

# NREL Research as Part of the Hydrogen Sorption Center of Excellence

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ST19

# Overview

## Timeline

- Center of Excellence start date: FY05
- Center of Excellence end date: FY10
- Percent complete: 60%

## Budget

- \$2.34 M in FY07
- \$2.53 M in FY08

## Barriers

**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.

## 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 (V. Crespi), U. Michigan (R. Yang), University of North Carolina (Y. Wu), U. Miami, Ohio (J. Zhou), ANL (D.J. Liu). U. Chicago (L. Yu) + others outside of the COE

# Objectives

**NREL's research in the HSCoE is targeted at addressing key technical barriers in DOE's Hydrogen Storage Program:**

- **Efficiency:** It is clear that the highest efficiency storage system will be achieved with a sorbent material which operates reversibly on-board with a hydrogen binding energy in the range of 15 - 20 kJ/mol (room T operation).
- **Refueling Time:** The fastest on-board refueling time will be found for a sorption system when the materials are not limited by heat transfer processes.
- **Weight and Volume:** When the sorption material has an optimized binding energy and thermal conductivity, non-sorbing system hardware can be kept to a minimum. Capacities of the system will then be approximated by the capacities of the materials.
- **Cost:** We are closing the gap between the idealized sorption materials that have been predicted and the synthesis of actual materials using low cost source materials and synthesis processes.

# Approach: NREL Contributes to the Research Conducted in Four Research Clusters

**RC1: “Engineered Nanospace”** Develop stable high surface area, minimally macroporous, light materials that can either stabilize large quantities of hydrogen directly (by physisorption), or provide frameworks for incorporating/stabilizing other species.

**RC2: “Doped Materials”** Increase concentration of substitutional dopants (e.g. B and N) in lattices to sorb dihydrogen directly (via donation), stabilize active species (e.g. TMs) against agglomeration, or provide anchor points for building more complex sorbents.

**RC3: “Strong Binding of H<sub>2</sub>”** Synthesize sorbents which can bind multiple dihydrogen ligands through metals that are capable of Kubas binding. Examples are chemical and gas phase syntheses of organometallic materials and MOFs.

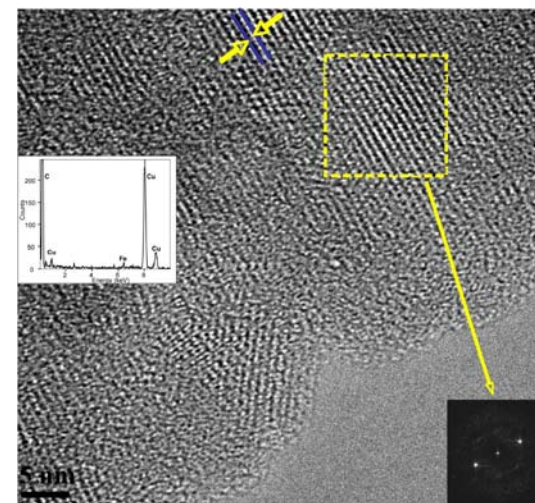
**RC4: “Storage by Spillover”** Develop methods to prepare catalytic species, bridges, receptors, and the activation processes to reproducibly prepare spillover materials with high capacities and good kinetics.

- **All RCs require balancing hydrogen and material reactivity with the density and stability of the sorption sites.**
- **RCs build on each other to make an optimized material: e.g. molecules developed in RC3 can be localized on doped (RC2) high surface area (RC1) materials.**

## RC3 Accomplishment: “Strong Binding of H<sub>2</sub>”

# Wrapping-up Synthesis of Organometallic Fullerenes

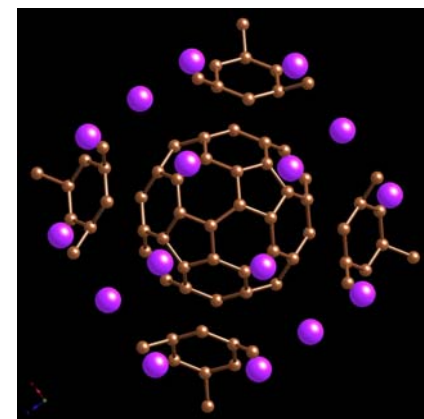
Compound	Hydrogen Capacity	Binding Energy (kJ/mol)	Structure	Hydride Formation
Fe(C <sub>60</sub> )	0.5 wt.%: 77 K, 2 bar 1 wt.%: 77K, 85 bar	6 kJ/mol	chain	no
12Li(C <sub>60</sub> )	0.8 wt.%: RT, STP 0.2 wt%: 77 K, 2 bar	6 kJ/mol	polymer	LiH
K <sub>6</sub> C <sub>60</sub>	0.004 wt.%: RT, 2 bar 0.06 wt.%: 77 K, 2 bar	N.A.	crystal	no
32Ca(C <sub>60</sub> )	1.04 wt.% RT, STP 0.25 wt.%: 77 K, 2 bar	> 100 kJ/mol 4 kJ/mol	polymer	CaH <sub>2</sub>
Na(C <sub>60</sub> )	1.1 wt.% RT,	~100 kJ/mol (onset)	ion	NaH



Purified C<sub>60</sub>-Fe-C<sub>60</sub>-Fe-C<sub>60</sub>

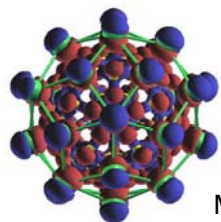
- Inspired by theoretical work of *Zhao et al. PRL 94 155504 (2005)* and *Q. Sun, et al. JACS 128 (2006) 9741*.
- Theoretical compounds proving to be difficult to make.
- Table shows subset of findings from many experiments which were designed to make the target species.
- C<sub>60</sub> serves as a model system that is easy to characterize and the synthetic knowledge obtained from these studies may be transferred to simpler systems based on less expensive starting materials.

Knowledge obtained from synthesis of C<sub>60</sub> compounds will shed light in organometallic synthesis of simpler systems designed to stabilize multiple di-hydrogen ligands.



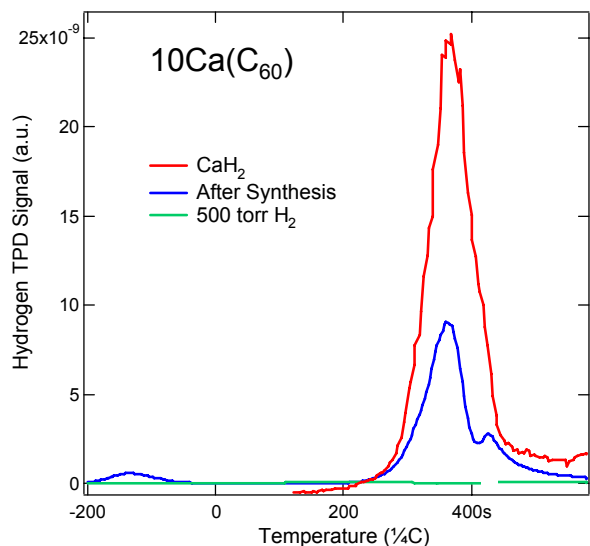
K<sub>6</sub>C<sub>60</sub> Crystal Structure

# RC3 Accomplishment: "Strong Binding of H<sub>2</sub>" Followed-Up on Prediction of New Ca<sub>32</sub>C<sub>60</sub> Compound



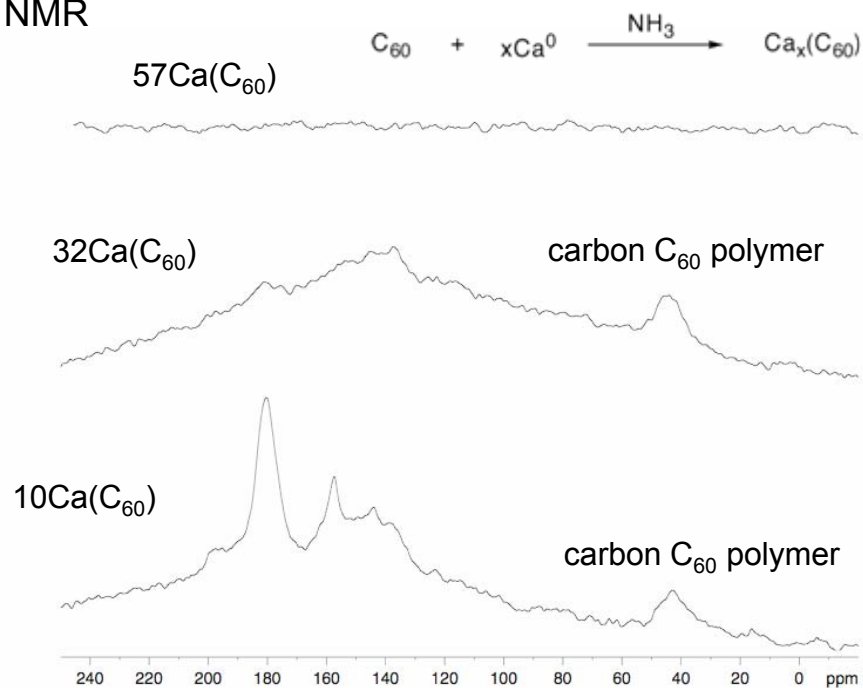
ORNL theory predicts  
Ca<sub>32</sub>C<sub>60</sub> ~8.4 wt% H<sub>2</sub> uptake  
at near ambient conditions.

M. Yoon et al. Phys. Rev. Lett. (under review)



- Temperature programmed desorption measurements revealed that for all samples, the calcium hydride is formed during synthesis but could not be regenerated with RT H<sub>2</sub> exposure. (TPD for 10CaC<sub>60</sub> is representative.)

NMR



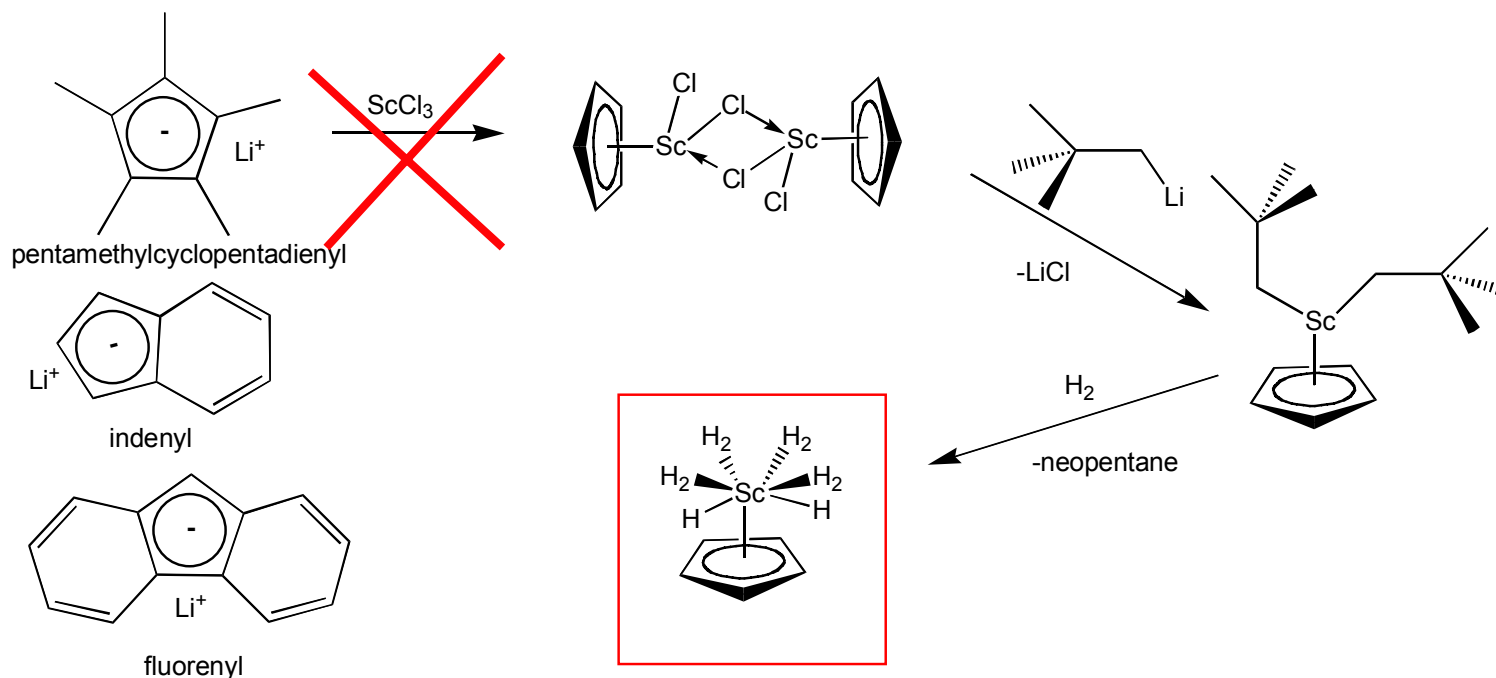
- At high Ca loading, it is not possible to resolve carbon peaks with NMR. At lower loadings, the NMR indicates new compounds with evidence of a more ordered structure for the 10Ca(C<sub>60</sub>).
- The theoretical compound was not made as evidenced by C<sub>60</sub> polymerization in the NMR spectrum.

- The highest capacity was observed for 57Ca(C<sub>60</sub>): 1.3 wt.% as-synthesized and 0.5 wt.% at 77 K and 2 bar.

**New Ca(C<sub>60</sub>) compounds were synthesized. In all cases formation of calcium hydride is observed. Theoretical molecule again difficult to achieve.**

## RC3 Accomplishment: "Strong Binding of H<sub>2</sub>"

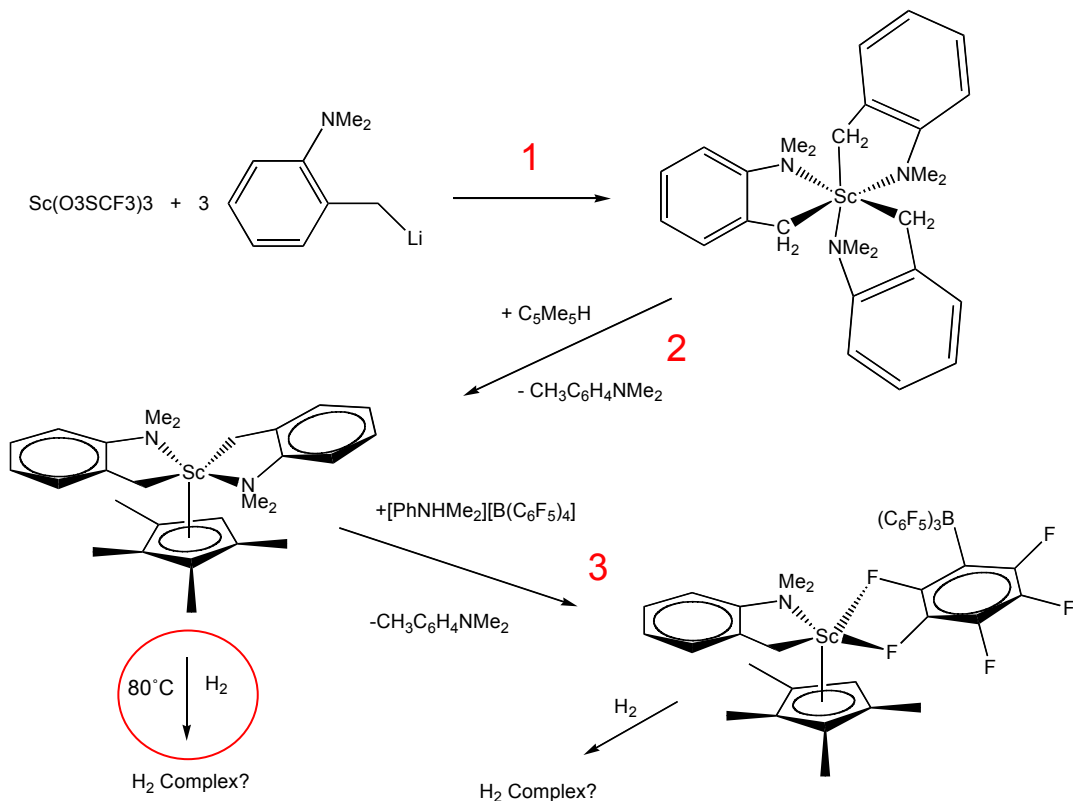
### Moving from C<sub>60</sub> Syntheses to Reactions on Simple Systems: Demonstrate Stabilization of Di-hydrogen Ligands



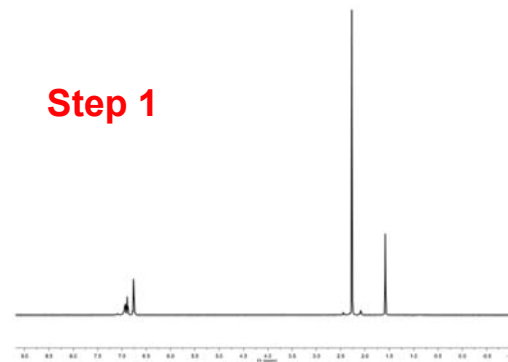
Attempts in performing the first step of this reaction were not successful so a new reaction scheme was developed and is moving forward.

## RC3 Accomplishment: “Strong Binding of H<sub>2</sub>”

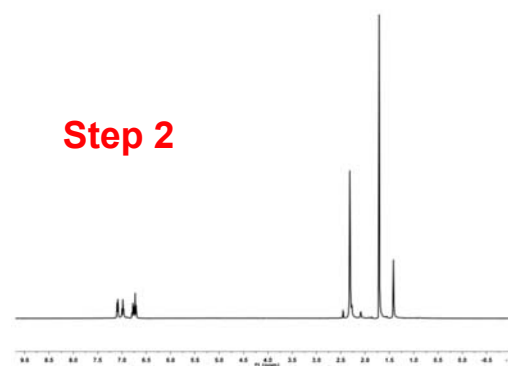
### Tractable Reactions to Demonstrate H<sub>2</sub> Ligands



Step 1



Step 2



- Product of step 2 was exposed to H<sub>2</sub> at 80 °C in an NMR tube.
- **NMR revealed the CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub> ligands are dislodged.**
- Neither Di-hydrogen ligands or Sc-H were detected with the NMR.
- These peaks may be overlapping with H<sub>2</sub> gas phase peak.
- Synthesis will be scaled up and/or other detection techniques tried.

NMR reveals high-yield formation of the substitution compound formed in both step 1 and step 2.

Stabilization of dihydrogen ligands on a first-row transition metal may have been achieved. Scale-up and further characterization required.

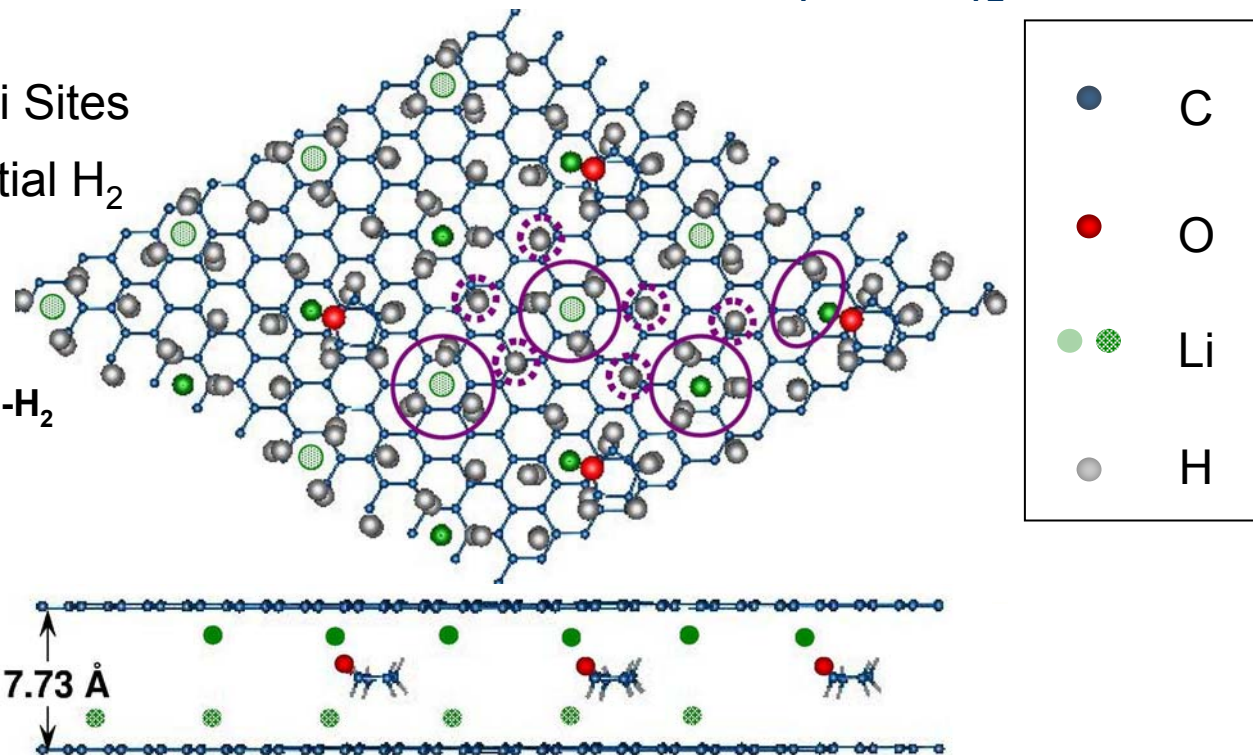


## Closing the gap between Predictions and Experiments

### Co-Intercalation of Graphite with Li and THF: Li<sub>4</sub>(THF)C<sub>72</sub>

○ H<sub>2</sub> at Li Sites

⊙ Interstitial H<sub>2</sub>



Capacity: 3.4 wt.%

H<sub>2</sub> coordinated with Li

Binding Energy: 9~22 kJ/mol-H<sub>2</sub>

Total capacity: 5.7 wt.%

Includes additional 2.3 wt%

physisorbed H<sub>2</sub>

(~ 5 kJ/mol-H<sub>2</sub>)

**The co-intercalant prevents clustering and expands the lattice to allow H<sub>2</sub> Adsorption**

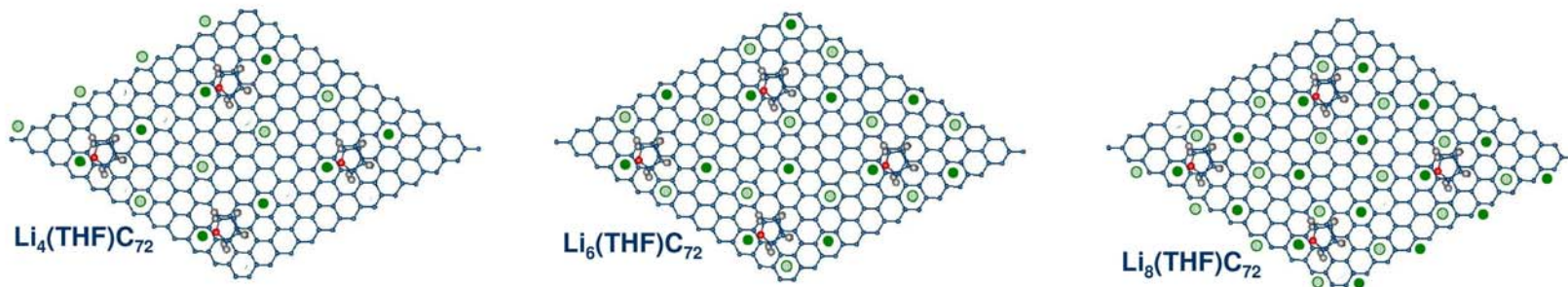
- Samples are readily synthesized by reacting alkali metal naphthalide with graphite in THF or DMTHF
- TPD confirms intercalation of THF. DMTHF does not intercalate providing a comparison.

Theoretical calculations were employed to predict a promising hydrogen sorption system that is easily synthesized.

# RC1 and RC3 Accomplishment: “Strong Binding of H<sub>2</sub>” and “Engineered Nanospace”

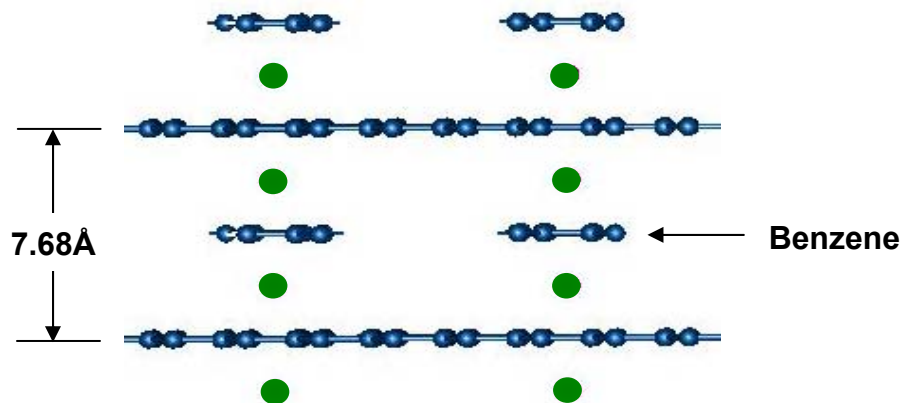
## Multiple Interesting aspects of Co-intercalation Concept

RC3: What density of Li maybe intercalated before clustering is observed?



- Metal clustering leads to the formation of a lithium hydride rather than stabilization of di-hydrogen ligands.
- $\text{Li}_4(\text{THF})\text{C}_{72}$  is found to be the structure with highest density of non-clustering Li.
- At this loading the Li-ions are stabilized by the graphene sheets

### RC1: Propping open structures with Li-Benzene (side View )

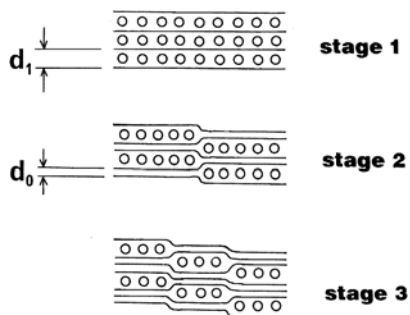


- More space is opened for enhanced physisorption ( $\sim 9$  kJ/mol- $\text{H}_2$ )
- No  $\text{H}_2$  binding to the Li atoms is observed.
- This is because the Li orbitals are fully saturated by the graphene sheets and the benzene molecules.

Different Li densities and different co-intercalants may be probed to theoretically guide experimental synthesis of most promising compound.

# Synthesis of Co-Intercalation Compounds in only Two Months

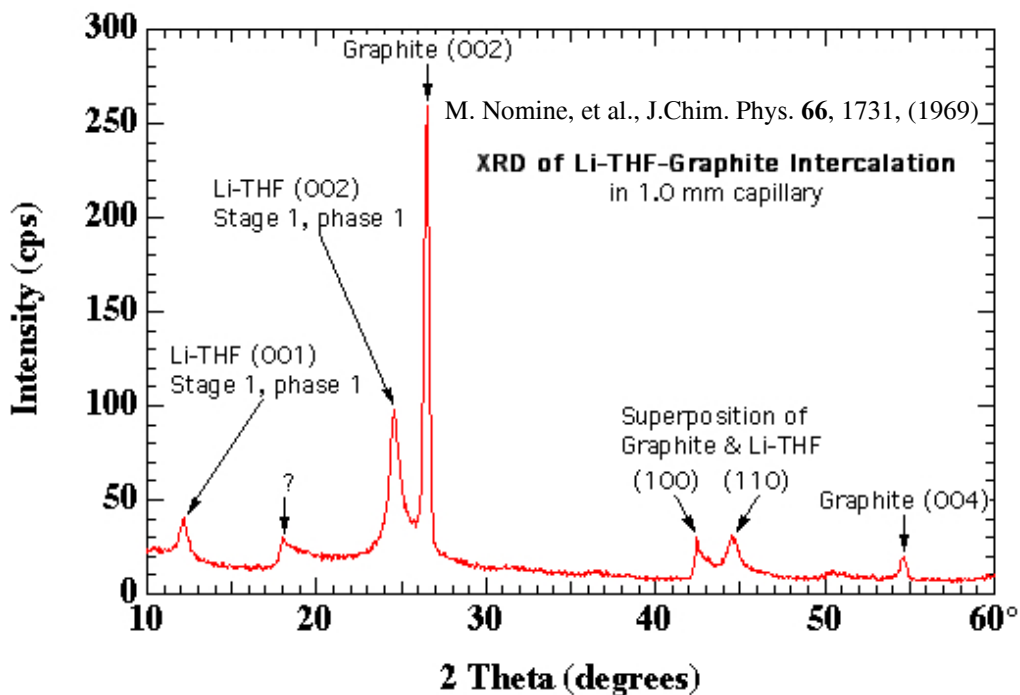
## Intercalation Compounds



H. Shioyama, Syn. Met. **114**, 1, (2000)

The Li/THF co-intercalant exhibits higher hydrogen capacity than Li intercalated graphite, consistent with the theoretically predicted results.

These are the only known H<sub>2</sub> adsorption studies on these promising materials.



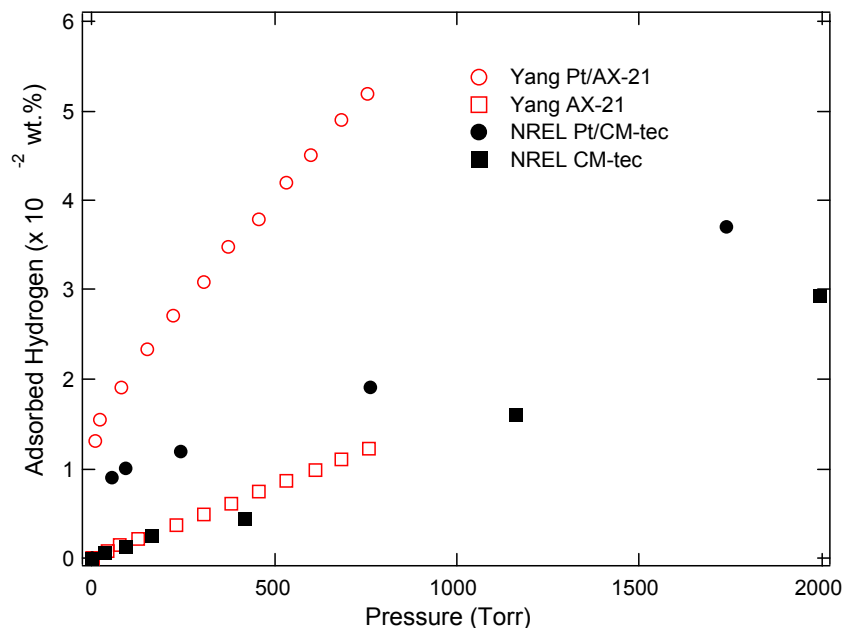
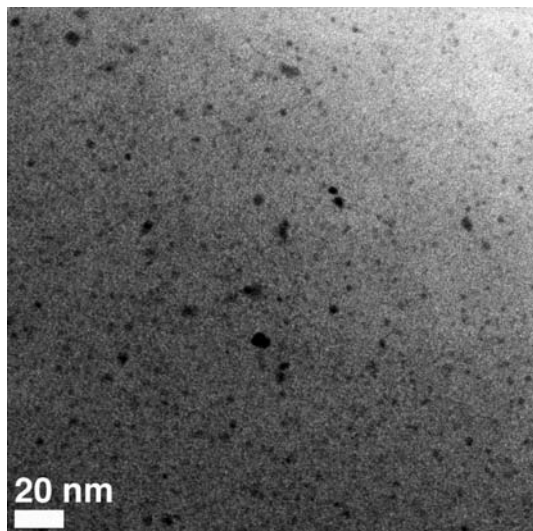
- Rapid, room temperature reactions are employed to form the co-intercalation compounds.
- XRD shows Li-THF co-intercalates into graphite to form stage 1 compounds.

Sample	RT Degas		100 °C degas		250 °C degas	
	Wt% H <sub>2</sub> @ RT	Wt% H <sub>2</sub> @ 77 K	Wt% H <sub>2</sub> @ RT	Wt% H <sub>2</sub> @ 77 K	Wt% H <sub>2</sub> @ RT	Wt% H <sub>2</sub> @ 77 K
Li / THF	0.08	0.34	0.04	0.42	0.06	0.52
Li	0.003	0.02	Negligible	0.02	0.005	0.02

Li-intercalated graphite was made for hydrogen adsorption comparison.

## NREL Reproduces U. Michigan Results at Low Pressure

TEM of NREL Sample



- NREL employed the same process to incorporate Pt in a large sample of CM-tec because AX-21 is no longer available.

- Several iterations were required to achieve well dispersed small particles of Pt (above TEM).

- Also found that activated carbon must be sulfur free.

- Yang observes ~ five-fold increase in H<sub>2</sub> adsorption at 800 Torr on Pt/AX-21 (spillover).

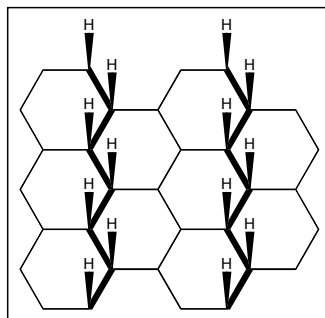
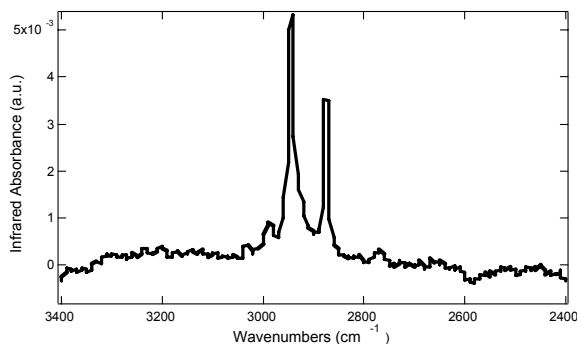
*Y. Li, and R. Yang J. Phys. Chem. C 111 (2007) 11086.*

- The Pt/CM-tec sample show ~ two-fold increase in H<sub>2</sub> adsorption at 800 Torr indicating spillover.

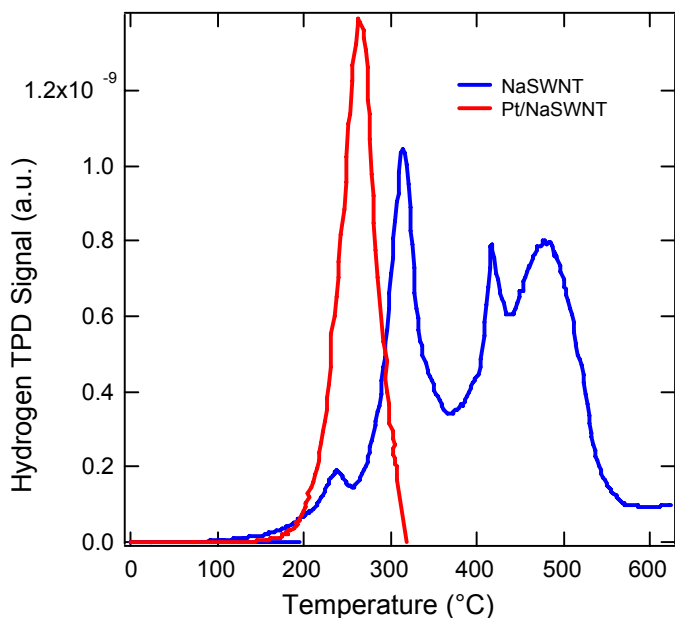
- The reduced spillover effect on the NREL sample may be attributed to the change in activated carbon or perhaps the Pt dispersion should still be improved.

Significant spillover for a Pt/activated carbon system has been observed at NREL 12  
employing the U. Michigan developed process.

## Exploration of Alternative Spillover Process



- A novel wet chemical route has been explored to hydrogenate  $sp^2$  hybridized carbons.
- The  $sp^2$  hybridized carbon are reduced with sodium naphthalide in THF.
- Infrared spectroscopy indicates ortho-hydrogenation.



- NaSWNT samples may be hydrogenated irreversibly to ~ 4 wt.%; *agreement with theory: Y. Zhao et al. Chem. C. 2007, 111, 13275.*
- ~2 wt.% is recovered reversibly following RT exposure when Pt catalyst on activated carbon is incorporated.
- The Pt/NaSWNT sample shows a lower reversible desorption temperature.
- The desorption temperature may be lowered further by introducing strain/dopants.

Mechanistic understanding of hydrogenation reaction and new spillover reaction have been realized. Future efforts will focus on lowering desorption temperature.

# Accomplishment All Clusters: Unique Measurement Capabilities Employed by Partners

New calibration methods have been developed: accurate high-pressure measurements may be performed on small samples. Detection at levels of  $\sim 40 \mu\text{moles}$  is achieved.

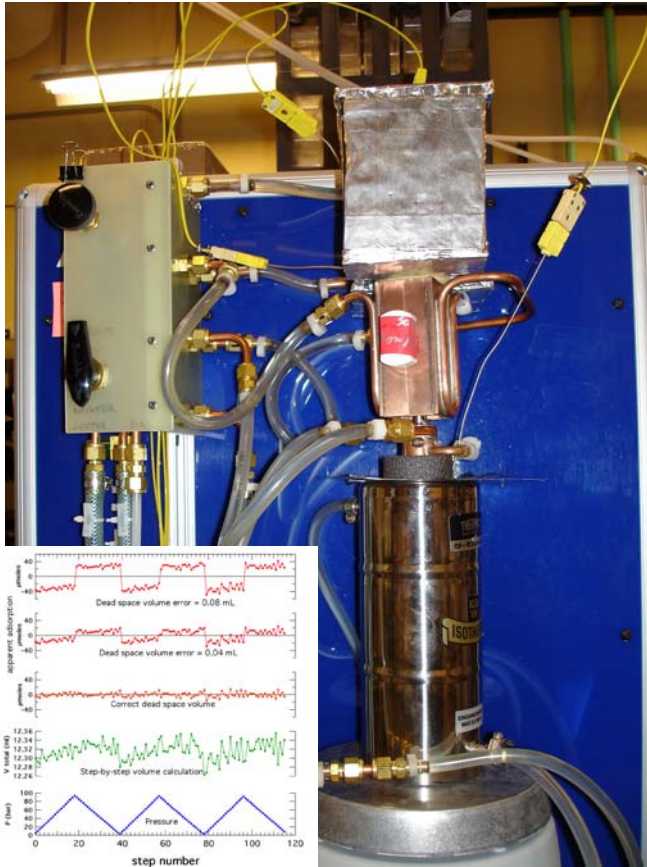
- Methods used: BET, TPD, TGA, low & high pressure Sieverts
- NREL has developed transfer procedures and equipment to allow for airless sample transport from external labs
- NREL works with Karl Gross to ensure best practices.

NREL worked with multiple institutes to provide measurements

- In FY08 69 samples have been analyzed for partners /collaborators (to date).
- Over 700 measurements have been performed on external and internal samples.
- More than doubles the number of samples evaluated for others in FY07.



BET surface area can be determined using  $\text{H}_2$  such that deviations from “Chahine’s Rule” may be better understood.

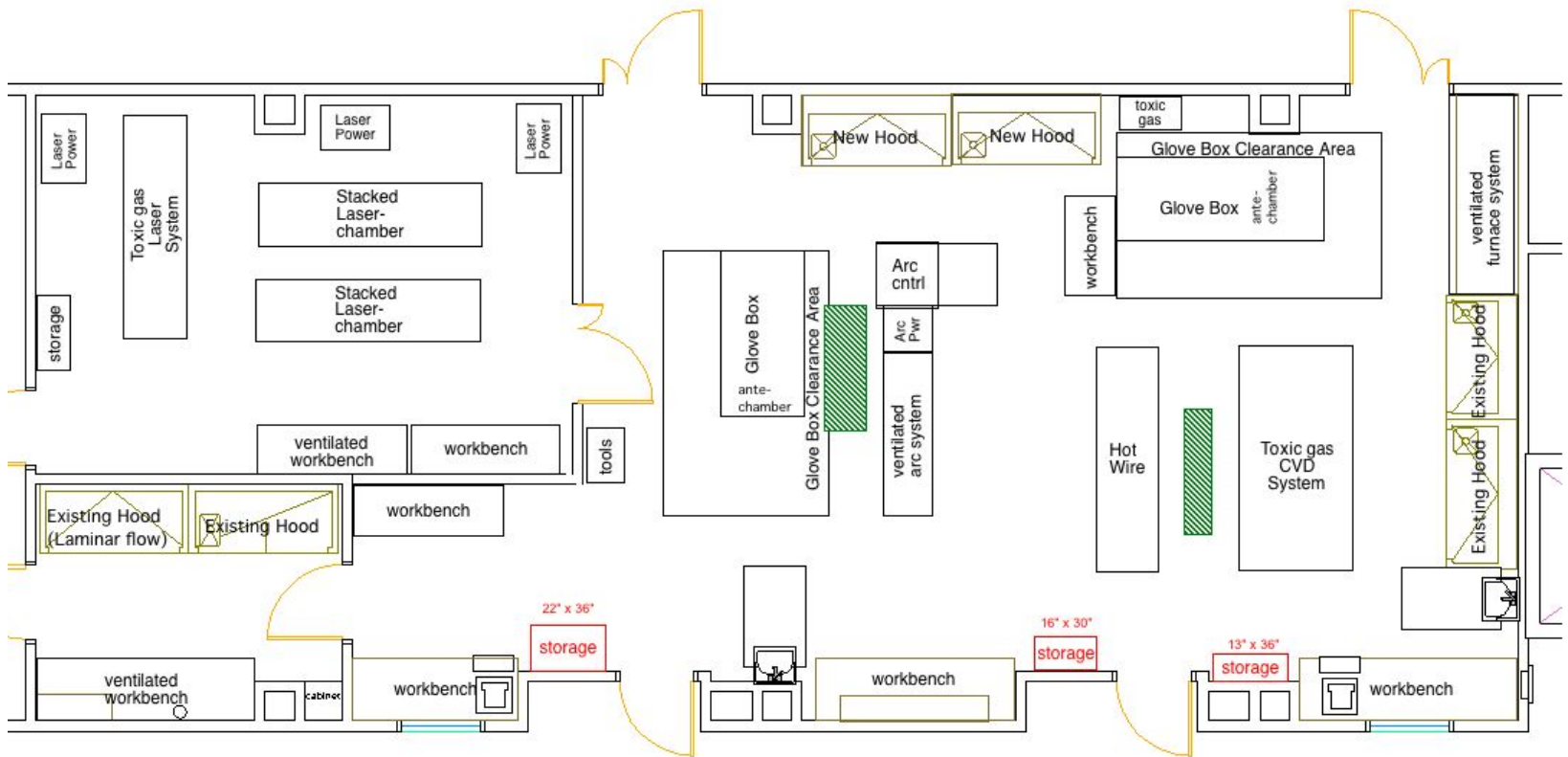


NREL continues to improve measurement capabilities to provide more accurate and unique hydrogen storage materials characterization at high throughput.

**Accomplishment: All Clusters**

# Technical Progress: New Materials Synthesis Laboratory

- Move-in is complete to 1500 ft<sup>2</sup> laboratory
- Laser, Arc, HWCVD, new glove box operational
- Nanomaterials safety issues addressed with ventilated handling areas
- Toxic gas capabilities in progress: incorporation of reactive gases such as diborane is anticipated to increase boron loading in carbon materials with gas-phase processes.



**New materials synthesis laboratory is operational.**

# Future Work

## FY08

- Demonstrate dihydrogen ligand stabilization employing tractable reactions and determine optimized reaction pathway.
- Improve synthesis of co-intercalation compounds such that theoretical compound is achieved.
- Reduce reversible desorption temperature for model Na-reduced carbons by incorporating strain or dopants into the carbon matrix.
- Continue to both verify Michigan spillover and develop new spillover processes.
- Employ reactive gases to increase boron loading in carbon materials.
- Calculate hydrogenation of metal intercalated graphite (another simple system) and continue to employ theoretical calculations to assist other synthetic efforts.
- Continue to develop state-of-the-art measurement techniques and to provide high-throughput measurement for partners.

## FY09

- Employ successful organometallic reactions to high surface-area substrates obtained from center partners such as functionalized aerogels (LLNL), MOFs (MUO), carbon nanohorns (ORNL) or nanotube scaffolds (Rice).
- Gas phase synthesis of targeted carbon and non-carbon sorbents.
- Accelerate theoretical efforts that directly support the development of potential materials.
- Determine optimal high-surface area system for organometallic chemistry, intercalation and/or spillover by working in conjunction with partners.
- Scale-up synthesis of most promising materials such that round-robin verification of samples may be achieved.



# Summary

- **Multiple organometallic fullerene compounds have been evaluated for hydrogen storage capabilities. Significant insight into relevant chemical processes for hydrogen storage have been ascertained.**
- **Tractable aromatic systems appear promising for their potential to stabilize di-hydrogen ligands.**
- **Theoretical calculations have been employed to probe a viable co-intercalation system for hydrogen storage that may be easily synthesized, and proof of concept synthesis was achieved in only two months.**
- **Spillover materials similar to those fabricated at U. Michigan have been synthesized at NREL.**
- **Alternate spillover materials have also been explored at NREL.**
- **NREL has continued to develop and employ high-throughput measurement capabilities to accelerate discovery, development and partner interactions.**
- **Improved gas phase synthesis capabilities such that boron doped materials may be readily made are in place.**

# Material Performance

Storage Parameters	Units	System Targets (2010)	SWNTs, validated <sup>a</sup>		B-SWNT		M(C <sub>60</sub> )			Li/THF co-intercalated graphite	Hydrogenated Materials			<4 Angstrom Pore Size Material
			FY06	FY05	FY06	FY06	FY07	FY08	FY08	FY06	FY07	FY08	FY07	
Specific Energy	Wt% H <sub>2</sub>	6	3	*	~2.2 <sup>b</sup>	0.5	1	0.8	0.5	4 <sup>c</sup>	5.3 <sup>c</sup>	2 <sup>d</sup>	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	STP	77 K, 2 bar	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 techniques develop.

c. Mostly irreversible. Demonstrates potential reversible capacity once dissociation material can be incorporated with lattice.

d. Reversible via gas phase dihydrogen

# Theoretical Materials Predictions

Storage Parameters	Units	System Targets (2010)	Organo-metallic Fullerenes <sup>a</sup>	MetCars <sup>b</sup>	Macro-molecules	Endohedral Metallo-fullerene <sup>c</sup>	Metallo-carborane <sup>d</sup>	THF-Li Co-intercalated Graphite	Ca intercalated Graphite <sup>e</sup>	Spillover on SWNT (NREL)
			FY05	FY06	FY06	FY07	FY07	FY08	FY08	FY07
Specific Energy	Wt% H <sub>2</sub>	6	~9	3.7-7.7	>5	6.1	10.5	3.4	>7	>7.7
Volumetric Energy Capacity	g/L	45	52-43	48-58	>40	*	52	>40	>60	~56
Comments			STP, 23-46 kJ/mol	STP, 15-32 kJ/mol	STP	~STP, 10-78 kJ/mol	STP	~STP, ~20 kJ/mol	~STP, ~20 kJ/mol	RT, 100 bar

\* Information not available

Volumetric capacities derived from material densities

a. Zhao et al. PRL 94, 15504 (2005). Similar predictions have appeared in the literature including, Yildirim and Ciraci, PRL 94, 175501 (2005); Shin, Yang, Goddard III, and Kang, APL 88, 053111 (2006); Deng et al. PRL 92, 166103 (2004); Lee, Choi, and Ihm, PRL 97, 056104 (2006); Q. Sun et al., J. Am. Chem. Soc. 128, 9741 (2006).

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

c. Y. Zhao et al. J. Phys. Chem. C 11, 13275 (2007).

d. Y. Zhao et al, Nanoletters 8, 157 (2008)

e. Y.-H. Kim et al submitted, may have volumetric densities higher than liquid hydrogen.