NREL Research as Part of the Hydrogen Sorption Center of Excellence


National Renewable Energy Laboratory
† Rochester Institute of Technology

DOE Annual Merit Review
May 15-18, 2006

Project ID ST 2

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Overview

Timeline
• Center of Excellence start date: FY05
• Center of Excellence end date: FY09
• Percent complete: 40%

Barriers
• See next slide

Budget
• $2.1 M in FY06 for NREL
• $2.1 M in FY07 for NREL
  – Center management funding not included

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: Cost and T: Efficiency

<table>
<thead>
<tr>
<th>DOE 2010 Technical Targets for Storage System</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Gravimetric</td>
</tr>
<tr>
<td>- Volumetric</td>
</tr>
</tbody>
</table>
Objectives

NREL is performing R&D and coordinating the Hydrogen Sorption Center of Excellence to develop the science base and technology advances required to meet DOE’s on-vehicle hydrogen storage targets.

- In FY 2006, NREL and DOE determined a No-Go decision for pure SWNTs.
- In FY 2007, NREL’s Research efforts have been refocused:
  - Using theory as a guide, actively pursue the synthesis of new promising compounds for reversible hydrogen storage with desired binding energies.
  - Determine structures of new compounds and correlate the structure with adsorption mechanisms, desired binding energies and capacities (volumetric and gravimetric).
  - Employ theory to explain and confirm observed experimental results as well as to establish optimized structures that have rational synthesis routes.
  - Expand hydrogen capacity measurement capabilities for rapid screening to improve round robin process / sample exchange with partners.
  - Continue theoretical efforts to predict / design new sorption materials consisting of light elements but not restricted to a carbon base.
This year NREL focused on accelerating the rational synthesis of multiple compounds that are promising for meeting DOE on-vehicle system targets. An emphasis is placed on finding structures with desirable binding energies.

**Approach: Optimize Hydrogen Binding Energy, Surface Area, and Site Density**

- Employ wet chemical routes to synthesize organometallic fullerenes after Zhao et al. *PRL* 94 155504 (2005). Correlate experimental findings with new theory.

- Examine new alternative non-fullerene-based compounds.


- Perform theoretical calculations to identify promising new materials and determine synthetic pathways.

- Develop high throughput measurement capabilities to accelerate discovery, development and partner interactions.
Technical Accomplishment: New M(C₆₀) Synthesis

Six Organometallic Fullerene Complexes Have Been Synthesized and New Structures Have Been Demonstrated.

<table>
<thead>
<tr>
<th>Material</th>
<th>Metal at%</th>
<th>Yield</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>20Li(C₆₀)</td>
<td>&gt;90%</td>
<td>Ionic / polymer</td>
<td></td>
</tr>
<tr>
<td>16Li(C₆₀)</td>
<td>&gt;90%</td>
<td>Ionic</td>
<td></td>
</tr>
<tr>
<td>Fe(C₆₀)</td>
<td>1-1.5% Fe</td>
<td>20-30%</td>
<td>Chain</td>
</tr>
<tr>
<td>Co(C₆₀)</td>
<td>16% Co</td>
<td>Co most likely coating or particulates</td>
<td></td>
</tr>
<tr>
<td>Sc(C₆₀)</td>
<td>1-1.5% Sc</td>
<td>20-30%</td>
<td>Chain</td>
</tr>
<tr>
<td>Cr(C₆₀)</td>
<td>&lt;10%</td>
<td>Structure still being determined</td>
<td></td>
</tr>
</tbody>
</table>

Example of Fe(C₆₀) and Sc(C₆₀) ¹³C NMR spectra used to determine that unique M(C₆₀) structures have been formed. **No non-C₆₀ peaks suggests chain-like structures.** (Note that the C₆₀ NMR line is at 143.7 ppm)

Six new organometallic C₆₀ compounds were synthesized and characterized as part of an effort to form materials with predicted high hydrogen storage capacities and to validate calculations.
Technical Accomplishment: Enhanced Binding Energy for $M(C_{60})$ is Observed for All New Fullerene Complexes

As an example, temperature programmed desorption shows unanticipated binding site for Fe($C_{60}$). $\sim 0.5$ wt% at 77 K, 2 bar with slow kinetics.

Desorption activation energy ($E_d$) described by: $\ln T_m = E_d / RT_m$ indicates enhanced binding energy of $\sim 6.2$ kJ/mol.

Theory indicates the Fe atoms in a chain-like structure stabilize di-hydrogen ligands.

The new organometallic $C_{60}$ compounds demonstrate sites with higher binding energies. Theory has been performed to confirm the most probable binding interaction for Fe($C_{60}$). Good agreement with experiment has been achieved.
Technical Accomplishment: Fe(C\textsubscript{60}) Synthesis Scale-up

TEM of Fe(C\textsubscript{60}) material
- Areas of unreacted Fe (pink) are oxidized upon exposure to air to form Fe\textsubscript{2}O\textsubscript{3}.
- Other areas reveal stable atomic Fe (yellow) indicating that 1 - 1.5 at.% Fe is complexed with C\textsubscript{60}.

Gram quantity synthesis enables accurate characterization measurements. Volumetric analysis at higher pressure now possible.

C\textsubscript{60}-Fe-C\textsubscript{60}-Fe-chains may result in porous framework with unique sites for hydrogen adsorption. Purification and/or increased Fe loading may increase H\textsubscript{2} capacity.

XRD consistent with loosely ordered aligned chains (porous network with atomically dispersed metal).
Technical Accomplishment: Synthesis Correlation Li(C₆₀) Structure with Adsorption

TPD of 16Li(C₆₀) material reveals a binding energy of ~ 6 kJ/mol. Agreement with Sun et al. JACS 128 (2006) 9741. ~0.2 wt.% , 77 K, 2 bar

Compound with excess Li shows 0.5 wt.% H₂ desorption at 200 °C perhaps due to weakly bound Li-H.

Previously 0.5 wt.% H₂ desorption at 200 °C attributed to polymerized structure, as 34Li(C₆₀) polymerized compound does not reveal this desorption site.

Hydrogen stabilized on Li(C₆₀) at room temperature with no over pressure may be due to a C-Li-H structure with the H binding energy lowered due to dispersion by the C₆₀ framework. (Bulk LiH formation is ~ 2 eV/H₂). The low-temperature binding energy is consistent with theory.
Technical Accom.: Synthesis of Hydrogenated Carbons

- Na⁺ reduced carbons show new binding sites for hydrogen.

- The aromatic carbon double bonds are weakened due to the formation of ionic species, and hydrogenation may occur.

- Deuterium experiments were employed to show that THF may serve as a source for hydrogen.

A new Na⁺ reduction process reveals unique hydrogen adsorption sites on aromatic carbon surfaces. Future efforts will focus on enhancing reversible capacity.
Technical Accomplishment: Synthesis
Arc-discharge for B-doping

Previously Reported: Laser vaporization was employed to produce B-SWNT. EELs and $^{13}$C NMR confirmed doping level 1-2%.

Blackburn et al., Chem. Mater. 18, 2558 (2006)

Unique Arc-Discharge Assembly

Catalysts: NiB, Ni$_2$B, Co$_3$B
Purification with HCl / CO$_2$, 800 °C
Still ~1-2 % B incorporation

Need to Increase B content
- New reactive processes are required.
New laboratory construction in progress.
New capabilities for reactive precursors, elevated temperatures etc.

The economical arc-discharge technique has been demonstrated for the production of B-doped nanotubes. New facilities are under construction to achieve higher boron loading and synthesize new materials.
Technical Accomplishment: Synthesis
NIST Neutron Scattering for B-doped SWNTs

Arc SWNTs have double peak structure. *Liu et al. in prep.* An enhanced binding energy is not detected, as in previous NMR studies, implying better sensitivity with NMR.

- Neutron scattering suggests different adsorption sites for arc tubes vs. laser tubes but better sensitivity is required to observe enhanced binding energy.
- Raman suggests these sites may arise from defects or impurities.
Volumetric measurements indicate that laser low B content SWNTs and pure SWNTs have similar $H_2$ adsorption properties. **Need higher B-loading to determine effects of boron doping.**
Technical Accomplishment: Theory
New Hydrogen Adsorbents

Metallaborane Nanostructures

Metallacarborane Nanostructures

Boron Replaces Carbon

\( B_{60}Sc_{20} \) ↔ \( B_{60}Sc_{20}H_{144} \)

\( \sim 8.6\% \) wt.\%, reversible, 52 kgH\(_2\)/m\(^3\)

~ 8.6% wt.% , reversible, 43 kgH\(_2\)/m\(^3\)

Calculations show both reversible and irreversible adsorption.

Discharged complex stability is probed at 1000 K. Aggregation / degradation is not observed.

New promising nanostructures have been identified. The structures emphasize boron as a replacement for carbon. These predictions will guide future synthetic efforts.
Technical Accomplishment: Theory
A New Concept: The Metal Inside
Hydrogenation of Endohedral Metallofullerenes

Endohedral Metallofullerenes are a new class of materials identified by NREL that may meet DOE hydrogen storage targets. NREL calculations indicate that Ca$_2$ is the optimal endohedral dopant for hydrogen storage. Similar endohedral fullerenes have been easily synthesized at high yield; e.g. Ge et al. JACS 127 (2005) 16292.

Charge transfer from Ca$_2$ both allows for reversible hydrogen storage as well as the stabilization of negative curvature in the fullerene. Zhao et al. JACS (submitted)

$\text{Ca}_2 \@ \text{C}_{60}$
$\text{Ca}_2 \@ \text{C}_{60} \text{H}_{52}$

6.1% wt.%, reversible, $\sim 50$ kg/m$^3$
Technical Accomplishment: Measurements
Unique Capabilities Available to Partners

NREL developed new temperature control system that enables BET, TPD, pore size, and volumetric meas. from 12 to 1300 K.

SSA measurements using $H_2$ and He

Methods used: BET, TPD, TGA, XRD, low & high pressure Sieverts

Samples can be measured as-received (after degassing) and after each NREL processing step (including anneals in various gases and wet chemical treatments)

NREL has transferred procedures and equipment to allow for airless sample transport from external labs

NREL worked with multiple institutes to provide measurements/consultation

FY06 performed 108 measurements on 36 samples

FY07 performed ~107 (to date) measurements on 31 samples

NREL improved the temp. control of our quartz tube sample holders. This enables more accurate measurements using external port configurations for higher throughput.

NREL continues to improve our measurements capabilities to provide more accurate and unique hydrogen storage materials characterization faster.
Future Work

• Purify Fe(C₆₀) compound, synthesize Cr(C₆₀) compound at higher yield and further evaluate excess Li(C₆₀) compound to increase capacity and meet year end milestone. Employ simpler systems to explore synthetic transformations and achieve higher hydrogen loading.

• Finalize lab space and construction of new reactors capable of employing reactive precursors for novel synthetic pathways that will lead to increased boron-doping and gas phase assembly of new structures.

• Continue to theoretically probe promising new materials including hybrid structures, intercalated graphite as well as non-carbon based adsorbents. Merge theoretical and experimental efforts such that theory will guide in the synthesis of promising compounds.

• Continue development of rapid throughput hydrogen storage capacity measurements and the evaluation of partner samples. Transfer NREL’s measurement expertise to other center members.
Summary

• Six novel organometallic fullerene compounds were synthesized each with unique hydrogen adsorption sites.
  – Structural characterization as well as H$_2$ capacity measurements (see table next slide) suggest these materials warrant further study.

• A new hydrogen adsorption mechanism has been revealed on Na$^+$ reduced (hydrogenated) carbon materials.

• Both arc and laser-generated B-doped SWNTs have been made and evaluated with neutron scattering (~2% B-loading).
  – New laboratory space / reactor facilities are under construction such that highly reactive gas phase precursors may be employed to improve boron loading as well as to synthesize new compounds.

• New classes of materials for hydrogen storage have been identified including metallaboranes, metallacarboranes and endohedral fullerenes. Theory has been employed to validate experiments.

• Hydrogen storage measurement capabilities have been improved to accelerate development of materials that can meet DOE storage targets.
## Summary Table of NREL Synthetic Results

### Material Performance

<table>
<thead>
<tr>
<th>Storage Parameters</th>
<th>Units</th>
<th>System Targets (2010)</th>
<th>Specific Energy Wt% H₂</th>
<th>Volumetric Energy Capacity g/L</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>FY06 FY05 FY06 FY06 FY07 FY07 FY07 FY07 FY07 FY07</td>
<td>FY06 FY07 FY07 FY07 FY07 FY07 FY07 FY07 FY07 FY07</td>
<td></td>
</tr>
<tr>
<td>SWNTs, validated ⁴</td>
<td>6</td>
<td>3</td>
<td>*</td>
<td>28</td>
<td>77 K, 20 bar</td>
</tr>
<tr>
<td>B-SWNT</td>
<td></td>
<td></td>
<td>~2.2 ²</td>
<td>*</td>
<td>77 K, 20 bar</td>
</tr>
<tr>
<td>Fe(C₆₀)</td>
<td></td>
<td></td>
<td>FY06 FY06 FY06 FY06</td>
<td>*</td>
<td>77 K, 20 bar</td>
</tr>
<tr>
<td>Cr(C₆₀)</td>
<td></td>
<td></td>
<td>FY06 FY06 FY06 FY06</td>
<td>*</td>
<td>77 K, 20 bar</td>
</tr>
<tr>
<td>Li(C₆₀)</td>
<td></td>
<td></td>
<td>FY07 FY07 FY07 FY07</td>
<td>*</td>
<td>77 K, 20 bar</td>
</tr>
<tr>
<td>Reduced SWNTs</td>
<td></td>
<td></td>
<td>FY07 FY07 FY07 FY07</td>
<td>*</td>
<td>77 K, 20 bar</td>
</tr>
<tr>
<td>Reduced AX-21</td>
<td></td>
<td></td>
<td>FY07 FY07 FY07 FY07</td>
<td>*</td>
<td>77 K, 20 bar</td>
</tr>
<tr>
<td>&lt;4 Angstrom Pore Size Material</td>
<td></td>
<td></td>
<td>FY07 FY07 FY07 FY07</td>
<td>*</td>
<td>77 K, 20 bar</td>
</tr>
</tbody>
</table>

* Information not available

Volumetric capacities derived from material densities

a. 3 wt% results reproduced at different laboratories.
b. Blackburn et al. Chem. Mat. 18 2558 (2006), B-doping level (~1-2% now) will be increased as precursors / techniques develop.
c. When excess Li is present.
d. Mostly irreversible. Demonstrates potential reversible capacity once dissociation material can be incorporated with lattice.
## Summary Table: NREL Predicted Materials

### NREL Theoretical Materials Predictions

<table>
<thead>
<tr>
<th>Storage Parameters</th>
<th>Units</th>
<th>System Targets (2010)</th>
<th>Organometallic Fullerenes&lt;sup&gt;a&lt;/sup&gt;</th>
<th>MetCars&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Macromolecules</th>
<th>Endohedral Metallofullerene&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Metallaborane</th>
<th>C&lt;sub&gt;3&lt;/sub&gt;B&lt;sub&gt;2&lt;/sub&gt;ScH&lt;sub&gt;12&lt;/sub&gt;</th>
<th>Spillover on SWNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Energy</td>
<td>Wt% H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>6</td>
<td>~9</td>
<td>3.7-7.7</td>
<td>&gt;5</td>
<td>6.1</td>
<td>8.6</td>
<td>10.5</td>
<td>10.5</td>
</tr>
<tr>
<td>Volumetric Energy Capacity</td>
<td>g/L</td>
<td>45</td>
<td>52-43</td>
<td>48-58</td>
<td>&gt;40</td>
<td>*</td>
<td>52</td>
<td>52</td>
<td>~56</td>
</tr>
<tr>
<td>Comments</td>
<td></td>
<td></td>
<td>STP, 23-46 kJ/mol</td>
<td>STP, 15-32 kJ/mol</td>
<td>STP</td>
<td>~STP, 10-78 kJ/mol</td>
<td>STP</td>
<td>STP</td>
<td>RT, 100 bar</td>
</tr>
</tbody>
</table>

* Information not available

Volumetric capacities derived from material densities

c. Y. Zhao et al. submitted to JACS.
Additional Slides
Assume organometallic fullerenes will pack in an FCC crystal consistent with C₆₀.
Assuming close packing C₆₀[ScH₂(H₂)₄]₁₂ and C₄₈B₁₂[ScH(H₂)₅]₁₂ center to center distance is ~ 17.6 Å each.
This could allow for approximately 42 kg/m³ and 52 kg/m³, respectively.

**Assuming a low overpressure will be employed, it will be possible to utilize a light container; then organometallic fullerenes could meet the 2010 volumetric targets.**
Reaction sequences: synthesis of 6 organometallic fullerene compounds.

\[
\begin{align*}
C_{60} + 6K & \rightarrow K_6C_{60} + C_pFe(CO)_2I \quad \text{THF} \quad \text{dry ice} \quad \text{Fe}(C_{60}) \\
\text{fulleride} & \quad \text{Chains?}
\end{align*}
\]

\[
\begin{align*}
C_{60} + 6K & \rightarrow K_6C_{60} + Sc(SO_3CF_3)_3 \quad \text{THF} \quad \text{dry ice} \quad \text{Sc}(C_{60}) \\
\text{fulleride} & \quad \text{Chains?}
\end{align*}
\]

\[
\begin{align*}
C_{60} + 12(CH_3CH_2CN)_3Cr(CO)_3 & \rightarrow \text{Cr}(C_{60}) \quad \text{THF} \quad \text{dry ice} \quad \text{Low Yield}
\end{align*}
\]

\[
\begin{align*}
C_{60} + 6Co_2(CO)_8 & \rightarrow \text{Co}(C_{60}) \quad \text{uv} \quad \text{Decorated?}
\end{align*}
\]

\[
\begin{align*}
C_{60} + xLi & \rightarrow \text{Li}_xC_{60} \quad \text{NH}_3 \quad \text{dry ice} \quad \text{Incomplete}
\end{align*}
\]

\[
\begin{align*}
C_{60} + 12Li & \rightarrow \text{Li}_{12}C_{60} \quad \text{NH}_3 \quad \text{dry ice} \rightarrow RT \quad \text{Reaction appears complete}
\end{align*}
\]
Solid State $^{13}$C Nuclear Magnetic Resonance Spectra

- Sharp feature at 143.7 ppm corresponds to $C_{60}$.
- The Li, Fe, Sc and Cr spectra indicate formation of new compounds.
- The Co spectrum may indicate some charge transfer.

Novel organometallic fullerene chemistry is demonstrated.

- $Li_xC_{60}$, with $x \sim 3-6$: yield $> 90\%$.
- $Fe(C_{60})$ with $\sim 1 - 1.5$ at.% Fe: yield $\sim 20 - 30\%$.
- $Sc(C_{60})$ likely $\sim 1-1.5$ at.% Fe: yield $\sim 20-30\%$.
- $Fe(C_{60})$ with Co most likely existing as coating or small particles.
- $Cr(C_{60})$ : yield $< 10\%$ making structure difficult to determine.
Technical Accomplishment: Enhanced Binding of M-C$_{60}$

Temperature programmed desorption (TPD) of Fe(C$_{60}$) indicate substantially enhanced hydrogen storage compared to C$_{60}$. Volumetric measurements indicate ~ 0.5 wt.% H$_2$ storage at 77 K and 2 bar. Slow kinetics at low T.

TPD of Cr(C$_{60}$), Sc(C$_{60}$), and Co(C$_{60}$) indicate higher hydrogen binding energies. Volumetric measurements of Cr(C$_{60}$) indicated ~ 0.5% wt% H$_2$ storage at 77K, 2 bar.

Comparison of TPD from Li, Sc, Co, Cr, and Fe- (C$_{60}$), materials indicates that Li (C$_{60}$) has substantially higher hydrogen storage capacities (~0.5 wt%) at ambient conditions.

- Samples showed no capacity degradation after cycling (mass spec. measurements).
- Uptake and discharge for TPD measurements over several minutes.

The new organometallic C$_{60}$ compounds demonstrate sites with higher binding energies. The Fe, Li and Cr complexes warrant further investigations to quantify the heats of adsorption and/or optimize the hydrogen storage capacities.
Commenting on our paper: Sun, Wang, Jena, & Kawazoe suggested that Metal Clustering Could Be a Problem - JACS 127, 14582 (2005)

- Comparison of thermodynamics of chosen initial and final configurations
- We showed by molecular dynamics that an energy barrier between these two states renders the initial state stable up to 1000 K

In any event, Boron incorporation pins the metals in place, rendering the metal-dispersed arrangement stable from even a thermodynamic point of view.

Zhao et al., NREL
Mechanism: The Role of Charge Transfer

Ca$_2@C_{60}$

0~36H

Ca$_2@C_{60}H_{36}$ - $T_h$

36~44H

Ca$_2@C_{60}H_{52}$ - $T_h$

44~52H
Metallacarborane Nanostructures

$\text{C}_3\text{B}_2\text{Sc}$

HOMO-LUMO: 0.32(sp6)/0.12(sp0) eV
C-C: $1.45/1.55$ Å (double/single)
C-B: $1.51/1.58$ Å (double/single)
Sc-C: $2.37(1)/2.10(2)$ Å
Sc-B: 2.38 Å
Sc-Sc: 5.62 Å

$\text{C}_3\text{B}_2\text{ScH}_{12}$: wt.% ~ 10.5%
0.40 eV/H$_2$
HOMO-LUMO: 1.48 eV

Volumetric: ~52 kg/m$^3$
Theoretical, ambient, reversible ~ 9 wt% on B-doped C\textsubscript{60}

\[ C_{48}B_{12}[\text{ScH}]_{12} \xrightleftharpoons{60H_2} C_{48}B_{12}[\text{ScH}(H_2)_5]_{12} \]

H\textsubscript{2} charge/discharge ~ 1atm
C\textsubscript{48}B\textsubscript{12} [ ScH]_{12} stable at 1000K


Theory predicts stable organometallic fullerene complexes for H\textsubscript{2} storage. We have experimentally demonstrated this concept with novel compounds.
Improved Laboratory Space

- Consolidation of all synthesis & purification processes (laser, arc, & hot wire)
- Improved environmental conditions will improve sample quality
- Larger space will allow increased production

Estimated completion in Summer, 2007


NREL Invited Presentations

7. "Nanoscience for Energy Conversion and Storage" M.J. Heben, University of Toledo, Department of Physics and Astronomy Colloquium, April 2, 2007.
NREL Contributed Presentations


1. Anne Dillon is leading the organization of a session entitled "The Hydrogen Economy" at the spring 2008 MRS meeting in San Francisco.


4. M.J. Heben co-organized a session on “Hydrogen Production, Transport, and Storage 2” at the ECS meeting in Chicago (May 6 -11, 2007).

5. M.J. Heben co-organized a symposium at the MRS Fall meeting, Boston, MA, in November 2006

6. M.J. Heben submitted a research plan for NREL's participation in a joint project with Richard Chahine (University of Quebec, Trois Rivieres) for the new IEA Annex 22

7. Anne Dillon interacted with and served on the International Program Committee for the 4th International Conference on Hot-Wire CVD (Cat-CVD) Process, Takayama, Japan, October 4-8, 2006.


