Hydrogen Storage in Single-wall Carbon Nanotubes

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DOE Office of Science, Division of Materials Science
Renewable Hydrogen Energy Economy


Oxygen

Outputs: Electricity, heat and Water

Stored Hydrogen

Water
Outline

• History of H storage on carbon.
• Application of carbon single-wall nanotubes (SWNTs)
• Experimental findings, methods and controls.
• Future work & directions.

- Cryogenic engineering study (Kidnay and Hiza, 1967)
  Coconut shell charcoal.
  *Excess* H of 2.15 wt% at 25 atm, 76 K.

- Hydrogen storage medium (Carpetis and Peshka, 1976)
  5.2 wt% for “F12/350” carbon at 41.5 atm, 65 K.
  Inverse relation between porosity and H wt%.

- Optimization (Schwartz, et al., 1980s, early ‘90s)
  Surface acidity, metal modification
  ~4.8 wt% at 59 atm and 87 K.

  ➔ Amount stored would be greater in an empty cylinder at same T, P.

Sites for Hydrogen Adsorption on Carbon Materials

Slit Pore

Planar Graphite

Activated Carbon

$\Delta H_{\text{ads}}$ vs Coverage

$\frac{kT}{2}$
SWNTs: An Ideal Adsorbent for Hydrogen?

Arc-Discharge materials available in 1995

- Areal densities of: SWNTs, amorphous and graphitic carbon, and Co particles by graphical integration.
- Heights measured by AFM.
- Densities of 2 g/cc and 8.9 g/cc for C and Co, respectively.
- SWNT densities ranged from 0.1 to 0.2 wt% in best samples.

Materials through Collaboration with:
Kiang and Bethune, IBM

A.C. Dillon, T.A. Bekkedahl, K.M. Jones, and M.J. Heben
Proceedings of the Electrochemical Society,
Volume 96-10, 716-727 (1996).
Temperature Programmed Desorption

- 90 to 1500 K
- $5 \times 10^{-9}$ to 1000 torr
- Mass Spectra
  - 0 - 300 amu

→ 1 wt%H on 1 mg
  - = $5 \mu$gm H$_2$
  - $\approx 0.1$ standard cc
  - $\approx \Delta P \sim 25$ mtorr

in 3 liters
Degas Spectrum on Arc-Discharge Materials

A.C. Dillon, M.D. Landry, J.D. Webb, K.M. Jones and M.J. Heben
Hydrogen Adsorption After Degassing

- New high temperature adsorption site
- Integrated H₂ was ~0.01 wt% of the total sample weight
- Storage densities between 5 and 10 wt% on a SWNT basis

Variation with Heating Rate shows 1st Order Desorption

- First order desorption:
  \[ \ln\left(\frac{T_p^2}{\beta}\right) = \frac{E_d}{RT_p} \]
  where:
  \(T_p\) is the peak T
  \(\beta\) is the heating rate (0.3 - 30 K/s)
  \(R\) is the universal gas constant
  \(E_d\) is the activation energy

- Straight line demonstrates non-dissociative adsorption with
  \(H_{\text{ads}} = 19.6 \text{ kJ/mol}\)

Enhanced Production Yield with Laser Vaporization

Arc-Discharge

Laser Vaporization
Quantitative Purification

- Reflux 16 hrs, 3M HNO₃
- 30 min at 550 °C in air

High Purity Samples

Characterized by: 
Raman, TGA, ICPS, XRD.

Final purity > 98 wt% when formation of graphite encapsulated metal is avoided.

Low defect density.
Very little amorphous carbon.
Less than 0.1 at% metal.

 prive: No RT H₂ desorption in TPD.

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**Chemical Cut**

Conc. 3:1 $\text{H}_2\text{SO}_4$:$\text{HNO}_3$

Destroys SWNTs

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**Probe Sonication Cut**

~10 mg sample, 5 M $\text{HNO}_3$,

16 hrs, 50W/cm$^2$

Introduces Ti-6Al-4V alloy

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Heben et al., Proceedings of the Fall 2000 meeting of the MRS

Dillon et al., Proceedings of the 1999 & 2000 DOE Hydrogen Program Review
Optimized cutting yields 6.5 - 7 wt% H₂ with incorporated Ti-6Al-4V alloy.

500 torr, RT dose, cool to 130K prior to evacuation

16 hrs.
4 M HNO₃
50 W/cm²

Long-pulse 1064 nm

6.5 wt% H
26 wt% alloy
Comparison of Installed H Storage Systems (1997)

<table>
<thead>
<tr>
<th>Material</th>
<th>Density</th>
<th>Temp</th>
<th>Pressure</th>
<th>Reference</th>
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<td></td>
<td>wt%</td>
<td>(K)</td>
<td>(MPa)</td>
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<td>Nutzenadel</td>
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<td>RT</td>
<td>echem</td>
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<td>RT</td>
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<td>0.5</td>
<td>RT</td>
<td>10</td>
<td>Wang</td>
<td>1999</td>
</tr>
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<td>0.1</td>
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<td>3.5</td>
<td>Tubbets</td>
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<td>0</td>
<td>RT</td>
<td>0.08</td>
<td>Hirscher</td>
<td>2001</td>
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</table>
Criticism of Our Findings

1. Some groups refute the claim that SWNTs adsorb any hydrogen at room temperature.

2. Believe that we have been misled by inaccurate equipment, poor calibration, and incomplete methods.

3. Conclude that all of the hydrogen we observe is simply explained by absorption on the Ti alloy fraction introduced during cutting.
Three Independent Calibrations of TPD

1) Decompose known amounts of CaH$_2$ in volumetric and TPD.

- Electrical Insulator
- Hygroscopic
- Inhomogeneous
- Variable Purity

Three Independent Calibrations of TPD (cont)

2) Charge and Release H from Pd powders in volumetric and TPD.

- Reversible
- Pressure / Temperature Charging Profiles Must be Identical
- Cooling is critical
- Special sample holder required
Three Independent Calibrations of TPD (cont)

3) Decompose TiH₂ in volumetric and TPD.
   • High purity samples available, not hygroscopic
   • No cooling required
   • Time integrated areas independent of temperature profile
Three Independent Calibrations of TPD (cont)

- All three methods indicated calibration constants for the TPD apparatus within 10%.
- TiH₂ method was found to be the most robust:
  - Vacuum stable, high-purity starting materials.
  - 4.03 ± .06 wt % for TiH₂
- TPD areas for known amounts of TiH₂ constant to < 5%
- TPD calibration constants varied by 15% over 8 months.
TPD Spectra from:

- Probe-generated alloy
- Cut graphite
- Cut SWNTs

....are similar in shape

But differ in magnitude!...

We became aware of the presence of the alloy in 1999

Presented information to the public at MH2000
Current SWNT Activation is Not Consistent

• Similar SWNT samples do not exhibit the same H capacity after cutting.
Probe-Cut SWNT Samples

Nd:YAG & Alexandrite Syntheses
Various Cutting Conditions
Post-cut Alloy Content Determination

• Employed three different methods to access alloy content: ICP, TGA, combustion/weighing.

• Both Goodfellow alloy and probe-generated samples showed good agreement between ICP and TGA data and confirmed oxidation pathway of alloy:

\[
\text{Ti}_{0.86}\text{Al}_{0.1}\text{V}_{0.04} \rightarrow \text{TiO}_2 + \text{Al}_2\text{O}_3 + \text{V}_2\text{O}_5
\]

• Alloy introduced by cutting simply evaluated by weighing samples before and after combustion in air with a sensitive balance.
Hydrogen Capacity of $\text{Ti}_{0.86}\text{Al}_{0.1}\text{V}_{0.04}$ Alloy

- Volumetric apparatus to investigate hydrogen uptake at room temperature and 500 torr.
- Applied high-temperature, high vacuum activation.
- 2.99 wt% on Goodfellow alloy (< 450 µm), consistent with literature.
- 2.5 wt% on ultrasonically-generated $\text{Ti}_{0.86}\text{Al}_{0.1}\text{V}_{0.04}$ by both volumetric and TPD.
Evaluating Storage Content of Tube Fraction

(1) \[ X_{\text{alloy}} + X_{\text{SWNT}} = 1 \]

(2) \[ (\text{wt}\% \ H_{\text{SWNT}} \cdot X_{\text{SWNT}}) + (\text{wt}\% \ H_{\text{alloy}} \cdot X_{\text{alloy}}) = \text{wt}\% \ H_{\text{sample}} \]

Where \( X_{\text{alloy}} \) and \( X_{\text{SWNT}} \) are weight fractions.

\[
\text{wt}\% \ H_{\text{SWNT}} = \frac{\text{wt}\% \ H_{\text{sample}} - (X_{\text{alloy}} \cdot \text{wt}\% \ H_{\text{alloy}})}{1 - X_{\text{alloy}}}
\]
Hydrogen Content on SWNTs

Hydrogen on SWNT Fraction (wt%) vs Metal Alloy Content (wt%).

- 2.99 wt% on alloy
Invited paper – Rapid

Hydrogen storage in sonicated carbon materials

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Table 1. List of different carbon materials sonicated using a Ti-alloy probe:
Total hydrogen storage capacity (TDS) an Ti content (ICP) an hypothetical H/Ti-6Al-4V content under the assumption that all hydrogen is absorbed by Ti-alloy particles

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sonication time [h]</th>
<th>Total H [wt %]</th>
<th>Ti [wt %]</th>
<th>H/Ti-6Al-4V [wt %]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWNTs Rice</td>
<td>1</td>
<td>0.04</td>
<td>8.5</td>
<td>0.42</td>
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<tr>
<td>SWNTs Rice</td>
<td>5</td>
<td>0.12</td>
<td>16.6</td>
<td>0.65</td>
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<td>SWNTs Rice</td>
<td>10</td>
<td>0.74</td>
<td>36.0</td>
<td>1.85</td>
</tr>
<tr>
<td>SWNTs Rice</td>
<td>16</td>
<td>0.94</td>
<td>45.5</td>
<td>1.86</td>
</tr>
<tr>
<td>SWNTs Rice</td>
<td>24</td>
<td>1.47</td>
<td>59.6</td>
<td>2.22</td>
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<tr>
<td>Graphite powder</td>
<td>16</td>
<td>1.4</td>
<td>≈ 50</td>
<td>2.52</td>
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<tr>
<td>Diamond powder</td>
<td>1</td>
<td>0.05</td>
<td>2.0</td>
<td>2.25</td>
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<tr>
<td>Diamond powder</td>
<td>5</td>
<td>0.19</td>
<td>7.8</td>
<td>2.19</td>
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<tr>
<td>Diamond powder</td>
<td>16</td>
<td>0.67</td>
<td>20.3</td>
<td>2.97</td>
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<tr>
<td>Diamond powder</td>
<td>24</td>
<td>0.94</td>
<td>25.9</td>
<td>3.27</td>
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</table>
Current SWNT Activation is Not Consistent

- Sonication produces differing degrees of cutting, amounts of metal, and metal particle sizes even with careful control of external parameters (time, sonication power, acid concentration, hydrodynamics).
- Samples having a large proportion of semiconducting tubes have shown some preference for activation.
- Decoupling of the cutting and metal introduction processes will be required for further understanding.
- This work is underway in our laboratory.
Dry Cutting

We have developed a general, dry cutting technique that is scalable. The method cuts purified SWNT without introducing impurities. Raman D-band spectroscopy can assess the degree of cutting.
What is the Mechanism?

- The inclusion of Ti may assist in the addition of hydrogen either via thermal effects associated with immediate contact, or by a catalytic effect.

- We have previously shown some Raman and thermopower evidence for partial electron transfer from H₂ to the SWNT.

- Recent quantum-mechanical molecular dynamics simulations show molecular adsorption energies as high as 45 kJ/mol at 600 K with partial electron transfer.

Hydrogen Storage with Carbon / Metal Hybrids
(very recent work)

• Mechanical milling of Mg and graphite lead to enhanced physical and electrochemical properties for H adsorption.

  Imamura et al., several pubs including:


• Cooper and Pez: US patent publication 2002/0096048A1

  “….carbon-metal hybrid materials…display an H\textsubscript{2} adsorption capacity that is greater than the sum of the capacities of the hybrid’s individual components…”
Conclusions

• We have demonstrated that SWNTs can adsorb hydrogen at room temperatures and pressures.

• A maximum of 8 wt% is observed on the SWNT fraction.

• The inclusion of a Ti alloy assists in the addition of hydrogen to the SWNT structure.

• More controlled cutting and metal introduction processes are required for to further elucidate the behavior of these systems.