DOE Carbon-based Hydrogen Storage Center of Excellence: Center Highlights and NREL Activities


National Renewable Energy Laboratory
† Rochester Institute of Technology

DOE Annual Merit Review
May 16-19, 2006

This presentation does not contain any proprietary or confidential information

NREL/PR-590-41726
Overview: Timeline and Budget

Timeline

• Center of Excellence start date: FY05
• Center of Excellence end date: FY09
• Percent complete: 20%

Barriers

• See next slide

Budget

• Center funding
  – $27.5 M for five-year CoE
  – $2.5 M Contractor share (20% of Contractor budget)
• $2 M in FY05 for NREL
• $2.1 M in FY06 for NREL

Partners

Rice (J. Tour), Rice (B. Yakobson, R. Hauge), Air Products (A. Cooper), Duke (J. Liu), CalTech (C. Ahn), LLNL (J. Satcher), NIST (D. Neumann, ORNL (D. Geohegan), Penn State (P. Eklund), U. Michigan (R. Yang), University of North Carolina (Y. Wu), U. Penn. (A. MacDiarmid) + others outside of the COE
Overview: Barriers & Targets

General
A. Cost.
B. Weight and Volume.
C. Efficiency.
E. Refueling Time

Reversible Solid-State Material
M. Hydrogen Capacity and Reversibility.
O. Test Protocols and Evaluation Facilities.

Crosscutting Relevance
Off-Board Hydrogen Storage Barriers S & T: Cost and Efficiency

DOE 2010 Technical Targets for Storage System
- Gravimetric 0.06 kg H₂/ kg
- Volumetric 0.045 kg H₂/m³
COE Interactions & Collaborations

8 university projects (at 7 universities), 4 government labs, 1 industrial partner

Also: IEA (R. Chahine, K. Ross), several IPHE collaborators, SwRI, Stanford GCEP, NIST, NASA, Virginia Commonwealth U. (G. Glaspell, P. Jena), Argonne National Lab (R. Ahluwalia), ATMI, synergy with two BES projects at NREL, and two BES projects at ORNL.

Organization of Conferences: IPHE (Lucca, 6’/05), MRS (Fall ‘04, Fall ‘05, Spring ‘06, Fall ‘07), ECS (Spring ‘06, Spring ‘07), APS ‘07
Objectives

• Investigate a variety of adsorbent materials known to store hydrogen to determine limits of performance.

• Design and synthesize materials that bind hydrogen as either (i) weakly and reversibly bound atoms or (ii) as strongly bound molecules.

• Understand possible mechanisms and the interplay between structure, binding, and material and storage densities (volumetric and gravimetric).

• Develop the experimental and computational tools to speed discovery, testing, and deployment of new materials that meet DOE system goals.

• Create a collaborative, nimble environment to permit expeditious exploration, research, and deployment (sum of whole > sum of parts).

• Enable new storage system concepts possible with “smart” materials to meet DOE system targets.
  • Conformal tanks with low T and moderate P (<100 bar) operation
  • Hybrid nano-engineered systems with near STP operation
Approach: Optimize H Binding Energy, Surface Area, and Site Density

A number of advanced materials are being investigated

Chemical hydrides > 100 kJ/mol
Metal hydrides 50 - 100 kJ/mol
Chemical hydrides > 100 kJ/mol

Materials with appropriate binding energies, sufficient surface area, low-weight and high material density will meet DOE hydrogen storage system targets and enable high-efficiency on-vehicle refueling.
Approach: Binding Energy Impacts System Design

- Optimized binding is essential to enable on-vehicle refueling and reduce overall costs
  - High hydrogen capacity is typically associated with high binding energy and/or irreversible chemical reactions
  - Properly designed materials can have high hydrogen capacities and desired intermediate binding energies (10 - 50 kJ/mol)

- Too large of a binding energy will lead to energy penalties during charge & discharge, prohibit on-board recharging, reduce system capacities (heat exchangers), increase costs of the system and the hydrogen fuel
- Too low of a binding energy will reduce system capacities (cooling & insulation), increase system costs
Approach: NREL Roles/Responsibilities

NREL in-house task areas

<table>
<thead>
<tr>
<th>Task 1: Hydrogen Adsorption Measurements (Parilla)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Task 2: Gas Phase Synthesis of Nanostructured Carbon-based Adsorbents (Heben)</td>
</tr>
<tr>
<td>Task 3: Chemical Synthesis of Nanostructured Carbon-based Adsorbents (Dillon)</td>
</tr>
<tr>
<td>Task 4: Theory of Hydrogen Storage in Nanomaterials (Zhang)</td>
</tr>
<tr>
<td>Task 5: Center Integration (Simpson)</td>
</tr>
</tbody>
</table>

- Perform activities in five task areas in support of DOE mission
- Insure COE activities are aligned with DOE goals
- Promote communication and collaboration to expedite progress towards targets
- Create a nimble research and technology development environment to pursue new opportunities as they arise, in support of DOE

NREL performs research and development on advanced adsorbents, provides technical and scientific leadership to the COE, and serves as a resource for the COE and the larger community
Center is organized into five areas - collaboration on projects across areas speeds development.
COE Accomplishment: Technical Interactions

NREL developed technical interactions with nearly all COE partners

- **UMich**
  - H₂ Spillover
  - Provided samples
  - Confirm capacities

- **Rice University**
  - SWNT samples for TPD and H₂ Uptake

- **CalTech**
  - H₂ Uptake Confirmation on purified SWNTS

- **PSU**
  - (B-C-N materials)
  - Samples for TPD

- **UNC**
  - NMR on purified and b-doped SWNTS

- **Duke**
  - SWNT - TPD and H₂ Uptake

- **UPenn**
  - Conducting Polymers for TPD and H₂ Uptake

- **NIST**
  - Oak Ridge
  - SWNH & Pt/SWNH for H₂ Uptake

- **Livermore**
  - (aerogels)

- **Steering Committee**
  - NREL
  - Materials, theory, measurement, systems, center integration

**COE mode accelerates research and development efforts to meet DOE hydrogen storage system targets. The COE is also working with SwRI, ATMI, U. Quebec, BES projects, and individuals outside of the COE.**
COE Accomplishment: B-doping Project

Motivation: Enhanced H\(_2\) binding

C-B-H\(_2\) theory
NREL

B-doped materials - PSU
Carbons and arc SWNTs

Materials Synthesis

B-doped materials - NREL
Laser SWNTs

Measurement & Characterization

Volumetric - PSU

Small volumetric & TPD - NREL

Neutron scattering
NIST

NMR - UNC

High Accuracy
Volumetric - APCI


COE technical interactions accelerate R&D efforts toward meeting DOE hydrogen storage system targets. Close interactions provide rapid feedback for development.
COE Accomplishments: Other Selected Accelerated Project Areas

COE technical interactions accelerate R&D efforts toward meeting DOE hydrogen storage system targets. Close interactions provide rapid feedback for development.
COE Accomplishment: Enhanced Spillover (Yang et al., U. Michigan)

- Last year’s spillover result of 1.8 wt% uptake has been increased to ~ 4 wt% at room temperature and ~ 100 bar
- Key is development of “bridge” structure between catalyst and receptor components
- Volumetric capacity on materials basis is estimates to be ~41 kg H₂/m³
- Samples currently being measured at NREL for validation

Comparison of hydrogen sorption as a function of pressure for receptor, catalyst/receptor and catalyst/bridge/receptor materials indicates a substantial enhancement when bridges are formed. Y. Li and R.T. Yang, JACS. 2006, 128, 726-727

For the first time, substantial hydrogen sorption/desorption at room temperature has been demonstrated via spillover. Improved bridge forming and integration processing need to be developed to increase capacity and rates.
COE Accomplishment: Improved MOF Uptake (*Yaghi et al., U. Michigan)

- Synthesized particular MOF material with 5800 m²/gm BET surface area
- Record 7 wt% storage at 77 K and ~ 60 bar
- Volumetric storage density in excess of 30 g/L on materials basis
- BET surface area more than twice the theoretical max for an infinite sheet of graphite (2650 m²/gm).

- High surface area is essential for high hydrogen storage capacities.
- Materials have hydrogen storage capacities close to that needed to meet DOE 2010 targets.
- COE partners must reproduce the results obtained on MOF structures with other nano-engineered materials, at higher T.

Volumetric and gravimetric densities are close to that needed to meet 2010 system targets. Binding energy need to be increased for operation at higher temperatures.


* O. Yaghi, previously at U. Michigan, is now at UCLA. His program is no longer part of the CoE.*
COE Accomplishment: New Carbon Structures (Yakobson, Tour, Hauge, et al., Rice)

- Identified processing for high surface area carbon structures with opened van der Waals spaces and minimal wasted volume
  - Optimized spacing could increase hydrogen binding and capacity
    - Superposition of potentials can enhance sorption w/ optimum spacing
      - Patchkovskii, Tse, et al. PNAS 2005
    - 3D Carbon foam
      - Ding, Yakobson, et al. in progress
    - Nanoengineered SWNTs
      - Tour, Hauge, et al. in progress

Optimized nano-engineered structures may meet DOE hydrogen storage targets according to theories. Proposed routes to “propping open” normally collapsed structures outlines rational construction approach for the first time. Theoretical and process development is critical to demonstrate full potential.
COE Accomplishment: Small Diameter Nanotube Synthesis (Liu et al., Duke)

- Theoretical calculations, from Air Products, predict that small diameter SWNTs (< 1 nm) will have higher hydrogen storage capacities and higher binding energies for dihydrogen than SWNTs with larger diameter. 
  Cheng et al., JACS 123: 5845 (2001); Kostov et al., PRL 89, 2002.
- Small-diameter nanotubes have not been synthesized in high yield previously, and have not been available for testing.

Progress:
- Discovered that the size of SWNTs are closely related to the CVD growth conditions, most importantly carbon feeding rates.
- Discovered that uniform small diameter SWNTs can be produced from non-uniform catalysts if the growth condition is controlled precisely.

The development of methods to synthesize small-diameter SWNTs will permit testing of predictions of their improved storage characteristics.
NREL Accomplishment: High Throughput, Accurate Volumetric Measurements

- Rate of materials discovery & measurement is dramatically increased by using small samples.
- Volumetric measurements, especially on small samples, are complicated by temperature gradients.
- NREL developed a simple method to improve measurement speed and accuracy
- Method is being extended to higher P, and will be transferred to partners, community and SwRI.

- Cu collar and clamp force $\Delta T$ to occur over a fixed distance
- Can be used with LN$_2$ or any fluid for variable temp measurements ($\Delta H$)
NREL Accomplishment: Repeatable Sample Prep and Measurement

• Developed synthesis and purification processes that reproducibly produced the same H₂ uptake (~3 wt% at saturation)
  – SWNT preparation involves repeated acid and high temp. oxidation steps
    • Nitric, sulfuric, hydrochloric acids
    • Heating in air, O₃ and/or CO₂
• H₂ uptake confirmed at 4 different institutions (including SwRI)
• Different institutions using similar processing created materials with similar H₂ uptake properties

• Partners are working together to increase H₂ storage capacities of base and nanoengineered materials.
• Interactions will accelerate development to meet DOE storage targets.
NREL Accomplishment: B-doped SWNTs made by Laser Vaporization

- B-SWNTs in high yield for first time using laser
- N₂ as carrier gas and NiB as a catalyst
- EELS spectrum indicative of sp²-bonded B in hexagonal lattice (confirmed by ¹³C NMR)
- Current doping level is 1-2% by EELS

Blackburn et al., Chem. Mat. accepted

B-doped materials are needed to enhance the H₂ binding energy, point the way to better adsorbents
Joint Accomplishment (NREL/UNC/NIST): NMR, Volumetric, and Neutron Scattering Show Stronger H₂ Binding

- Variable pressure NMR spectra show adsorbed and free H₂
- Binding energy of 11.6 kJ/mol - in good agreement with theory (12 kJ/mol)
- See STP41 - Wu et al.

- Step in adsorption isotherm shows B sites are populated first, consistent with NMR and neutron data (see ST25 - Neumann et al.)
- Prompt gamma analysis shows B content of 1.2% in samples, consistent with EELS
- At least 25% B is possible (BC₃)

BC₃ nanotubes
12 kJ/mol
~ 4.2 wt%


B-SWNTs and carbons will enable RT sorption at moderate pressures. Must increase boron doping content and determine affects on neighboring carbon sites.
NREL Accomplishment: Volumetric Performance of Predicted OBBs (Organometallic Bucky Balls)

- Calculations have shown that first-row transition metals complexed to C\textsubscript{60} can bind H\textsubscript{2} with near-optimal binding energies (20 - 30 kJ/mol); Zhao et al., PRL 94, 155504 (2005)
- 8.8 wt\% reversible, near ambient P and T, capacity was found for Sc complexed to B-doped fullerenes
- Assuming that OBBs form FCC crystals as does C\textsubscript{60}, but with an expanded lattice parameter, a volumetric capacity between 42 and 52 kg H\textsubscript{2}/m\textsuperscript{3} can be expected.

\[
\text{C}_{48}\text{B}_{12}\left[\text{Sc}\text{H}\right]_{12} \rightarrow 60\text{H}_2 \rightarrow \text{C}_{48}\text{B}_{12}\left[\text{Sc}\text{H(H}_2\text{)}_6\right]_{12}
\]
NREL Progress: Synthesis of OBB Adsorbents

Stabilizing Dihydrogen Ligands Requires Non-classical Coordination

- Metal d to $\sigma^*$ H-H back-donation is key to $\sigma$-bond coordination and the stabilization of dihydrogen ligands.
- However, too much electron donation results in dissociation and formation of monohydride species.
- Problem: $C_{60}$ organometallic chemistry is generally olefinic (2 e$^-$ donor)
- But Fe $\eta^5$ chemistry is known

First demonstration in 1983

Bulky phosphine ligands allow for H$_2$ to be stabilized with a $\sigma$-bond.

Enhanced d-$\sigma^*$ metal:H$_2$ interaction with Ir complexes as $X = I > Br > Cl$

$IrXH_2(H_2)(PR_3)_2$ ($X = Cl$, Br, I)

NREL Accomplishment: Non-olefinic coordination to C$_{60}$

- Initial attempts with Fe due to known $\eta^5$ coordination (ferrocene)
- Reaction chemistry cannot be revealed at this time, but NMR is consistent with $\eta^5$ coordination
- Fe detected at just above detection limits by EDS in TEM
- EPR confirms the presence of Fe$^{+3}$
- Proposed Bucky-dumbell structure
- First metal $\eta^5$ coordination to C$_{60}$?

Solid State $^{13}$C NMR of Starting C$_{60}$

After reaction: No non-fullerene related peaks in $^{13}$C NMR spectrum

non-olefinic coordination to C$_{60}$ is important first step to OBB synthesis.
NREL Accomplishment: Temperature Programmed Desorption of C$_{60}$-Fe-C$_{60}$

- H$_2$ adsorption sites after exposure to H$_2$ at 500 Torr for 5 min.
- Peaks increase as sample is progressively heated in vacuum up to 250°C.
- Measured binding energy of 6.2 kJ/mol lower than expected from DFT calculations on C$_{60}$-Fe-Cp.

DFT over estimates physisorption binding energy: 14.27 kJ/mol

Next steps:
- Confirm structure
- Dislodge C$_{60}$ and replace with H$_2$
- Increase # of Fe species
- Develop chemistries for other metals
- Demonstrate metal/structure stability
Dihydrogen uptake by transition metals (TMs) on fullerenes and nanotubes has stimulated new thinking for designing optimal adsorbents. Zhao et al., PRL 94, 155504 (2005); Yildirim et al., PRL 94, 175501 (2005)

Metal clustering reduces H capacity. $n$ TM-TM bonds reduces dihydrogen ligands bound to TM by $n$. $^1$Sun et al., JACS 127, 14582 (2005)

The issue of clustering / disproportionation is critical for all hybrid systems (e.g. Li/C), and is being investigated

- Conversion at 200°C (MD simulations) with a gain 1.22 eV/Sc, or ~2 eV/Ti
- Driving force lowered with first hydride bond
- TM dispersal is favored with B-doping, or charged TMs, which reduces TM-TM bonding and promotes stronger TM-cage bonding

TM atoms must be kept separated for high-capacity H storage. Coalescence can be avoided by increasing TM-C bond while decreasing TM-TM interactions
NREL Accomplishment: New Materials

- Identified new approaches to stabilize large hydrogen capacities at STP
- Emphasis on stable materials
- Self-catalyzed H₂ dissociation with MetCar
  - Forms hydrides with barriers less than 0.25 eV
  - Potential gravimetric capacity of 7.7 wt%
  - Model system for spillover shows both H and H₂ binding (Y. Zhao et al. Chem. Phys. Lett. accepted)
- Dendrimers or Macroscopic Molecules
  - Gravimetric capacity > 5 wt%
- Porous carbons used to keep TM atoms isolated
  - High storage on TM atoms
  - Also get storage with carbon matrix

Developing new macroscopic molecules with hydrogen sorption capacities that can meet DOE system targets

Other hybrid structures that are easier to produce are being identified that can meet DOE hydrogen storage targets

Hydrogen decorated transition metals implanted in a highly porous carbon matrix
NREL Progress: 4 wt% Milestone Focused on Pure SWNTs for Reproducibility in Processing

• As previously discussed, we demonstrated reproducible processing and volumetric measurement of hydrogen uptake on SWNTs across 4 labs.
• The measured uptake was ~ 3 wt% at 30 bar and 77 K.
• Samples have been sent to R. Chahine (U. Quebec, Trois-Rivieres) to be processed by a method that should yield 4.5 wt% uptake

1000 °C anneal

\[ Q_{st} \approx 0.12 \text{ eV} \]

8 wt% on SWNTs at 80K, 100 bar
Ye, et al., APL 74, 2307 (1999)

6 wt% on SWNTs at 77K, 2 bar
Pradhan, et al., JMR 17, 2209 (2002)

The performance reported in the literature was not found, although sample processing may have differed. Efforts to improve performance are continuing.
Plan to Meet 6 wt% SWNT Go/No-Go

6 wt% at RT means:
• BET S.A of 3000 m²/g and increased binding energy
• According to “Chahine’s Rule”: 1 wt% per 500 m² of S.A.
• Chahine’s rule may be improved upon with enhance binding energies due to a high density of small pores.

• 12 kJ/mol shown by Pradhan et al. suggests milestone can be met at RT.
• Various expected adsorption sites have not been resolved.
• The 3 wt% saturation capacity suggests that the existing surface area is not accessible.
• Directions: small diameter tubes, open ends, un-bundled, loosely bundled, or propped open tubes, cross-linking, defects, dopants, …
• If research on pure SWNT adsorbents should be stopped as a result of a No-Go decision, SWNTs should still be considered as building block components for possible nanoengineered adsorbents.

SWNTs alone or as functional components in designed adsorbents hold promise for meeting DOE storage targets if appropriate processing can be developed.
Technical Accomplishments and Progress:

- Substantial interactions involving all partners were established to accelerate R&D
- Strong teaming across institutions / topics / expertise
- Partner collaborations have enabled boron doped carbons that bind H₂ at ~ 12 kJ/mol: May enable ~RT and moderate pressure H₂ storage system
- MOF materials with > 5800 m²/g surface areas where made and sorbed ~ 7 wt% hydrogen
- Small diameter tubes have been made in high yield
- Developed nanoengineering strategies to construct better adsorbents
- Demonstrated substantial (~ 4 wt%) hydrogen sorption/desorption at RT via spillover
- Theory of spillover has been developed which shows energetic pathway from gas phase dihydrogen to chemisorbed hydrogen on model Metcars systems
- Demonstrated substantial (> 4 wt%) irreversible hydrogen capacity of hybrid materials at STP
- Strong interplay between theory and experiment is identifying weaknesses in approaches, and determining new paths forward.
- Organization and management of Center has been enhanced
  - Website and ftp site are operational
  - Regular webcasts on topical areas
  - Steering Committee has been engaged
  - Milestones, Go/No-Gos, Safety plans for all partners

For other Progress, see talks and posters from COE partners!
Future FY06 Work at NREL

• Complete development/testing of commercial high pressure volumetric system for use in laboratory scale (~10 mg samples) analysis to help accelerate materials development. Transition to community.

• Continue SWNT development efforts to meet 6 wt% Go/No-Go by Sept. 2006
  • Improve purification/debundling techniques to maximize surface area
  • Develop nano-engineering to keep tubes separated and aligned in appropriate structures
  • Demonstrate that diameter and/or intrinsic doping significantly increases hydrogen uptake
    • e.g. Demonstrate B-SWNT with ~ 10 at% B with >0.5 wt% hydrogen sorption at ~ RT

• Continue developing processes to nano-engineer hybrid materials
  • Demonstrate TM-C$_{60}$ structures that have appropriate structures close to theoretical predictions
  • Identify/demonstrate synthesis of other new materials
    • Demonstrate TM-SWNT, Catalyst-SWNT, and Alkali metal-carbon structures with room temperature hydrogen sorption significantly higher than the base materials
    • e.g. Pt/Pd decorated carbons with 2-4 X increase in hydrogen sorption at ~ RT
  • Integrate work with other spillover and materials development activities in the COE

• Perform calculations to identify new materials that could meet DOE targets
  • Complete calculations investigating the affects of alkali metal with carbon to bind H$_2$
  • Complete initial models for spillover in the MetCar systems. Apply to other cases.

• Continue Center activities to accelerate H$_2$ storage materials development
  • Work with others to provide rapid materials characterization and develop new materials
  • Work with DOE/GO to ensure optimum functioning of the Center
Future FY07 Work at NREL

• Develop new lab scale testing to accelerate H₂ materials development
  – e.g. BET surface area measurements that accurately correlate to H₂ capacity

• Develop intrinsic mat. w/ high surface areas, H₂ uptake > 6 wt%, 45 g/L
  – e.g. Nano-engineered carbon structures with enhanced binding (> 10 kJ/mol)

• Nano-engineer hybrid materials with STP H₂ uptake > 6 wt% 45 g/L
  – Develop synthetic processing to construct structures predicted to meet DOE targets

• Continue to identify new materials that meet DOE targets
  • Identify new synthetic processing to make meta-stable materials
  • Improve fundamental understanding of different adsorption processes
  • Search for good sorbent materials, both experimentally and computationally, that are readily synthesized and likely to be stable.

• Coordinate Center activities to accelerate H₂ storage materials development
  • Work with others to provide rapid materials characterization and develop new materials / approaches.
  • Work with DOE/GO and partners to ensure optimum functioning of the Center
  • Redirect activities away from unproductive materials and approaches toward more productive ones.
## Summary Table of Selected CbHS COE Results

**On-Board Hydrogen Storage System Targets**  
(*Data is based on material only, not system value*)

NA: Not Available

<table>
<thead>
<tr>
<th>Storage Parameter</th>
<th>Unit(s)</th>
<th>2010 System Target</th>
<th>MOF ** FY05</th>
<th>Spillover ** FY05</th>
<th>SWNT ** FY05</th>
<th>B-SWNTs ** FY05</th>
<th>FY06 Alkali Metal decorated SWNT**</th>
<th>FY06 Aerogels **</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Energy</td>
<td>wt. % H₂</td>
<td>6</td>
<td>2.5</td>
<td>7</td>
<td>1.6</td>
<td>~4</td>
<td>3†</td>
<td>~3 Cold 0.5 RT</td>
</tr>
<tr>
<td>Volumetric Energy Capacity</td>
<td>g/L</td>
<td>45</td>
<td>NA</td>
<td>31</td>
<td>NA</td>
<td>41</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Comments</td>
<td></td>
<td>77K, 40 bar</td>
<td>RT</td>
<td>100 bar FY06</td>
<td>77K, 20 bar</td>
<td>77K, 20 bar</td>
<td>77K, 20 bar</td>
<td>STP Irreversible</td>
</tr>
</tbody>
</table>

- **Reported results are preliminary.**
- **Reproduced at different labs.**
- **B-doping level is only 1-2% presently, result is similar to C-SWNT**
- **Previous reports are inconsistent.**
- **77K, 20 bar results are reported.**

---

*Notes:

- a. 28 g/L assuming a ~20% expanded lattice. Will be ~56 g/L at 6 wt% H₂ with this same assumption.*
## Summary Table of Selected CbHS COE Results (Predicted)

On-Board Hydrogen Storage System Targets

(**Data is based on material only, not system value)

NA: Not Available

<table>
<thead>
<tr>
<th>Storage Parameter</th>
<th>Units</th>
<th>2010 System Target</th>
<th>Organometalic Fullerenes Predicted ** FY05</th>
<th>Organometalic Fullerenes Measured Fe-C₆₀ ** FY06</th>
<th>MetCars Predicted ** FY06</th>
<th>Macromolecules Predicted ** FY06</th>
<th>Spillover on SWNTs Predicted ** FY06</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Energy</td>
<td>wt. % H₂</td>
<td>6</td>
<td>~9</td>
<td>0.4</td>
<td>&gt;7.7</td>
<td>&gt;5</td>
<td>~7.7</td>
</tr>
<tr>
<td>Volumetric Energy Capacity</td>
<td>g/L</td>
<td>45</td>
<td>52 - 43</td>
<td>NA</td>
<td>NA</td>
<td>&gt;40</td>
<td>~56</td>
</tr>
<tr>
<td>Comments</td>
<td></td>
<td></td>
<td>STP</td>
<td>77K 2 bar</td>
<td>STP</td>
<td>STP</td>
<td>STP Preliminary Result</td>
</tr>
</tbody>
</table>

Notes:
- STP: Standard Temperature and Pressure
- Preliminary Result
Back-Up Slides
Response to Past Reviewer Comments

Comment: Revisiting the pseudo cold/pressure region is recommended, this may be the "sweet spot" or at least the happy medium where overall system efficiencies can be acceptable in terms of compression/cooling energies and transfer from forecourts to vehicle tanks - especially if bulk transport of hydrogen will continue to favor liquid hydrogen.

Response: We agree. High density carbon nanostructures, such as tubes or foams, may improve the volumetric performance which has hindered past adsorbents in comparison to cryo-compressed tanks. Relatively modest increases in binding energy through doping or materials engineering may permit operating pressures to be reduced or temperatures to be increased. Low pressure operation will permit conformal tanks. A combination of a portion of hydrogen stored strongly at high binding energy sites and a high capacity at lower T would improve dormancy and allow for less insulation.

Comments: (1) Should give more attention to the projected volumetric H2 density of these modified C60 structures. In a relatively optimistic case, the projected density is 43 kgH2/m3; do these materials have (even theoretically) a chance to meet the 2010 or 2015 goals? (2) The key issue with these materials is the volumetric storage.

Response: We agree and have insisted that volumetric performance be as important as gravimetric performance. As can be seen from the Summary Table, several systems are currently close to or predicted to exceed the 2010 targets on a materials basis. This emphasis will continue in the future.
Response to Past Reviewer Comments

Comment: Broad and well respected collaborations. Only possible concern is that there may be too many institutions working on too many things to be able to adequately manage and direct.

Response: The Center is now ~ 1 year old and we have improved the management and organization so that the participants are clustered around focus areas (e.g. enhanced physisorption, Kubas-type interactions, spillover, materials production and measurement)

Comments: (1) Should increase flexibility. (2) Need to establish the internal material selection process/criteria. (3) Ensure an appropriate mechanism is put in place for the effective management of the Center of Excellence; this could be challenging in view of the size of the consortium and the diversity of the expertise there.

Response: Sufficient time must be allotted for the partners to pursue their SOWs sufficiently that informed decision can be made. Go/No-Go decision points are in place for all projects. However, we need to be as flexible as possible to pursue new opportunities as they arise, and to enhance support of promising areas. These issues are continuously discussed with DOE HQ and GO management. Management of Center has been improved by addition of a Deputy Director (Lin Simpson), addition of dedicated manager at GO (Jesse Adams), breakdown of internal NREL work into Tasks, use of communication tools such as webcasts, and a more active Steering Committee.
Response to Past Reviewer Comments

Comment: Showed binding energy for single metal atom on a single pentagonal ring. However, is there metal-metal interaction (i.e., is the binding still strong for a fully covered C60 molecule with 12 Sc atoms?). Is the fully-doped system stable with respect to decomposition into C60 + metal or C60 + metal hydride?

Response: These concerns are valid and are generally relevant to hybrid materials being investigated here as well as those proposed elsewhere. We have addressed the specific comment above computationally, and will continue to do so, both computationally and experimentally, for other systems and new approaches as they arise.

Comments: (1) The highlight of the last year is the portfolio diversification of the possible carbon-based storage molecules. It is critical to continue this pathway and create a well-balanced program with proper risk mitigation. (2) Center should continue to expand activities beyond carbon work. It seems that all materials with low bonding energy 10 to 50kJ/mol would be appropriate for this center and the systems would be similar.

Response: We agree that the concepts, techniques, and tools are well-suited to any types of materials or molecules with low binding energy and wish to expand the scope under study to include those promising adsorbents that do not contain carbon.


NREL Invited Presentations

NREL Invited Presentations (Cont.)

22. “On-Board Hydrogen Storage—Breakthroughs and Barriers”, Instructors: Tom Autrey, Weifeng Luo & Philip Parilla, Symposia ‘A’ (Tutorial), Fall MRS Meeting, Boston, MA, 11/27/05
23. “Carbon-Based Nanostructures for Hydrogen Storage” Thomas Gennett, Anne C. Dillon, Phillip Parilla, Jeffrey Blackburn, Sheng Bai Zhang, Michael J. Heben, (invited speaker) The 25th Annual Esther and Bingham J. Humphrey Memorial Symposium in Chemistry Saturday, September 30, 2006, University of Vermont
NREL Contributed Presentations


NREL Service


Critical Assumptions and Issues

• Success with a low binding energy approach is critical to permit efficient charge/discharge on-board vehicle and to avoid increasing the effective cost of hydrogen back through the hydrogen supply.

• Effective adsorbents can be identified which can meet all of the DOE targets when deployed in a system.

• Though our effort is research-based at this time, we assume that viable, low-cost synthesis methods can be developed once the best candidate(s) have been identified.

• The issues of stability, clustering, and disproportionation are extremely important when considering the use of dispersed metals in combination with carbons for hydrogen storage.

• The COE mode of operation is desired to accelerate discovery, research, and development of optimize adsorbents.
Reversible Condition (at room temperature): $\delta E \sim 10$-$30$ kJ/mol-$H_2$
Energy Pathway Calculated for MetCars

• Dihydrogen in gas phase is first adsorbed as dihydrogen by Ti atoms
• Adsorbed dihydrogen “spills-over” onto carbon