes at low pressures," J. Mater. Res., Vol. 17, No. 9, pg. 2209 (2002).
8. V. V. Simonyan and J. K. Johnson, "Hydrogen storage in carbon nanotubes and graphitic nanofibers," Journal of Alloys and Compounds 330–332 (2002) 659–665.
9. A. C. Dillon and M. J. Heben, "Hydrogen storage using carbon adsorbents: past, present and future," Appl. Phys. A 72, 133–142 (2001).
10. L. Schlapbach and A. Züttel, "Hydrogen-storage materials for mobile applications," Nature, Vol. 414, pg. 353 (2001).
11. S. M. Lee and Y. H. Lee, "Hydrogen storage in single-walled carbon nanotubes," Appl. Phys. Lett., Vol. 76, No. 20, pg. 2877 (2000).
12. M. J. Heben, A. C. Dillon, et al., "Rapid, Room Temperature, High-Density Hydrogen Adsorption on Single-Walled Carbon Nanotubes at Atmospheric Pressure Assisted by a Metal Alloy," Extended abstract, Materials Research Society Meeting, Boston (2000).
13. Y. Ye, C. C. Ahn, et al., "Hydrogen adsorption and cohesive energy of single-walled carbon nanotubes," Applied Physics Letters, Vol. 74, No 16, pg. 2307 (1999).
14. Q. Wang and J. K. Johnson, "Optimization of Carbon Nanotube Arrays for Hydrogen Adsorption," J. Phys. Chem. B, 103, 4809-4813 (1999).
15. V. V. Simonyan, P. Diep, and J. K. Johnson, "Molecular simulation of hydrogen adsorption in charged single-walled carbon nanotubes," Journal of Chemical Physics, Vol. 111, No. 21, pg. 9778 (1999).
16. A. C. Dillon, K. M. Jones, et al., "Storage of hydrogen in single-walled carbon nanotubes," Letter to Nature, Vol. 386, pg. 377 (1997).
17. K. Atkinson, S. Roth et al., "Carbon nanostructures: "An efficient hydrogen storage medium for fuel cells?", Fuel Cells Bulletin No. 38, pg. 9 (2001).

Input from Federal Register Notice

1. “Position Paper on Manufacturing Carbon Nanotubes for Hydrogen Storage,” R. W. Pike, Director, Minerals Processing Research Institute, Louisiana State University, Baton Rouge, LA.
2. H. Cheng et al., “Molecular Dynamics Simulations on the Effects of Diameter and Chirality on Hydrogen Adsorption in Single Walled Carbon Nanotubes,” J. Phys. Chem. B, 2005, 109, 3780-3786.
3. “Nanoengineered SWNT Structures for Efficient Hydrogen Storage: Position paper for the DOE notice in the Federal Register, August 24, 2006. page 50052,” Professor James M. Tour, Director, Carbon Nanotechnology Laboratory, Rice University.