NREL Research as Part of the Hydrogen Sorption Center of Excellence

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National Renewable Energy Laboratory
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Project ID ST 2

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.
N. Lack of Understanding of Hydrogen Physi- and Chemisorption.
O. Test Protocols and Evaluation Facilities.

Crosscutting Relevance

Compressed Gas Systems Barrier H: Sufficient Fuel Storage for Acceptable Vehicle Range.
Off-Board Hydrogen Storage Barriers S: Cost and T: Efficiency

DOE 2010 Technical Targets for Storage System

- Gravimetric 0.06 kg H_2/ kg
- Volumetric 0.045 kg H_2/m^3

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.

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.**
- **Continue to develop gas phase processes to generate boron doped materials after *Kim et al. PRL 96 016102 (2006).***
- **Perform theoretical calculations to identify promising new materials and determine synthetic pathways.**
- **Develop high throughput measurement capabilities to accelerate discovery, development and partner interactions.**

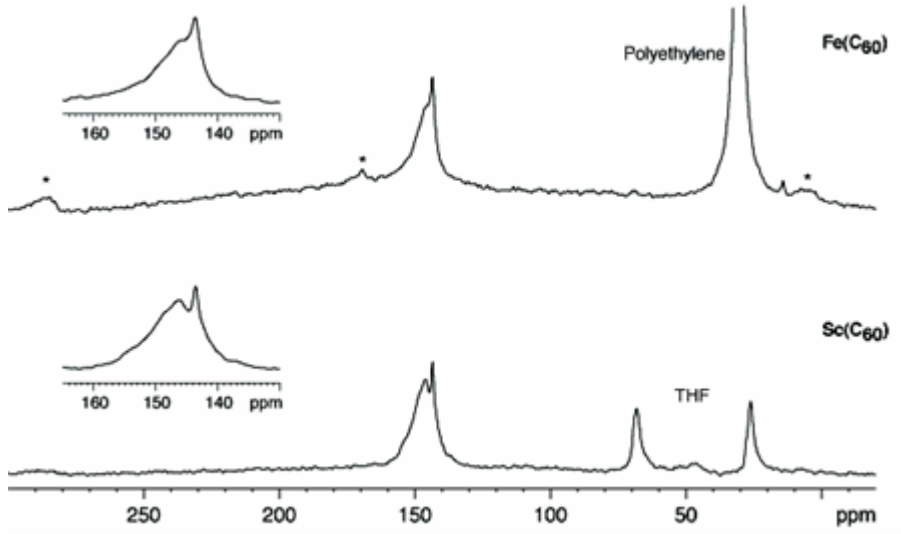
This year NREL focused on accelerating the rational synthesis of multiple compounds that are promising for meeting DOE on-vehicle system targets. An emphasis is placed on finding structures with desirable binding energies.

Technical Accomplishment: New M(C_{60}) Synthesis

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

Summary of different M(C_{60}) compounds synthesized

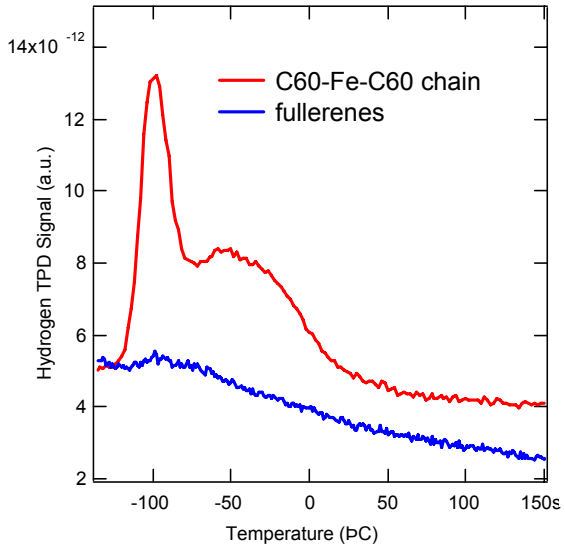
Material	Metal at%	Yield	Comment
20Li(C_{60})		>90%	Ionic / polymer
16Li(C_{60})		>90%	Ionic
Fe(C_{60})	1-1.5% Fe	20-30%	Chain
Co(C_{60})	16% Co		Co most likely coating or particulates
Sc(C_{60})	1-1.5 % Sc	20-30%	Chain
Cr(C_{60})		<10%	Structure still being determined

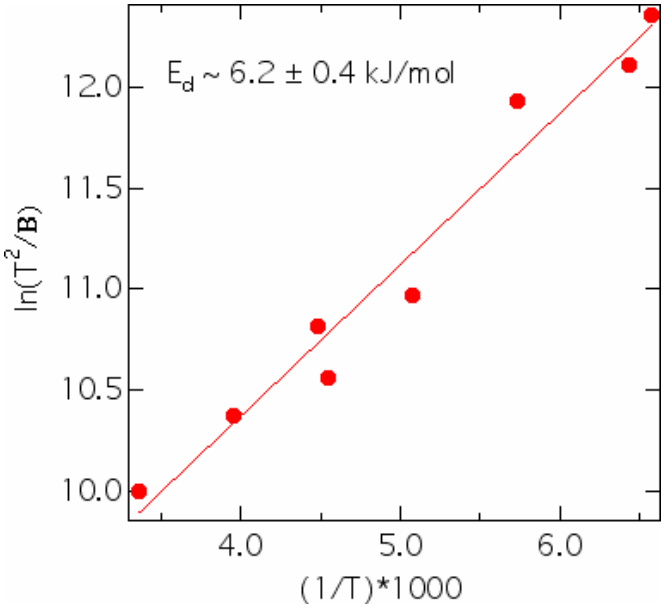


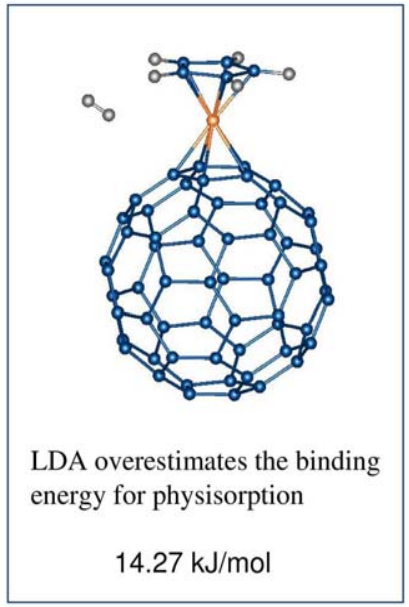
Example of Fe(C_{60}) and Sc(C_{60}) ^{13}C NMR spectra used to determine that unique M(C_{60}) structures have been formed.
No non-C_{60} peaks suggests chain-like structures.
(Note that the C_{60} NMR line is at 143.7 ppm)

Six new organometallic C_{60} 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







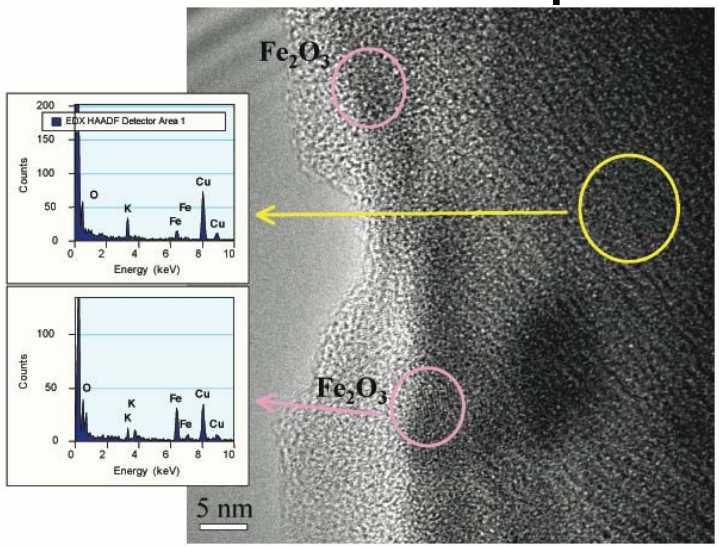
As an example, temperature programmed desorption shows unanticipated binding site for $Fe(C_{60})$. **~ 0.5 wt% at 77 K, 2 bar with slow kinetics.**

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

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

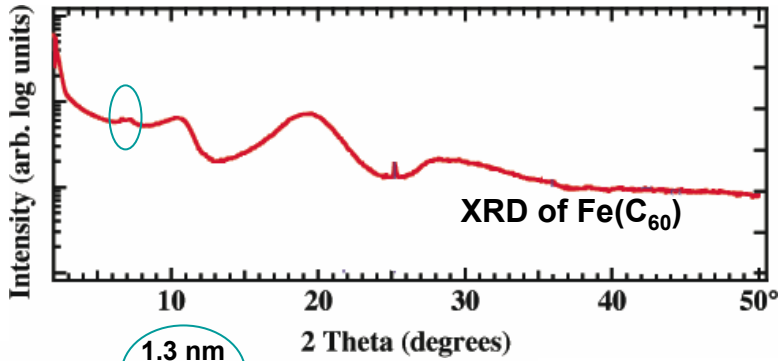
The new organometallic C_{60} compounds demonstrate sites with higher binding energies. Theory has been performed to confirm the most probable binding interaction for $Fe(C_{60})$. Good agreement with experiment has been achieved.

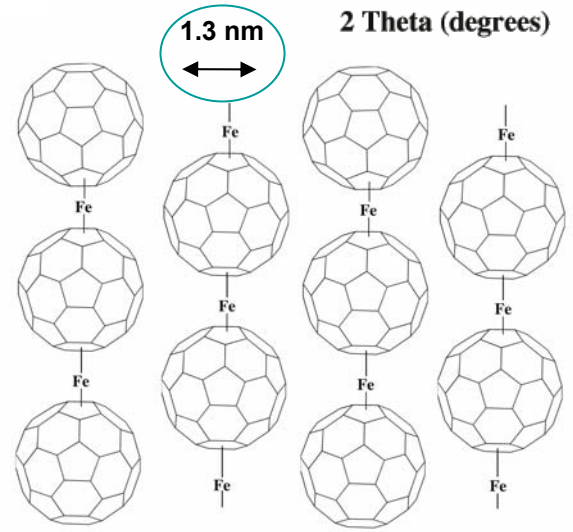
Technical Accomplishment: Fe(C_{60}) Synthesis Scale-up



TEM of Fe(C_{60}) material

- Areas of unreacted Fe (pink) are oxidized upon exposure to air to form Fe_2O_3.
- Other areas reveal stable atomic Fe (yellow) indicating that 1 -1.5 at.% Fe is complexed with C_{60}.



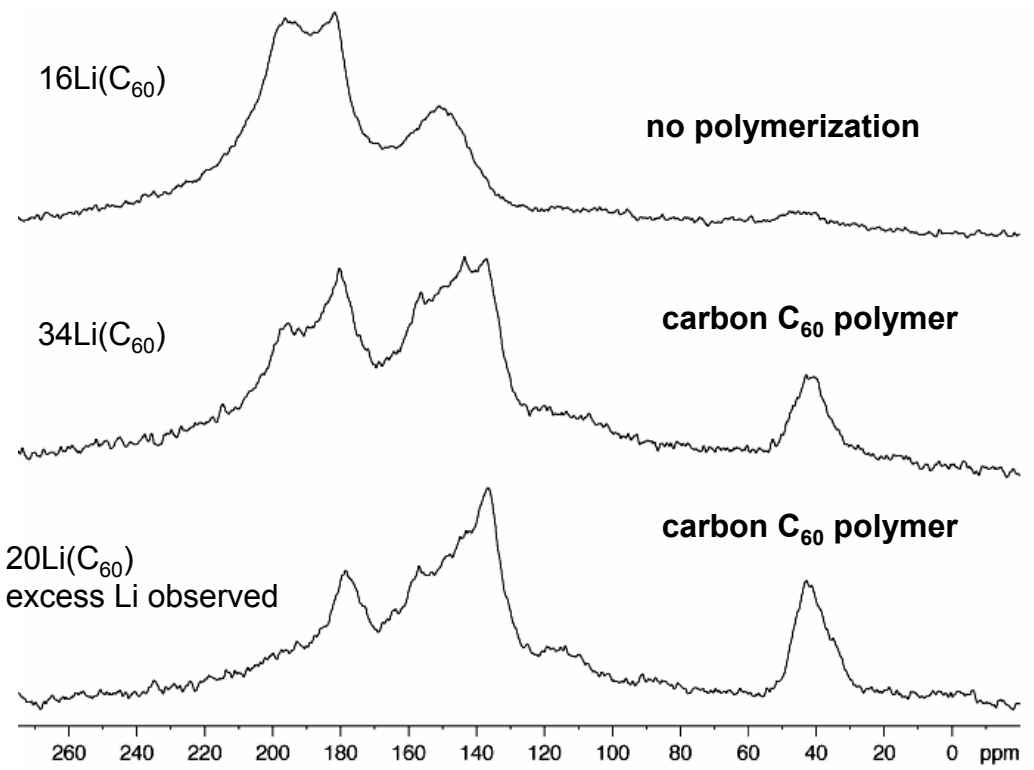


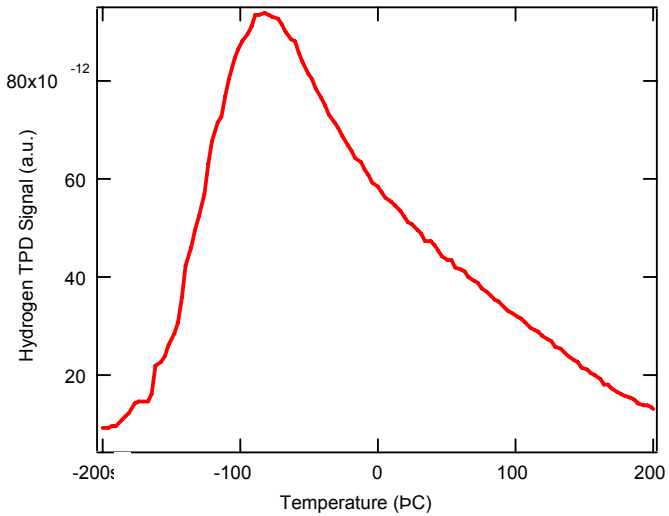
XRD consistent with loosely ordered aligned chains (porous network with atomically dispersed metal).

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

C_{60}-Fe-C_{60}-Fe-chains may result in porous framework with unique sites for hydrogen adsorption. Purification and/or increased Fe loading may increase H_2 capacity.

Technical Accomplishment: Synthesis Correlation Li(C_{60}) Structure with Adsorption





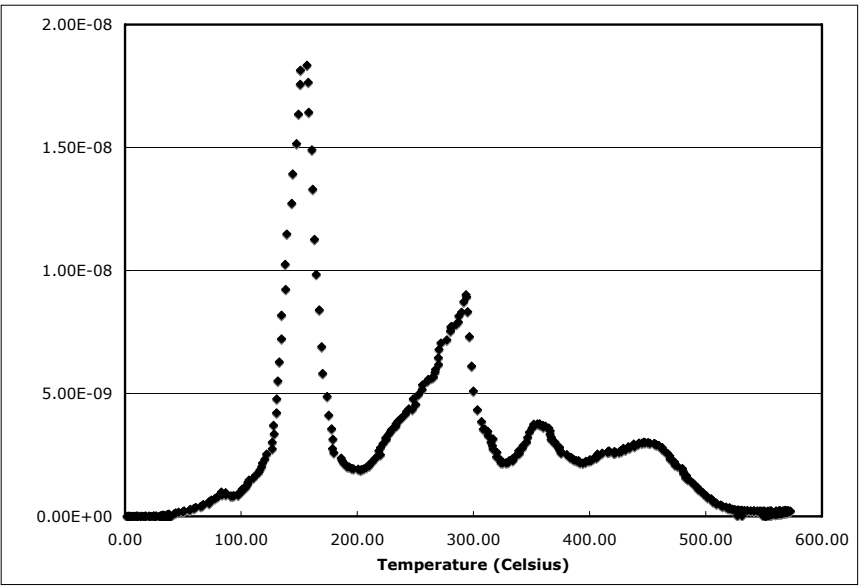
TPD of 16Li(C_{60}) material reveals a binding energy of ~ 6 kJ/mol. Agreement with *Sun et al. JACS 128 (2006) 9741*.
~0.2 wt.% , 77 K, 2 bar

Compound with excess Li shows 0.5 wt.% H_2 desorption at 200 ˚C perhaps due to weakly bound Li-H.

Previously 0.5 wt.% H_2 desorption at 200 ˚C attributed to polymerized structure, as 34Li(C_{60}) polymerized compound does not reveal this desorption site.

Hydrogen stabilized on Li(C_{60}) 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 C_{60} framework. (Bulk LiH formation is ~ 2 eV/H_2). The low- temperature binding energy is consistent with theory.

Technical Accom.: Synthesis of Hydrogenated Carbons



TPD reveals Na^+ reduced AX-21 acquires ~5 wt.% hydrogen from THF.
Na^+ reduced SWNTs acquire ~3.5 - 4 wt.% hydrogen.

~ 0.5 wt.% may be reversibly charged.

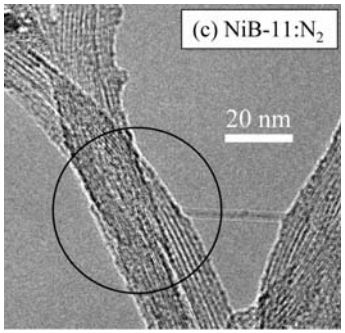
- **Na+ reduced carbons show new binding sites for hydrogen.**
- **The aromatic carbon double bonds are weakened due to the formation of ionic species, and hydrogenation may occur.**
- **Deuterium experiments were employed to show that THF may serve as a source for hydrogen.**

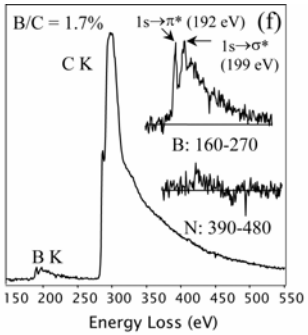
THF

$$+ \ SWNT\text{-}Na \rightarrow SWNT\text{-}H + C_2H_4 + (C_2H_3O)^- Na^+$$

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

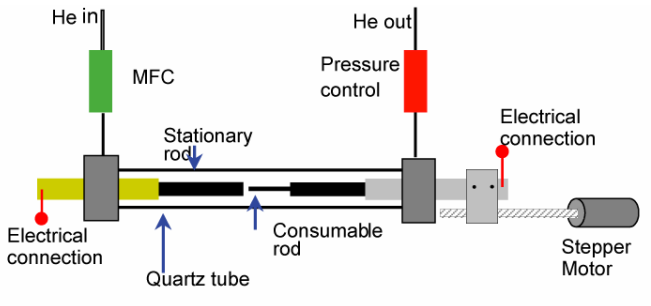




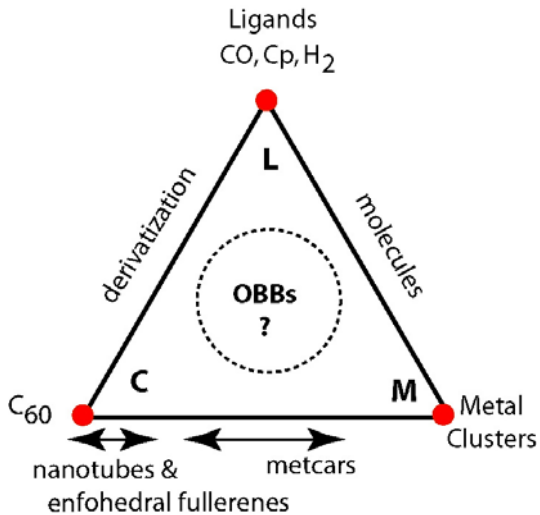
Previously Reported: Laser vaporization was employed to produce B-SWNT. EELs and ^{13}C NMR confirmed doping level 1-2%.

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

Unique Arc-Discharge Assembly



Catalysts: NiB, Ni_2B, Co_3B
Purification with HCl / CO_2, 800 ˚C
Still ~1-2 % B incorporation



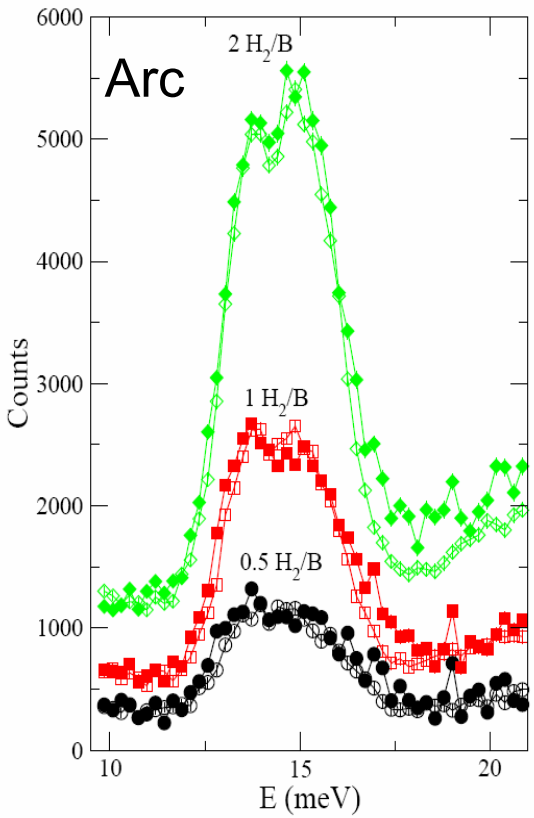
Need to Increase B content
- New reactive processes are required.

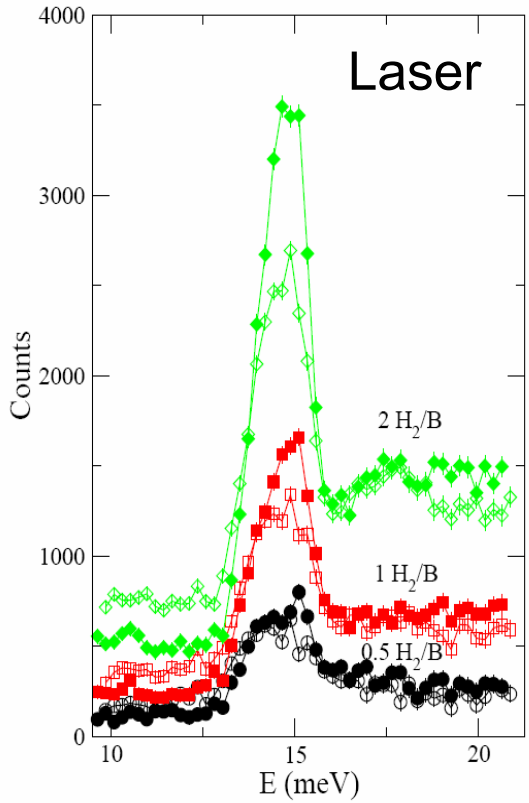
New laboratory construction in progress.

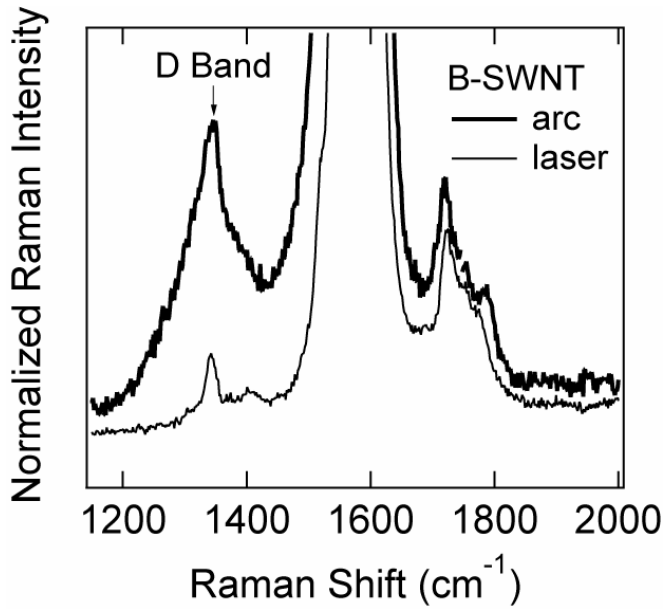
New capabilities for reactive precursors, elevated temperatures etc.

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







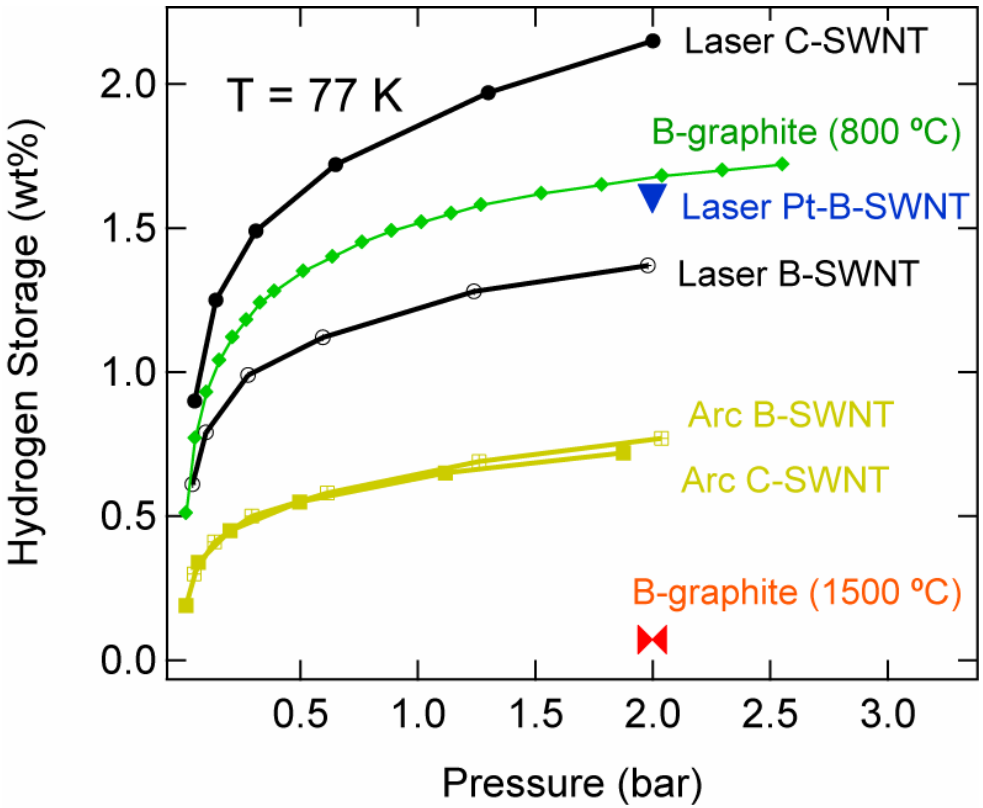
Raman suggests that splitting/broadening may be due to defects and/or impurities in arc SWNTs?

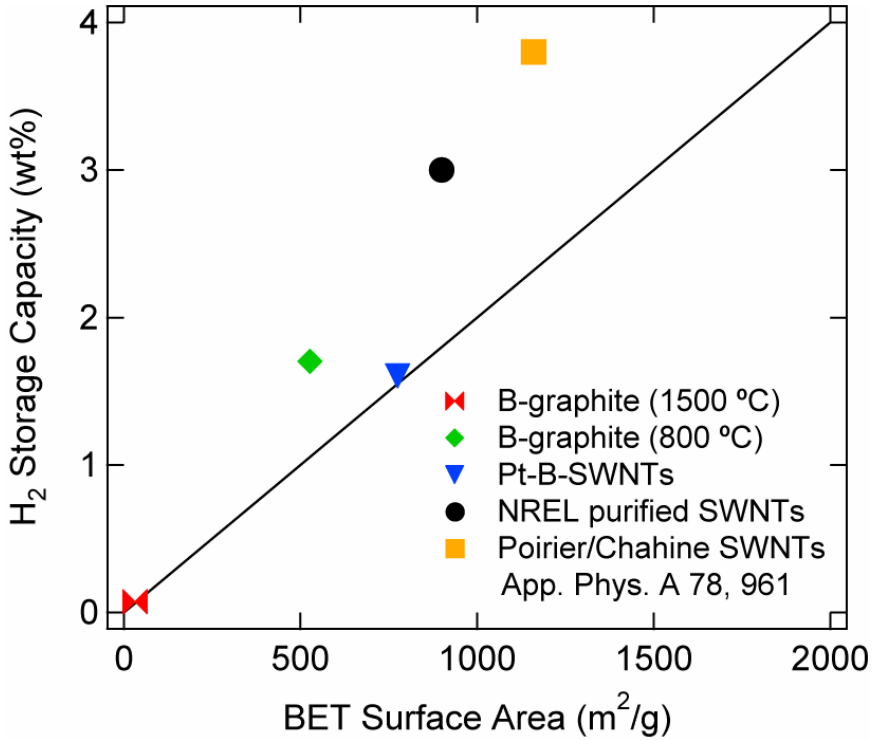
Arc SWNTs have double peak structure. *Liu et al. in prep.*

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.

Technical Accomplishment: Synthesis Volumetric Measurements B-doped Materials





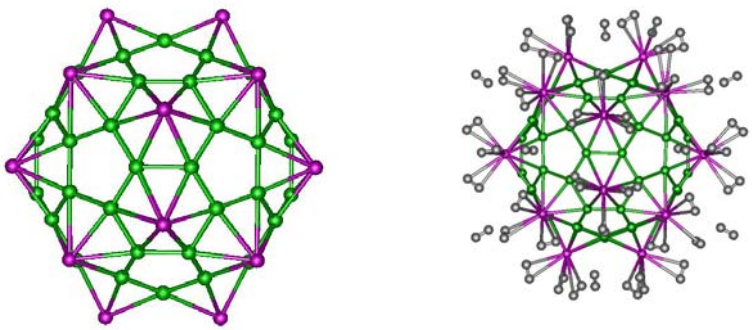
- Anneal T very important for B-graphite (Penn State)
- **Need to increase B-loading and decrease impurities to reveal boron-doping effect.**

- "Chahine Rule": AC ~1 wt% per 500 m^2/g
- Purified SWNTs have ~50% higher H_2 adsorption compared to activated carbon
- H_2 adsorption of B-SWNTs similar to other purified SWNTs on a per SSA basis

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
Boron Replaces Carbon

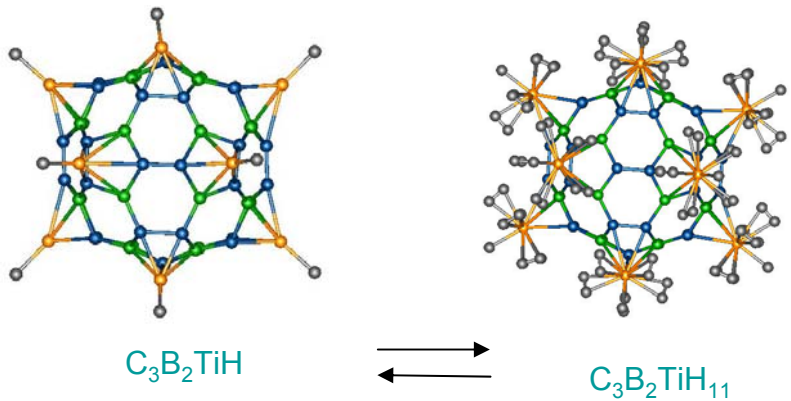


$B_{60}Sc_{20}$ ⇌ $B_{60}Sc_{20}H_{144}$

~ 8.6% wt.%, reversible, 52 kgH_2/m^3

Boron Scandium

Metallacarborane Nanostructures



C_3B_2TiH ⇌ $C_3B_2TiH_{11}$

~ 8.6% wt.%, reversible, 43 kgH_2/m^3

Boron Titanium Carbon

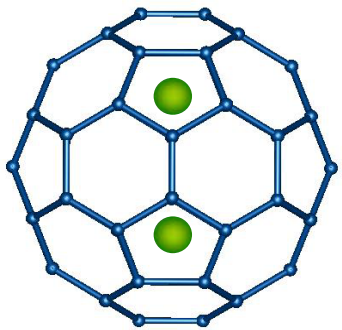
New promising nanostructures have been identified. The structures emphasize boron as a replacement for carbon. These predictions will guide future synthetic efforts.

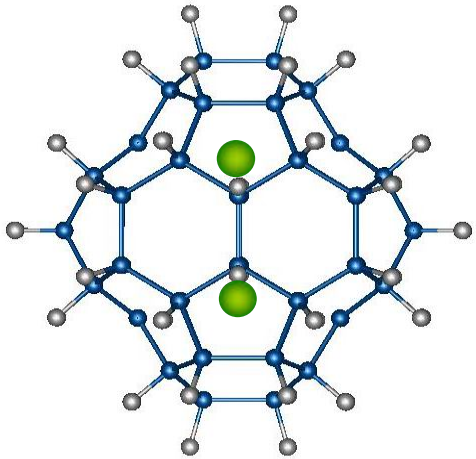
- Calculations show both reversible and irreversible adsorption.
- Discharged complex stability is probed at 1000 K. Aggregation / degredation is not observed.

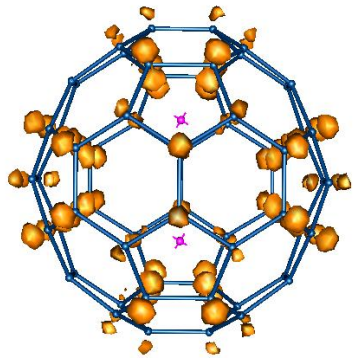
Technical Accomplishment: Theory

A New Concept: *The Metal Inside*

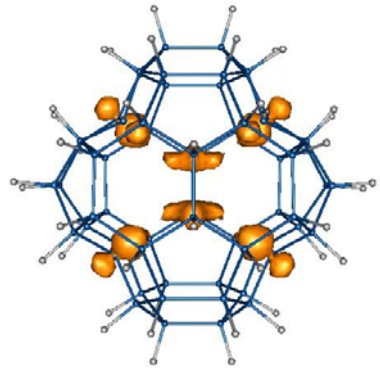
Hydrogenation of Endohedral Metallofullerenes







$Ca_2@C_{60}$



$Ca_2@C_{60}H_{52}$

$Ca_2@C_{60} \rightleftharpoons Ca_2@C_{60}H_{52}$

6.1% wt.%, reversible, ~50 kg/m^3

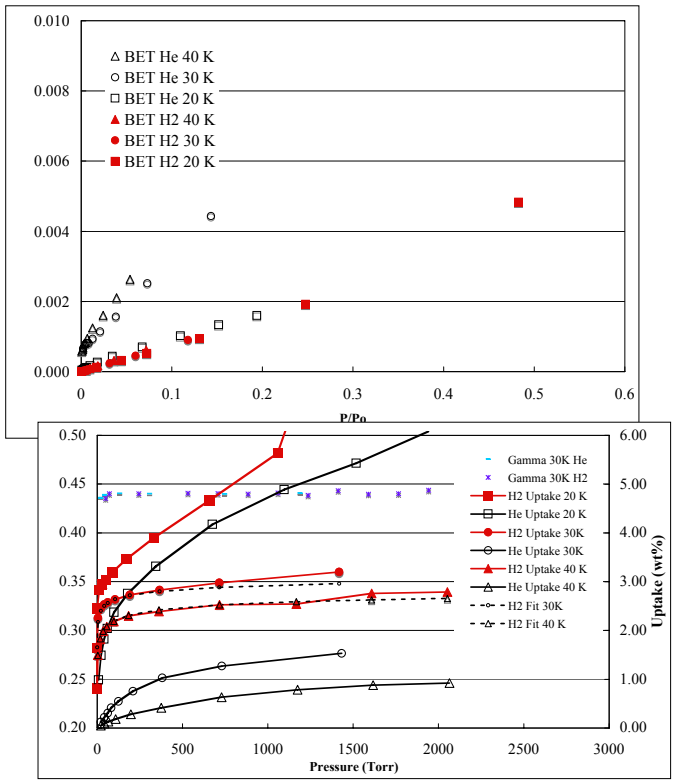
Charge transfer from Ca_2 both allows for reversible hydrogen storage as well as the stabilization of negative curvature in the fullerene. **Zhao et al. JACS (submitted)**

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.*

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

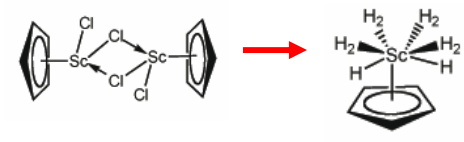
–FY07 performed ~107 (to date) measurements on 31 samples

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

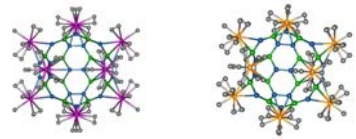
NREL continues to improve our measurements capabilities to provide more accurate and unique hydrogen storage materials characterization faster.

Future Work

- **Purify Fe(C_{60}) compound, synthesize Cr(C_{60}) compound at higher yield and further evaluate excess Li(C_{60}) compound to increase capacity and meet year end milestone. Employ simpler systems to explore synthetic transformations and achieve higher hydrogen loading.**

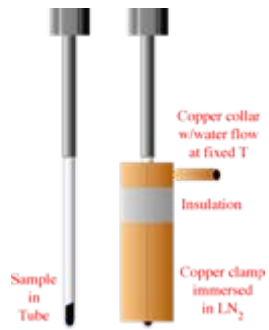


- **Finalize lab space and construction of new reactors capable of employing reactive precursors for novel synthetic pathways that will lead to increased boron-doping and gas phase assembly of new structures.**



- **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													
Storage Parameters	Units	System Targets (2010)	SWNTs, validated[a]	B-SWNT		$Fe(C_{60})$		$Cr(C_{60})$	$Li(C_{60})$	Reduced SWNTs		Reduced AX-21	<4 Angstrom Pore Size Material
			FY06	FY05	FY06	FY06	FY07	FY07	FY07	FY06	FY07	FY07	FY07
Specific Energy	Wt% H2	6	3	*	~2.2[b]	0.5	1	0.5	0.5[c]	4[d]	4[d]	5[d]	1.5
Volumetric Energy Capacity	g/L	45	28	*	20	*	*	*	*	37	37	*	*
Comments			77 K, 20 bar		77 K, 20 bar	77 K, 2 bar	77 K, 85 bar	77 K, 2 bar	STP	STP	STP	STP	77 K, 2 bar

* 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									
Storage Parameters	Units	System Targets (2010)	Organo-metallic Fullerenes [a]	MetCars[b]	Macro-molecules	Endohedral Metallo-fullerene[c]	Metalla-borane	$C_3B_2ScH_{12}$	Spillover on SWNT
			FY05	FY06	FY06	FY07	FY07	FY07	FY07
Specific Energy	Wt% H2	6	~9	3.7-7.7	>5	6.1	8.6	10.5	>7.7
Volumetric Energy Capacity	g/L	45	52-43	48-58	>40	*	52	52	~56
Comments			STP, 23-46 kJ/mol	STP, 15-32 kJ/mol	STP	~STP, 10-78 kJ/mol	STP	STP	RT, 100 bar

* Information not available
Volumetric capacities derived from material densities

a. Zhao etal. PRL 94, 15504 (2005).

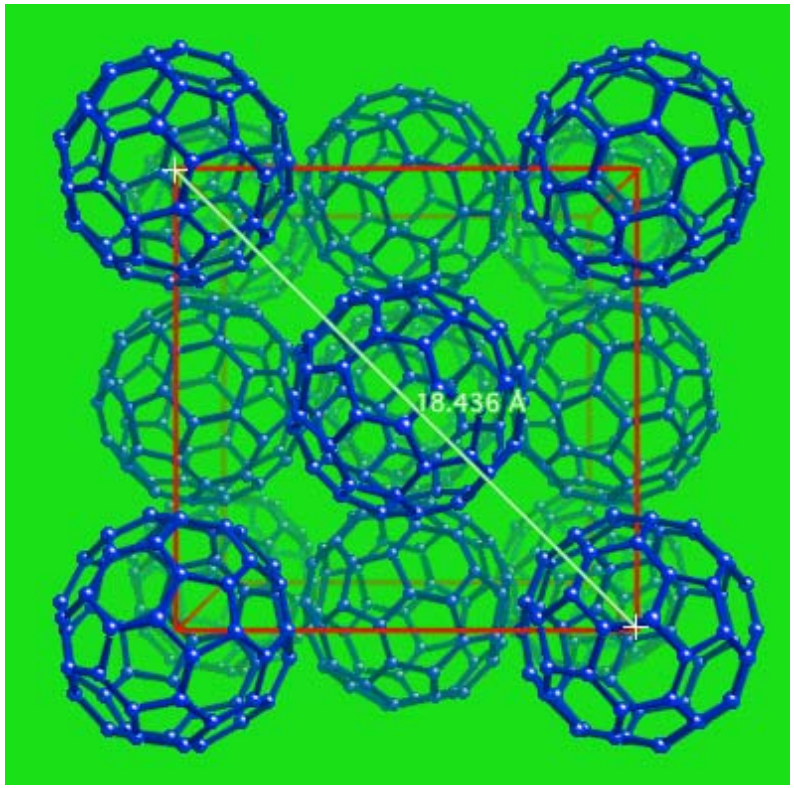
b. Chem. Phys. Lett. 425, 273 (2006).

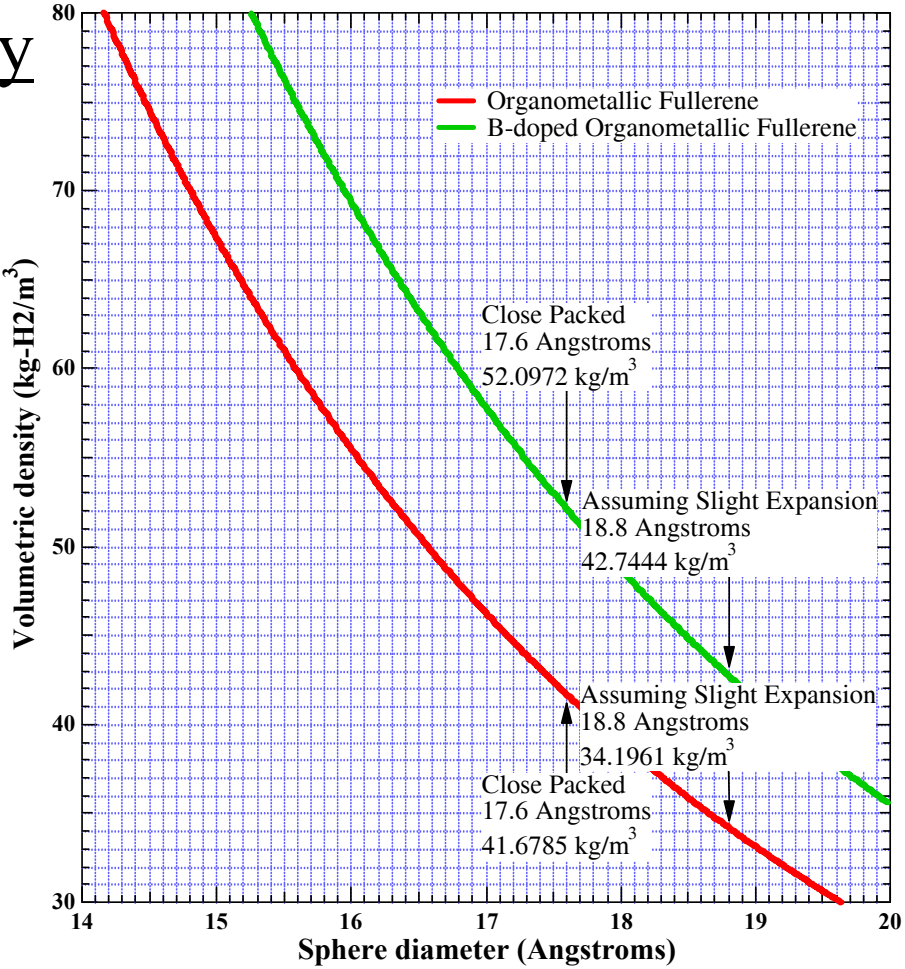
c. Y. Zhao et al. submitted to JACS.

Additional Slides

Probable Volumetric Capacity

C_{60} FCC crystal





- Assume organometallic fullerenes will pack in an FCC crystal consistent with C_{60}.
- Assuming close packing $C_{60}[ScH_2(H_2)_4]_{12}$ and $C_{48}B_{12}[ScH(H_2)_5]_{12}$ center to center distance is ~ 17.6 Å each.
- This could allow for approximately 42 kg /m^3 and 52 kg/ m^3, 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.

$$C_{60} + 6K \xrightarrow[\sim 4\ \text{days}]{250\ ^\circ C} K_6C_{60} + C_pFe(CO)_2I \xrightarrow[dry\ ice]{THF} Fe(C_{60})$$

fulleride — *Chains?*

$$C_{60} + 6K \xrightarrow[\sim 4\ \text{days}]{250\ ^\circ C} K_6C_{60} + Sc(SO_3CF_3)_3 \xrightarrow[dry\ ice]{THF} Sc(C_{60})$$

fulleride — *Chains?*

$$C_{60} + 12(CH_3CH_2CN)_3Cr(CO)_3 \xrightarrow[dry\ ice]{THF} Cr(C_{60})$$

Low Yield

$$C_{60} + 6Co_2(CO)_8 \xrightarrow{uv} Co(C_{60})$$

Decorated?

$$C_{60} + xLi \xrightarrow[dry\ ice]{NH_3} Li_xC_{60}$$

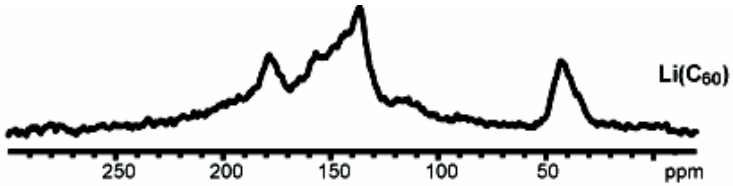
Incomplete

$$C_{60} + 12Li \xrightarrow[dry\ ice\ ->\ RT]{NH_3} Li_{12}C_{60}$$

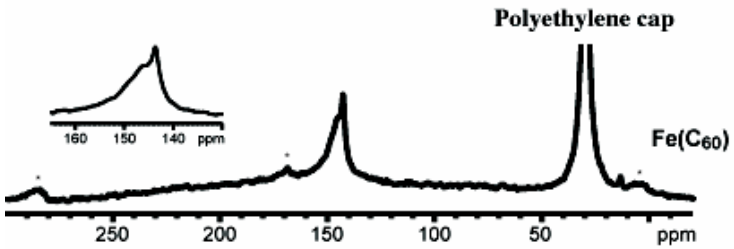
Reaction appears complete

Solid State ^{13}C Nuclear Magnetic Resonance Spectra

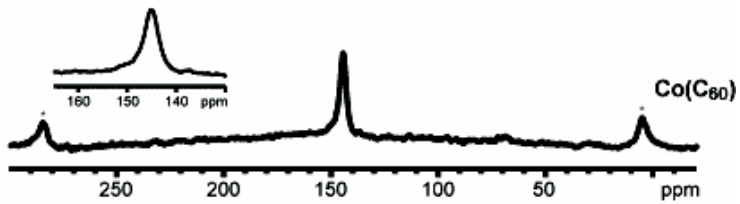
Li_xC_{60}, with x ~ 3-6: yield > 90%.



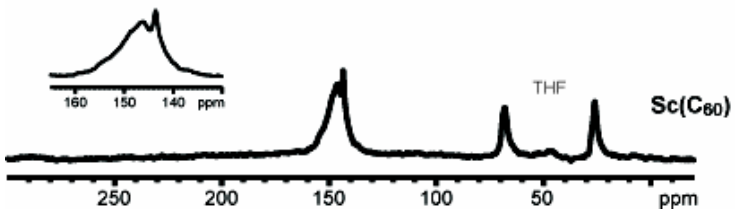
$Fe(C_{60})$ with ~ 1 -1.5 at.% Fe: yield ~ 20-30%.



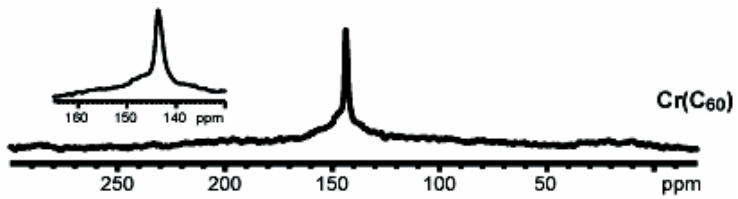
$Fe(C_{60})$ with Co most likely existing as coating or small particles.



$Sc(C_{60})$ likely ~ 1-1.5 at.% Fe: yield ~ 20-30%.



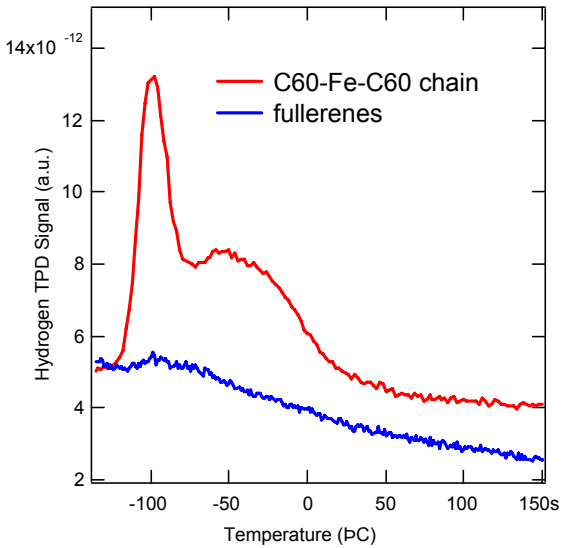
$Cr(C_{60})$: yield < 10% making structure difficult to determine.



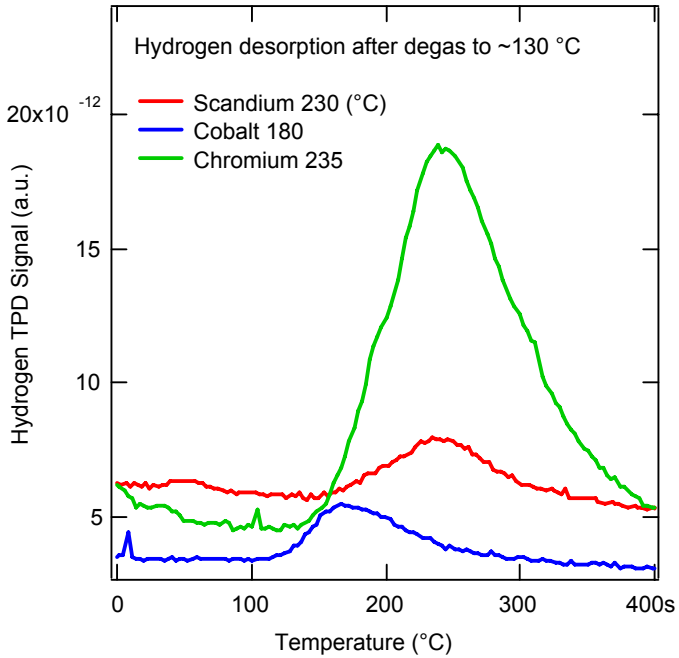
- Sharp feature at 143.7 ppm corresponds to C_{60}.
- The Li, Fe, Sc and Cr spectra indicate formation of new compounds.
- The Co spectrum may indicate some charge transfer.

Novel organometallic fullerene chemistry is demonstrated.

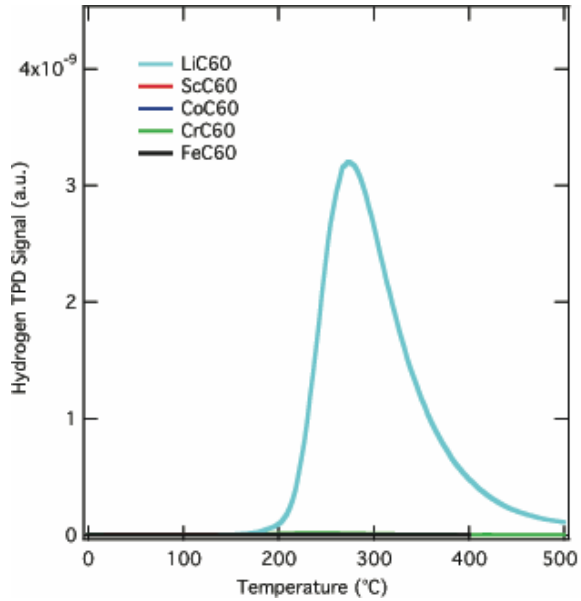
Technical Accomplishment: Enhanced Binding of M-C_{60}



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

initial

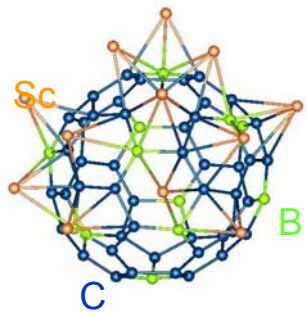
2.07 eV/Ti

final

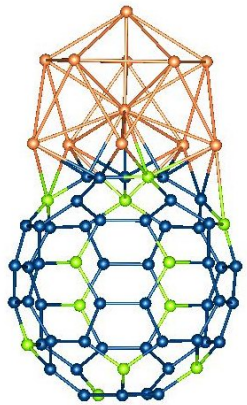
0.0 eV/Ti

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

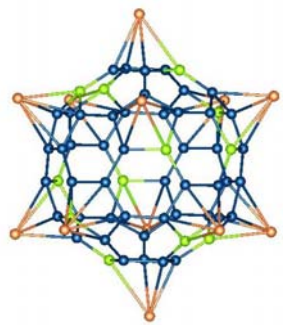
Zhao et al., NREL



-0.07

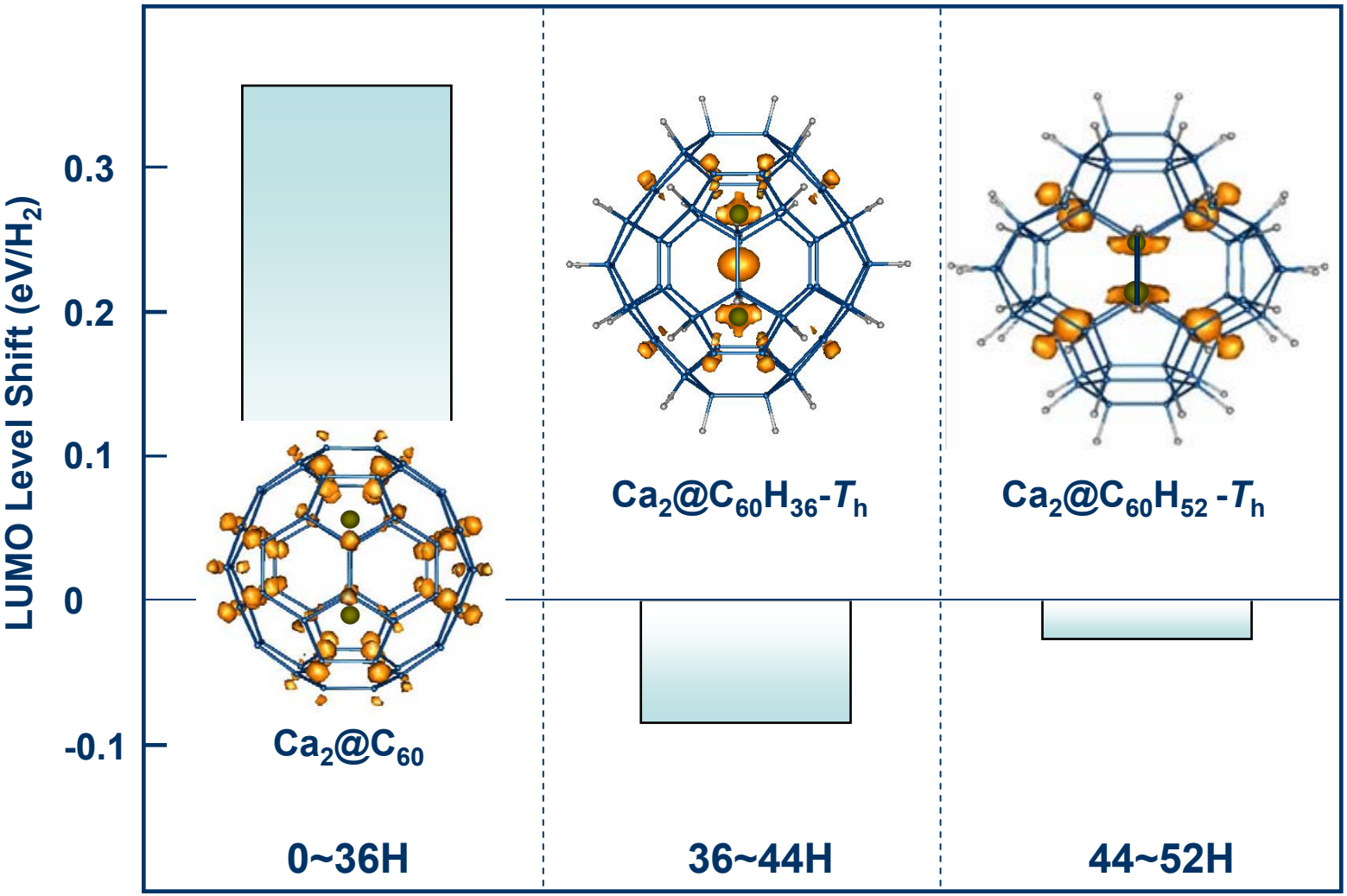


0.0

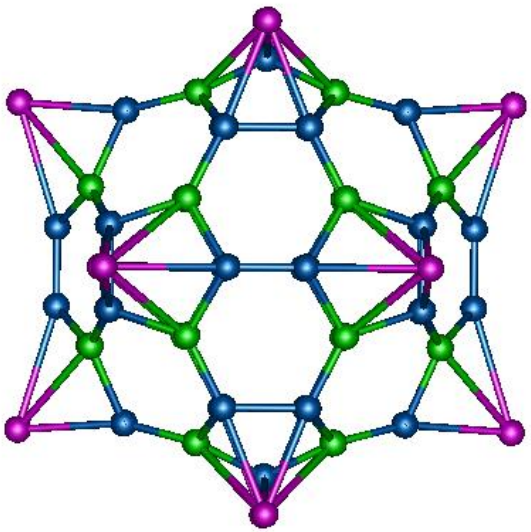


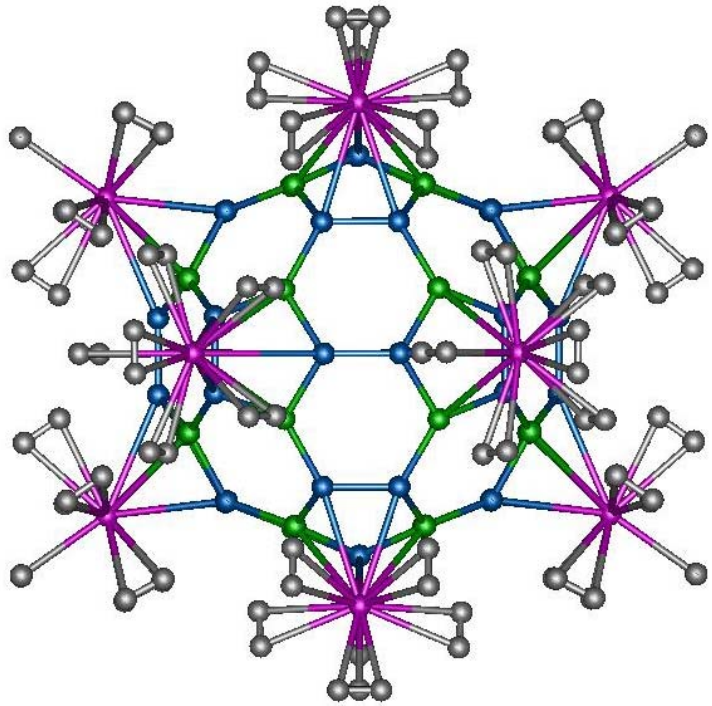
0.86 eV/Sc

Mechanism: The Role of Charge Transfer



Metallacarborane Nanostructures





C_3B_2Sc

HOMO-LUMO: 0.32(sp6)/0.12(sp0) eV

C-C: 1.45/1.55 A (double/single)

C-B: 1.51/1.58 A (double/single)

Sc-C: 2.37(1)/2.10(2) A

Sc-B: 2.38 A

Sc-Sc: 5.62 A

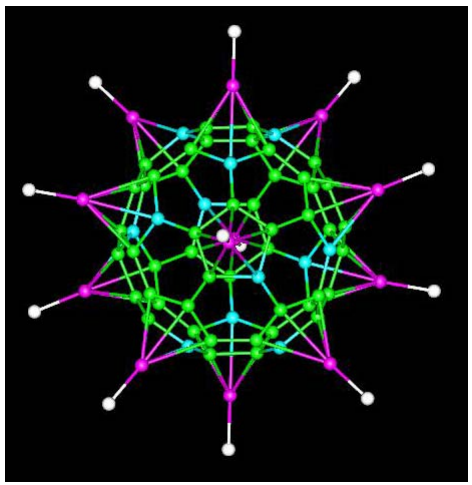
$C_3B_2ScH_{12}$: wt.% ~ 10.5%

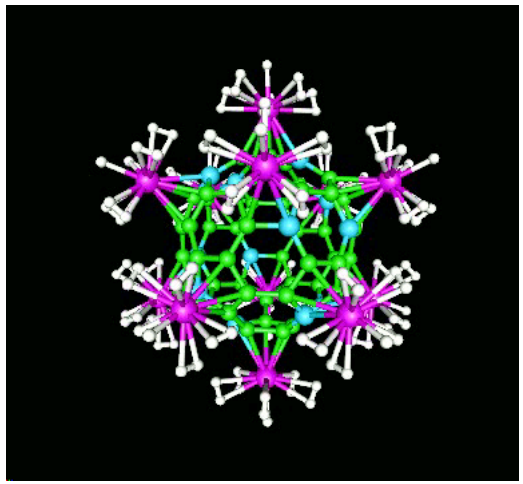
0.40 eV/H_2

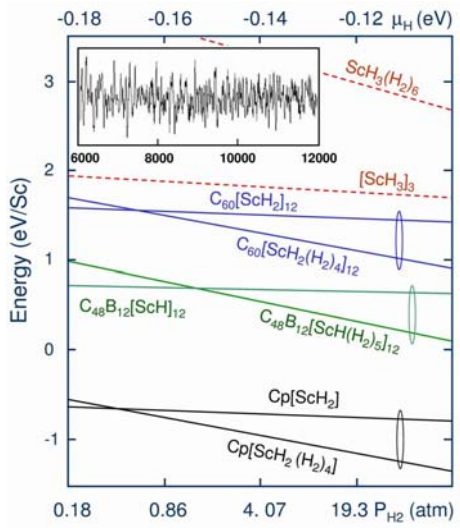
HOMO-LUMO: 1.48 eV

Volumetric: ~52 kg/m3

Theoretical, ambient, reversible ~ 9 wt% on B-doped C_{60}







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

H_2 charge/discharge ~ 1atm

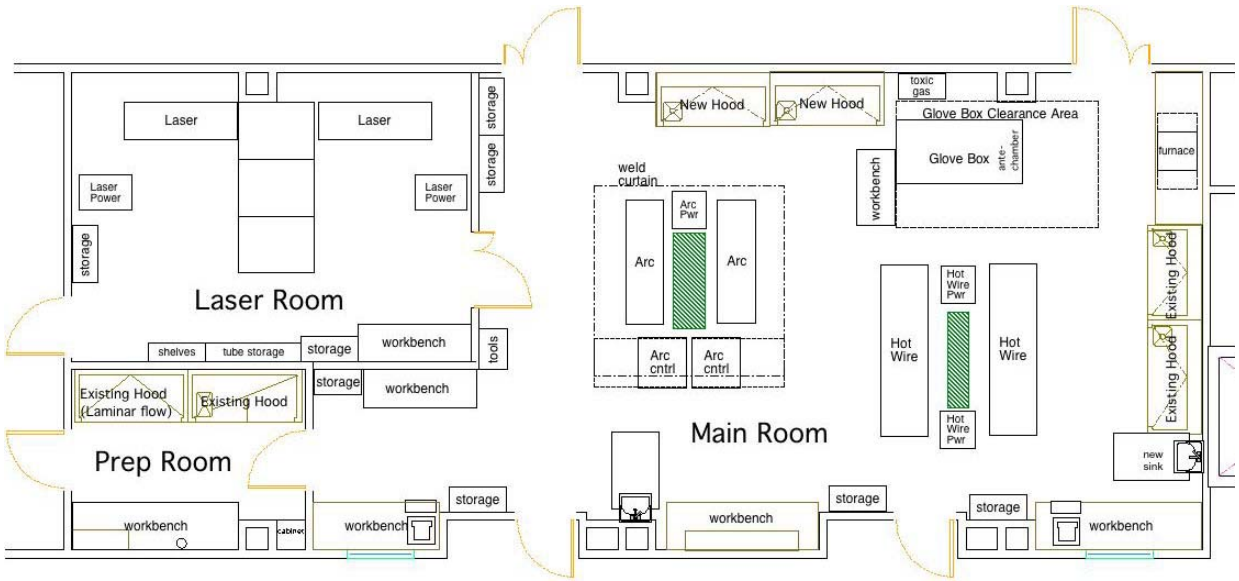
$C_{48}B_{12}$ [ScH]$_{12}$ stable at 1000K

Y. Zhao, Y-H. Kim, A.C. Dillon, M.J. Heben and S.B. Zhang PRL 94 (2005) 155504.

Theory predicts stable organometallic fullerene complexes for H_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 Publications

1. "Sorption Materials for Hydrogen Storage", J.L. Blackburn, A.C. Dillon, C. Engtrakul, M.J. Heben, Y.H-. Kim, P.A. Parilla, L.J. Simpson, E. Whitney, S.B. Zhang, and Y. Zhao, Chemical Reviews, submitted (2007).
2. "Hydrogen storage in carbon-based materials" P. Bénard, R. Chahine, P.A. Chandonia, D. Cossement, G. Dorval-Douville, L. Lafi, and E. Poirier, J.L. Blackburn, C. Curtis, A.C. Dillon, T. Gennett, M.J. Heben, Y.-H. Kim, P.A. Parilla, L.J. Simpson, E.S. Whitney, S.B. Zhang, and Y. Zhao, Final report for Task C1 for the International Energy Agency Hydrogen Implementing Agreement, Task 17, Final Report, 2007.
3. "Measurement of the Reversible Hydrogen Storage Capacity of milligram Ti-6Al-4V alloy samples with Temperature Programmed Desorption and Volumetric Techniques," Jeff L. Blackburn, Philip A. Parilla, Thomas Gennett*, Katherine E. Hurst, Anne C. Dillon, Michael J. Heben, Journal of Alloys and Compounds, Published online January 5 (2007).
4. "Effects of Surfactant and Boron Doping on the BWF Feature in the Raman Spectrum of Single-wall Carbon Nanotube Aqueous Dispersions, "Blackburn, J. L., Engtrakul, C., McDonald, T., Dillon, A. C., and Heben, M. J., Journal of Physical Chemistry, 110, 25551 (2006).
5. "Inelastic Neutron Scattering of H2 Adsorbed on Boron Substituted SWNTs," Y. Liu, C. M. Brown, J. L. Blackburn, D. A. Neumann, T. Gennett, L. J. Simpson, P. A. Parilla, A. C. Dillon, M. J. Heben, Journal of Alloys and Compounds, Special Issue, MH2006
6. "Is the Endohedral metallofullerene a "Smart Material" for Hydorgen Storage?," Y Zhao, M. J. Heben, L. J. Simpson, Y.-H. Kim, A. C. Dillon, P. A. Parilla, and S. B. Zhang, J. Amer. Chemical. Soc. (Submitted)
7. "Non-dissociative adsorption of H2 molecules in light-element doped fullerenes", Y.-H. Kim, Y. Zhao, A. Williamson, M.J. Heben, and S. B. Zhang, Physical Review Letters **96**, 016102 (2006)
8. "Self-catalyzed Hydrogenation and Dihydrogen Adsorption on titanium carbide nanoparticles," Y. Zhao, A. C. Dillon, Y.-H. Kim, M. J. Heben, and S. B. Zhang, Chem. Phys. Lett. **425**, 273 (2006).
9. "Synthesis and Characterization of Boron-doped Single-wall Carbon Nanotubes Produced by the Laser Vaporization Technique"**,** Jeff L. Blackburn, Yanfa Yan, Chaiwat Engtrakul, Philip A. Parilla, Kim Jones, Thomas Gennett, Anne C. Dillon, Michael J. Heben. Chemistry of Materials 18(10), 2558 2006.
10. "High Throughput, High Purity Single Wall Carbon nanotube Synthesis in a Volumetric Confined Arc Chamber," T. Gennett, C. Engtrakul, K. J. Franz, J. A. Alleman, P. A. Parilla, K.M. Jones, J. Blackburn, K .E. H. Gilbert, Jamie Ellis, A. C. Dillon, M. Heben, to be submitted.
11. "Alkali-Metal Induced Hydrogenation Reactions of Single Wall Carbon Nanotubes;" T. Gennett, C. Engtrakul, C. Curtis, J.E. Ellis, L.J. Simpson, J. Blackburn, A. Dillon, M. Heben., manuscript in preparation.
12. "SWNT Materials Applicable to High Charge-Discharge Rate Battery Systems'" T. Gennett, R. Morris, B. Gall, B. G. Dixon, J. Blackburn, C. Curtis and M. Heben. Manuscript in preparation.
13. "Rapid, accurate, *in situ,* calibration of a mass spectrometer for temperature programmed desorption studies", K.E.H. Gilbert, P.A. Parilla, J.L. Blackburn, T. Gennett, A.C. Dillon, and M.J. Heben, manuscript in preparation.
14. "Competitive adsorption between carbon dioxide and methane on carbon nanotube materials" K.E.H. Gilbert, P.A. Parilla, J.L. Blackburn, T. Gennett, A.C. Dillon, and M.J. Heben, manuscript in preparation
15. "Hydrogen Storage in Novel Carbon-based Nanostructured Materials," E.S. Whitney, C.J. Curtis, C. Engtrakul, M.R. Davis, T. Su, P.A. Parilla, L.J. Simpson, J.L. Blackburn, Y. Zhao, Y-H. Kim, S.B. Zhang, M.J. Heben and A.C. Dillon Mat Res. Soc. Proc., Fall 2006.
16. "Nano-octahedra of MoS2 and MoSe2: Global Topological Constraints on Bonding and Stoichiometry", Philip A. Parilla, Anne C. Dillon, Bruce A. Parkinson, Kim M. Jones, Jeff Alleman, David S. Ginley & Michael J. Heben, extended abstract for the ECS Meeting, Denver, CO, May 2006
17. "Metal-doped single-walled carbon nanotubes and production thereof," A. C. Dillon, M. J. Heben, T. Gennett, P. A. Parilla, PCT Patent WO03/085178.

NREL Invited Presentations

1. "DOE Carbon CoE Overview," M. Heben (invited talk) DOE Annual Merit Review, Alexandria, VA, May 15-18, 2007
2. "NREL Reseearch as Part of the Carbon CoE," A. Dillon (invited talk) DOE Annual Merit Review, Alexandria, VA, May 15-18, 2007
3. "DOE Carbon-based Hydrogen Storage CoE Overview," L. J. Simpson (invited poster) DOE Annual Merit Review, Alexandria, VA, May 15-18, 2007
4. "Nanoscience for Energy Conversion and Storage" M.J. Heben, University of Maryland, University of Maryland Energy Research Center Colloquium, April 23, 2007.
5. "Nanoscience for Energy Conversion and Storage," M.J. Heben, Colorado School of Mines, Chemistry Department Colloquium, April 12, 2007.
6. "First-Principles Materials Theory: The Promises and Challenges", Shengbai Zhang, Colloquium, Department of Physics and Astronomy, Washington State University, Pullman, April 5, 2007.
7. "Nanoscience for Energy Conversion and Storage" M.J. Heben, University of Toledo, Department of Physics and Astronomy Colloquium, April 2, 2007.
8. "Group IV Clusters: New Symmetry and Novel Storage Materials", Shengbai Zhang, Colloquium, Depart. of Chem., U. of Nebraska, Lincoln, March 23, 2007.
9. "Novel Organometallic Fullerene Complexes for Vehicular Hydrogen Storage" A. C.. Dillon (invited) International Winter School on Electronic Properties of Novel Materials, Kirschberg, Austria, March 14, (2007).
10. "Theory for hydrogen storage: the organometallic approaches" Yufeng Zhao, (invited Colloquium) Dept. Physics, Colo. Sch. of Mines, Golden, CO ,Jan. 16, (2007).
11. "First-principles study of nanostructured materials for room-temperature reversible hydrogen storage," Shenbai Zhang (invited talk and also session chair) International Workshop on "Clusters - A Bridge Across Disciplines" on Jekyll Island, Georgia, Dec 16-20, 2006.
12. "Update on activities for NREL's Hydrogen Storage Research Program ," Phil Parilla, (invited talk and panelist) Storage Systems Analysis Working Group (SSAWG), Washington, DC 12/12/06.
13. "On the Road to Viable Hydrogen Storage Systems," Mike Heben (invited talk and session chair) Boston, MA, Fall 2006 MRS conference.
14. "Novel Nanostructured Materials for Renewable Energy Applications," Anne Dillon, Seminar at the U. of Colorado, Boulder, Department of Physics, Oct 19, 2006.
15. "Addressing the Carbon SWNT Go/No-Go Decision Point," Michael Heben, (invited talk), DOE Hydrogen Storage Tech Team, Washington, DC, Sept. 21, 2006.
16. "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.
17. "Nanostructured Materials for Room-Temperature Reversible Hydrogen Storage: A First-Principles Study," Shengbai Zhang, Yufeng Zhao, Yong-Hyun Kim, Andrew Williamson, Anne C. Dillon, and Michael J. Heben, (invited talk) International Symposium on Materials Issues in Hydrogen Production and Storage, Santa Barbara, CA, August 25, 2006.
18. "Using Nanoscience to Design Hydrogen Adsorbents," Michael Heben, (iInvited talk) at the University of Toledo, August 20, 2006.
19. "Building Hydrogen Adsorbents with Nanoscience: Overview of Motivation and State of the Art", M.J. Heben, (invited talk), Fourth International Workshop On Polymer Routes to Multifunctional Ceramics for Advanced Energy and Propulsion Applications, July 30 - August 05 (2006).
20. "Novel Nanostructured Materials for a Variety of Renewable Energy Applications" A.C. Dillon, (Invited Talk) International Conference on Composites and Nano-engineering, July 7, 2006 Boulder, CO.
21. "Fullerenes and Nanostructured Materials for Room-Temperature Reversible Hydrogen Storage: A First-Principles Study", S. B. Zhang, Y. Zhao, Y.-H. Kim, A. Williamson, A. C. Dillon, M. J. Heben, (invited talk), The 209th Electrochemical Society (ECS) Meeting, Denver, CO, May 7, 2006.
22. "Hydrogen Storage in Novel Carbon-based Nanostructured Materials" A.C. Dillon, (invited talk / session chair), Materials Research Society Meeting, April 30, 2006, San Francisco, CA.

NREL Contributed Presentations

1. "Hydrogen Storage Materials Investigations of Nanostructured Sorbents," L.J. Simpson, P. Parilla, J. Blackburn, K. O'Neill, T. Gennett, C. Engtrakul, E. Whitney, A. Dillon and M. Heben, (contributed talk) Electrochemical Society Conference, Chicago, IL May 5-11 (2007)
2. "High Charge-Discharge Rate Performance of Single Wall Carbon Nanotube Based Anodes," T. Gennett, R. Morris, B. Gall, B. G. Dixon, J. Blackburn, C. Curtis and M. Heben. (contributed talk) Electrochemical Society International Meeting, Chicago, Illinois, May 2007.
3. "Alkali Metal Reduced Carbon Single- Walled Nanotubes as Primary Hydrogen Storage Materials," T. Gennett, C. Curtis, C. Engtrakul, J. Ellis and M. Heben (contributed talk) Electrochemical Society International Meeting, Chicago, Illinois, May 2007.
4. "Novel H2 Sorption Measurements of Nanostructured Materials," L.J. Simpson, P. Parilla, J. Blackburn, K. O'Neill, T. Gennett, C. Engtrakul, E. Whitney, A. Dillon and M. Heben, (contributed talk) American Physical Society, Denver CO March 5-9 (2007).
5. "High Pressure Volumetric Sorption Measurements On Small Samples At Low Temperatures", P. A. Parilla, L.J Simpson, J.L. Blackburn, A.C. Dillon, and M.J. Heben, (contributed talk), March APS Meeting, Denver, CO, March 2007.
6. "Smart-Material Behavior for Endohedral Metallofullerenes in Hydrogen Storage" Yufeng Zhao, M. J. Heben, A. C. Dillion, L. Simpson, J. L. Blackburn, H. C. Dorn,and S. B. Zhang, (contibuted talk), APS March Meeting, Denver, CO March 2007.
7. "Hydrogen Storage in Novel Carbon-based Nanostructures: Fe-C60," Erin Whitney (contributed talk) Gordon Conference on Renewable Fuels in Ventura Beach, California, Jan. 21-26, 2007.
8. "Hydrogen Storage in Novel Organometallic Fullerene Complexes," Erin Whitney (contributed talk) Fall MRS Conf., Boston, MA, Nov. 2006.
9. "Hydrogen Storage Properties of Boron-doped Carbon Nanotubes," Jeff Blackburn, A. Dillon, T. Gennett, P. A. Parilla, Y. H. Kim, Y. Zhao, S. Zhang, Y. Yanfa, K. Jones, L. J. Simpson. J. A. Alleman, M. J. Heben, (contributed Talk) Fall MRS Meeting in Boston, Nov. 27- Dec.1 2006.
10. "Lithium Capacity and Electrochemical Performance of Boron Doped Single Wall Carbon Nanotubes," T. Gennett, R. S. Morris, B. Dixon, B. Gall, T. Gennett, J. Blackburn, M. J. Heben, (contibuted talk) MRS Conference, Boston, MA November 2006.
11. "Absorption Cross Section and Quantum Efficiency of Pristine and Boron-doped Single-walled Carbon Nanotubes,". J. L Blackburn, T. J McDonald, T. Gennett, Y. Yan, K. M. Jones, C. Engtrakul, K. Knutson, R. J. Ellingson, G. Rumbles and M. J Heben; (contributed talk) MRS Meeting, Boston, MA, December 2006.
12. "Endohedral Metallofullerenes:A Smart Material for Hydrogen Storage" Yufeng Zhao, M. J. Heben, A. C. Dillion, L. Simpson, J. L. Blackburn, H. C. Dorn,and S. B. Zhang, (contibuted talk) MRS Conference, Boston, MA November 2006.
13. "Hydrogen adsorption in boron doped graphite and single walled carbon nanotubes probed by 1H nuclear magnetic Resonance measurements," Shenghua Mao, A. Kleinhammes, Q. Chen, Y. Wu, M. Chung, J. Blackburn, M. J. Heben, (contributed talk) MRS Fall Meeting, Boston, Nov. 2006. Abstract No. Z6.7.
14. "NMR-a sensitive tool for probing minority adsorption sites in carbon based hydrogen storage materials," Alfred Kleinhammes, Shenghua Mao, Qiang Chen, Yue Wu, Michael Chung, Jeff Blackburn, Michael J. Heben, (contributed Talk) MRS Fall Meeting, Boston, Nov. 2006. Abstract No. MM1.3.
15. "Carbon Based Hydrogen Storage; Boron-Substituted SWNTs," Craig Brown, (contributed talk with NREL material) MH2006-International Symposium on zMetal-Hydrogen systems, Fundamentals and Applications, Lahaina, Maui, Hawaii, October 1-6, 2006.
16. "Hydrogen Storage in Novel Organometallic Fullerene Complexes," Anne Dillon (poster) CU/NREL Research Symposium, Oct 3, 2006.
17. "Hydrogen Storage in Novel Carbon-based Nanostructured Materials," E. Whitney, (contributed talk) ACS Green Chem. Workshop, Wash. D.C. June 22-24, 2006
18. "Novel Organometallic Functionalization of Fullerenes for Hydrogen Storage Applications" A.C. Dillon, (contributed talk), Spring ECS May 2006.
19. "Nano-octahedra of MoS_2 and $MoSe_2$: Global Topological Constraints on Bonding and Stoichiometry", Philip A. Parilla, Anne C. Dillon, Bruce A. Parkinson, Kim M. Jones, Jeff Alleman, David S. Ginley & Michael J. Heben, (contributed talk), ECS Meeting, Denver, CO, May 2006
20. "Hydrogen Volumetric Sorption Measurements On Small Samples At Low Temperatures", P. A. Parilla, L.J Simpson, J.L. Blackburn, A.C. Dillon, T. Gennett, K.E.H. Gilbert, & M.J. Heben, (contributed talk), Spring MRS Meeting, San Francisco, CA, April 2006.
21. "Hydrogen Storage Properties of Laser-generated Boron-doped Carbon Nanotubes." Jeff Blackburn, Anne Dillon, Thomas Gennett, Phil Parilla, Lin Simpson, Katie Gilbert, Yong-Hyun Kim, Yufeng Zhao, Shangbai Zhang, Yanfa Yan, Kim Jones, Michael Heben, (contributed talk), Electrochemical Society Meeting, Spring 2006, Denver, CO.
22. "Hydrogen Storage using Carbon Nanomaterials", L.J. Simpson, P.A. Parilla, J.L. Blackburn, T. G. Gennett, C. Engtrakul, A.C. Dillon, and M.J. Heben. (contributed talk) Electrochemical Society Meeting, May 2006.
23. "Alkali Metal Reduction of Carbon Single-Walled nanotubes," C. J. Curtis, T. Gennett and M. J. Heben, ECS International Meeting, Denver Colorado, May 2006.
24. "High Yield Synthesis of Boron-doped Single-walled Nanotubes by Pulsed Laser Vaporization and their Optical and Vibrational Properties," J. L. Blackburn, T. J. McDonald, T. Gennett, et al., MRS International Meeting April 2006.

NREL Services

1. Anne Dillon is leading the organization of a session entitled "The Hydrogen Economy" at the spring 2008 MRS meeting in San Francisco.
2. Anne Dillon is co-organizing a Symposium entitled "Life-Cycle Analysis" at the Materials Research Society (MRS) Fall Meeting, Boston, MA Nov. 26-30, 2007.
3. Anne Dillon is on the International Organizing Committee for the "International Symposium on Materials Issues in a Hydrogen Economy" to be held in Richmond, Virginia during November 12-15, 2007.
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.
8. Anne Dillon participated in The National Academy of Engineering's U.S. of Frontiers of Engineering Symposium, Dearborn, MI, Sept. 21-23, 2006, discussing energy related topics.
9. L.J. Simpson and M.J. Heben, edited the HS CoE contribution to the DOE 2006 Annual Report
10. M.J. Heben co-organized the “Symposium on Hydrogen Production, Transport, ad Storage” at the Spring meeting of the ECS , Denver CO, May 8-12, 2006.
11. M.J. Heben co-organized and edited the proceedings volume for the “Symposium EE, Hydrogen Storage Materials" at the Spring Meeting of the MRS, San Francisco CA, April 17 -21, 2006.