

# Overview of the DOE Hydrogen Sorption Center of Excellence

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**National Renewable Energy Laboratory**

**DOE Hydrogen and Fuel Cell Technology  
Program Annual Merit Review**

**June 9, 2010**

**ST014**

This presentation does not contain any proprietary, confidential, or otherwise restricted information

# Overview

## Barriers Addressed

- Cost.
- Weight and volume.
- Efficiency.
- Refueling time.
- Hydrogen capacity and reversibility.
- Understanding of physi- and chemisorption.
- Test protocols and evaluation facilities.

## Timeline

Start date: FY2005  
End date: FY2010  
Percent complete: 100%

## Budget

Center Management - \$300K

**Partners: 9 universities, 5 government labs, 1 company**

**Steering Committee Members: APCI, Caltech, NIST, NREL, UM**

*Also, many other interactions with independent projects (BES and EERE), the other CoEs, IPHE, IEA, and companies.... see back-up slides for details.*



# HSCoE Goals and Objectives

Design and develop high-capacity sorbent materials with the potential to operate toward ambient temperatures and be efficiently and quickly charged on-board with minimum energy requirements and minimum penalties to the hydrogen fuel infrastructure. Overcome barriers to DOE's new 2015 system targets and identify pathways to meet DOE's ultimate targets.

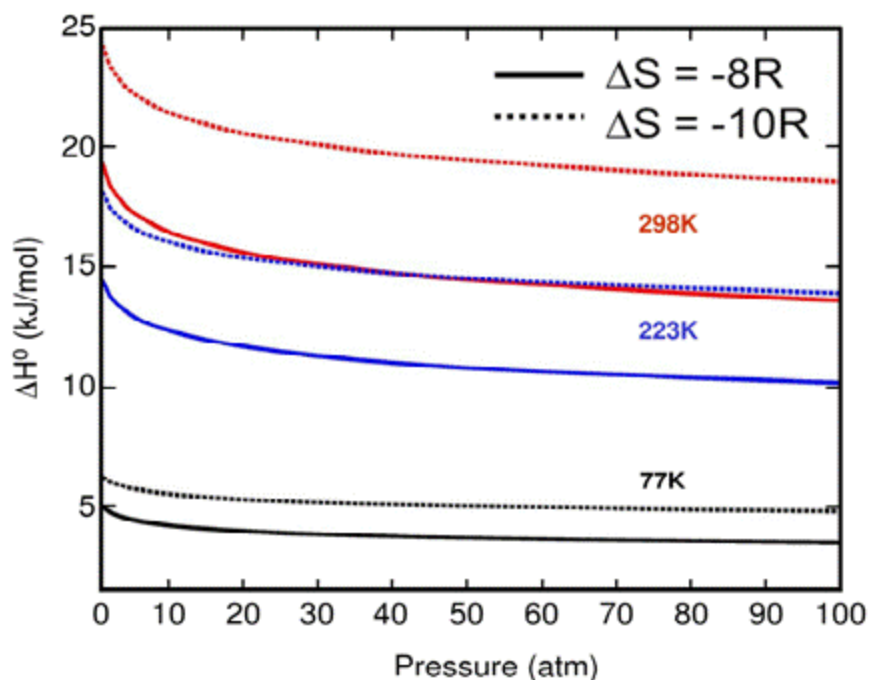
- **Optimize sorbent materials with high surface area and high density to meet both gravimetric and volumetric targets simultaneously with rapid kinetics.**
- **Develop materials which utilize mechanisms that bind H<sub>2</sub> with an optimal energy for near ambient operation (10 - 40 kJ/mol H<sub>2</sub>).**
- **Devise facile synthetic routes using low cost approaches.**

**HSCoE has worked exclusively on the very difficult problem of developing materials for on-vehicle hydrogen refueling and storage. Sorbents provide possible materials solutions to meet DOE 2015 and ultimate targets and may be the easiest to adapt for early market applications**

## **DOE's new 2015 Technical Targets for Storage System**

- **Gravimetric**      **0.55 kg H<sub>2</sub>/kg**
- **Volumetric**      **0.040 kg H<sub>2</sub>/L**

# Approach Optimizing Enthalpy of Adsorption



$$\Delta H_{\text{opt}} = T\Delta S + RT \ln\left(\frac{P_1 P_2}{P_0}\right)$$

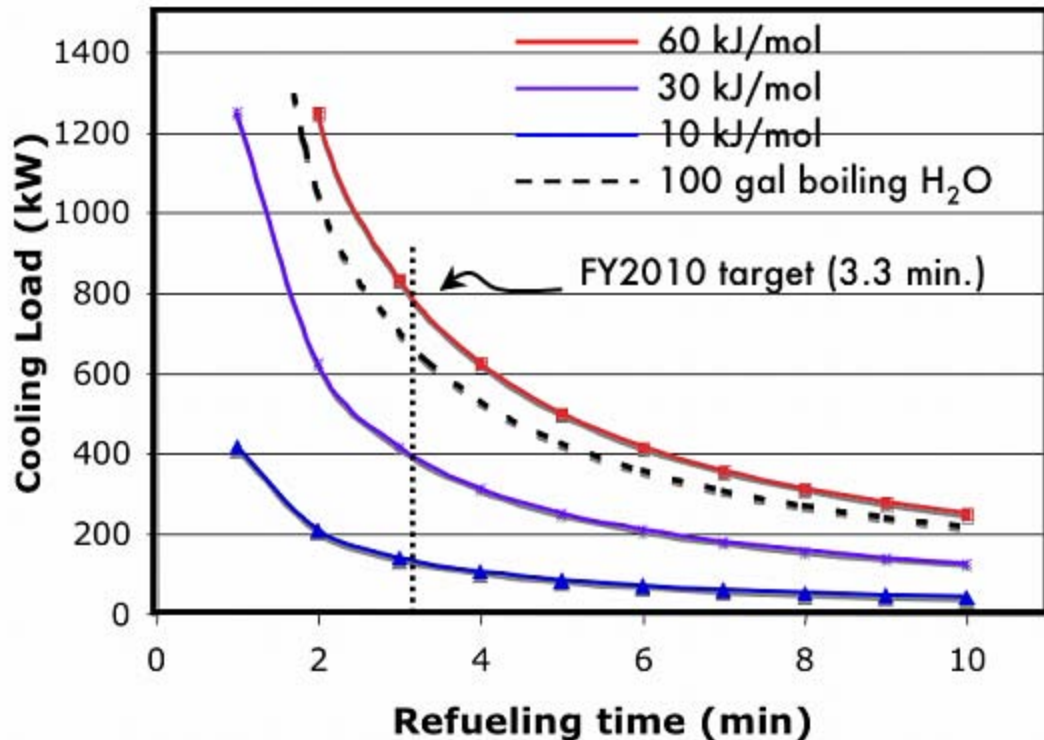
Charge to  $P_2$  and discharge to  $P_1$  (1.5 atm)  
Entropy values for theoretical slit pore (-8R)  
and intercalated graphite (-10R).

- The binding energy of physisorbed hydrogen is ~ 4-6 kJ/mol  $H_2$  requiring tank operation at sub-ambient temperatures to meet DOE 2015 capacity targets.
- To meet DOE targets at ~298 K requires a minimum binding energy of ~ 15 - 20 kJ/mol  $H_2$ .

After Bhatia & Myers, *Langmuir* 2006, 22, 1688.

HSCoE focuses on increasing the binding energy for dihydrogen in order to increase the tank operating temperature which will decrease system costs.

# Approach: Optimized Enthalpy Reduces Heat Dissipation



Cooling load for 5 kg of adsorbed H<sub>2</sub> assuming binding energies of 10, 30 and 60 kJ/mol. For reference the power dissipation provided in boiling 100 gal of water is plotted.

- Hydrogen enthalpy of adsorption dictates that cooling is employed during refueling.
- System demands are increased for rapid refueling times.
- Sorbent materials offer a path for onboard refueling; both metal and chemical hydrides bind H<sub>2</sub> too strongly.

**Onboard refueling rate targets dictates that  $\Delta H$  is minimized.  
Sorbent materials offer the only material path for onboard refueling.**

# Approach: Relevance to DOE

- Typically, sorbents meet 13 of 16 DOE storage targets
  - Paths available to meet 2015 and perhaps ultimate targets
  - Potentially require least engineering to meet HSECoE Phase I and II goals

Storage Parameter	Units	2010	2015	Ultimate
System net Gravimetric <sup>a</sup>	kg H <sub>2</sub> /kg system	0.045	0.055	0.075
System Net Volumetric	kg H <sub>2</sub> /L system	0.028	0.040	0.070
Storage system cost <sup>b</sup>	\$/kg H <sub>2</sub>	133	67	TBD
Durability/Operability				
1. Operating ambient T <sup>d</sup>	°C	-30/50 (sun)	-40/60 (sun)	-40/60 (sun)
2. Min/max delivery T	°C	-40/85	-40/85	-40/85
3. Cycle life (1/4 tank to full) <sup>e</sup>	Cycles	1000	1500	1500
4. Cycle life variation <sup>f</sup>	% mean (min) at % confidence	90/90	99/90	99/90
5. Min del. P from storage	Atm (abs)	4FC/35 ICE	3FC/35 ICE	3FC/35 ICE
6. Max del. P from storage <sup>g</sup>	Atm (abs)	100	100	100
Charge/discharge Rates				
• System fill time (5-kg H <sub>2</sub> )	min	4.2 min	3.3 min	2.5 min
• Minimum full flow rate	(Kg H <sub>2</sub> /min)	(1.2 kg/min)	(1.5 kg/min)	(2.0 kg/min)
• Start time to full flow (20°C) <sup>h</sup>	(g/s)/kW	0.02	0.02	0.02
• Start time to full flow (-20°C) <sup>h</sup>	s	5	5	5
• T . Resp. 10%-90%, 90% -0% <sup>i</sup>	s	15	15	15
	s	0.75	0.75	0.75
Fuel Purity (H <sub>2</sub> storage) <sup>j</sup>	% H <sub>2</sub>	99.99 (dry basis)		
Env. Health & Safety		Meets or exceeds applicable standards		
• Permeation & leakage <sup>k</sup>	Scch/h			
• Toxicity	-			
• Safety	-			
• Loss of useable H <sub>2</sub> <sup>l</sup>	(g/h)/kg H <sub>2</sub> stored	0.1	0.05	0.05

Depending on the exact sorption mechanisms and materials used, **only cost and capacity are typically an issue for sorbents.**

- Most HSCoE efforts focused on these 3
- HSCoE may have several materials that will meet DOE 2010 system targets
- HSCoE may have materials that meet HSECoE phase II goals
- HSCoE works to meet ultimate targets

\*The storage system costs are currently under review and will be changed at a future date

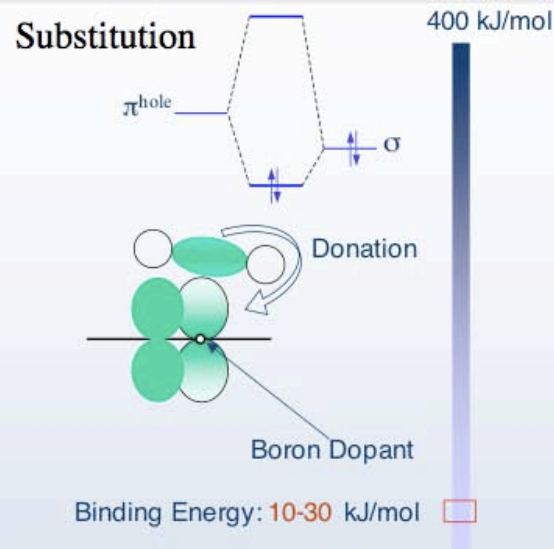
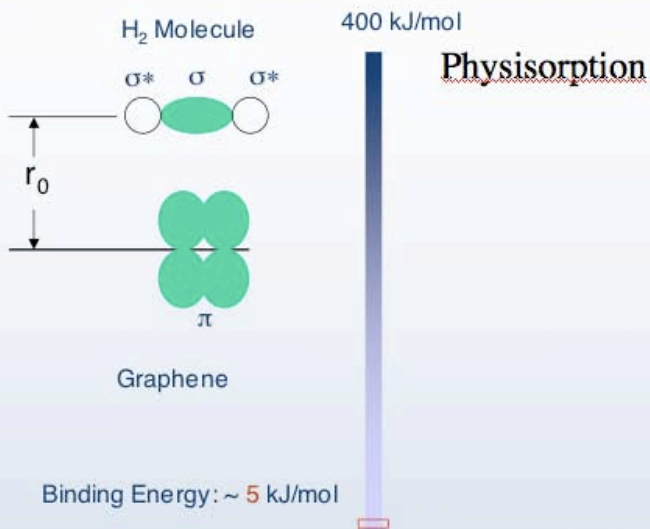
Green: low risk, high probability to meet.

Yellow: medium risk, medium probability to meet.

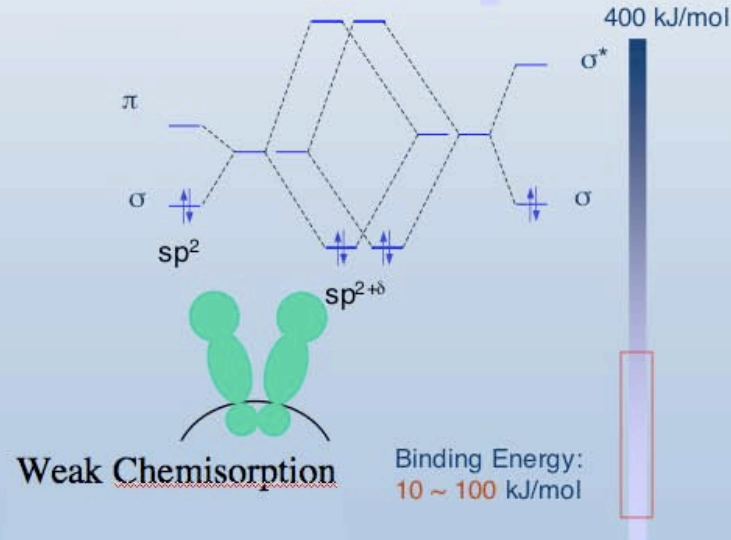
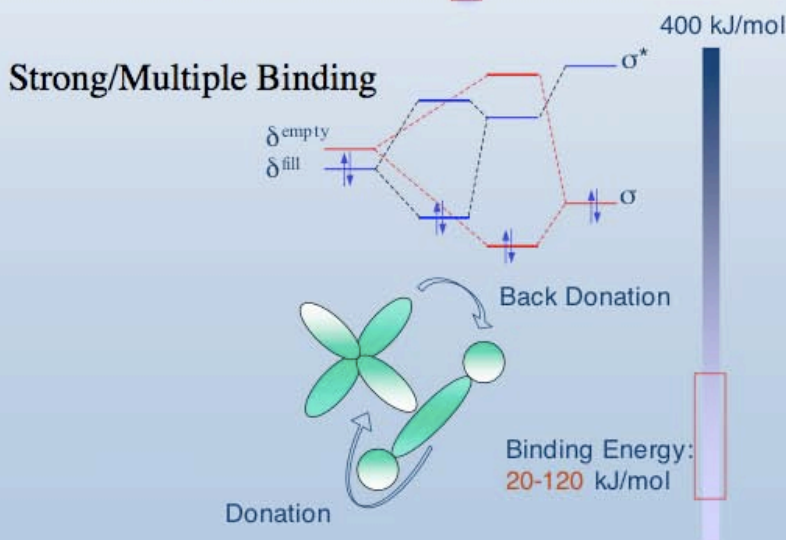
Red: High risk, low probability to meet.

# Approach: Four Mechanism to Store H<sub>2</sub> with Sorbents

- Physisorption (van-der Waals): optimize material density and surface area.
- Substituted Materials: e.g. BC<sub>3</sub> to enhance binding energy.
- Strong Binding: e.g. stronger interaction with atomic metal atoms.
- Weak Chemisorption (e.g. Spillover): e.g. catalytic dissociative adsorption.



**The HSCoE organized development efforts based on these storage mechanisms and developed materials optimized to take advantage of these mechanisms**



# Accomplishments Overview: Access to Optimized Sites

- Developed new materials that increased the gravimetric (~40%, e.g. from ~5 to >7 wt % at 77K) and volumetric (~150%, e.g. from ~15 to >35 g/L at 77K) hydrogen storage by physisorption onto high specific surface area (SAA) sorbents by optimizing pore sizes (0.7 to 1.5 nm) to increase SAA and packing density.
  - DOE 2015 hydrogen storage system capacity targets could be met with physisorption based optimized material at cryogenic temperatures and relatively low pressures (i.e. 10 to 50 bar). The decreased pressures, compared to high pressure 350 to 700 bar storage systems, enabled by relatively inexpensive carbon based sorbents could substantially reduce tank and balance-of- plant costs.
    - » Synthesized new high SSA physisorption materials with optimized uniform pore size using a variety of scalable/inexpensive processes
    - » High SSA physisorption materials may be used to meet DOE 2010 and possibly 2015 on-vehicle refuelable hydrogen storage system targets at cryo-compressed conditions



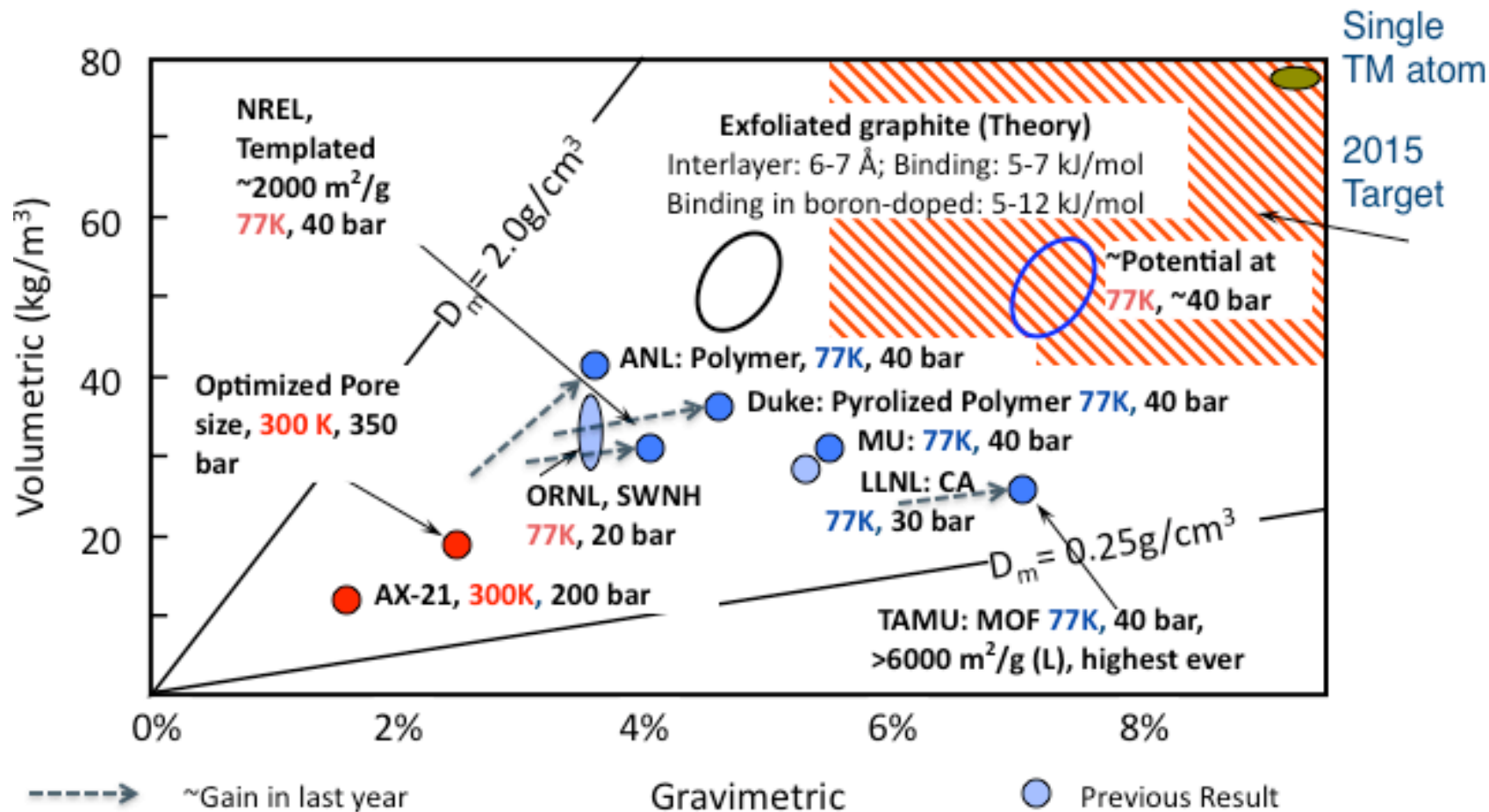
# Accomplishments Overview: Access to Optimized Sites

- Confirmed that standard physisorption based dihydrogen adsorption scales with specific surface area. To date, no validated experimental evidence exists that any substantial capacity enhancements occurs due to geometric configurations.
  - At the outset of the Center, numerous publications had reported extraordinary results for high specific surface area materials where the enhanced capacities where potentially a result of novel geometries or structures within the material. In general, heats of adsorption can be increased with multiple wall interactions, but this ultimately reduces capacities. The Center did not validate any single element material or any materials with unexceptional electronic states that have substantially higher hydrogen storage capacities beyond what is expected based on the specific surface area and specific storage conditions.
    - » **e.g. Down-selected pure carbon nanotubes as ambient temperature hydrogen storage material**

# Accomplishments Overview: Access to Optimized Sites

- Synthesized new high SSA physisorption materials with optimized uniform pore size using a variety of scalable/inexpensive processes, e.g:
  - **Aerogels:** LLNL: scaffolding
  - **Chemical or Vapor Synthesis**
    - » TAMU-MOFs, ORNL-SWNH, Rice, NREL, ANL-polymers
      - » TAMU created MOFs with highest SSA (Langmuir  $\sim 6100 \text{ m}^2/\text{g}$ ) and hydrogen uptake ( $\sim 7.3 \text{ wt}\%$ )
      - » ANL:  $>1 \text{ g/ml}$  porous polymer material with  $\sim 2000 \text{ m}^2/\text{g}$ ; will look at activation to increase SSA
  - **Graphene:** high conductivity and durability
    - » Rice: Exfoliated Graphite, CNT scaffolds/foams
    - » NREL: co-intercalated graphite
    - » Caltech: intercalated graphite, uniform higher binding for all loading
  - **Pyrolization**
    - » Duke: PEEK,  $>5 \text{ wt}\%$  with  $\sim 0.7 \text{ g/L}$  density and  $>3000 \text{ m}^2/\text{g}$  SSA
    - » Missouri-corncoobs
  - **Templating:** NREL, Rice, Duke, enables exact materials and structures to be formed
    - »  $\sim 7 \text{ wt}\%$  demonstrated at 77K and 50 bar
  - **Carbon nanotubes:**
    - » Purification is a major problem
    - » No exceptional capacity observed

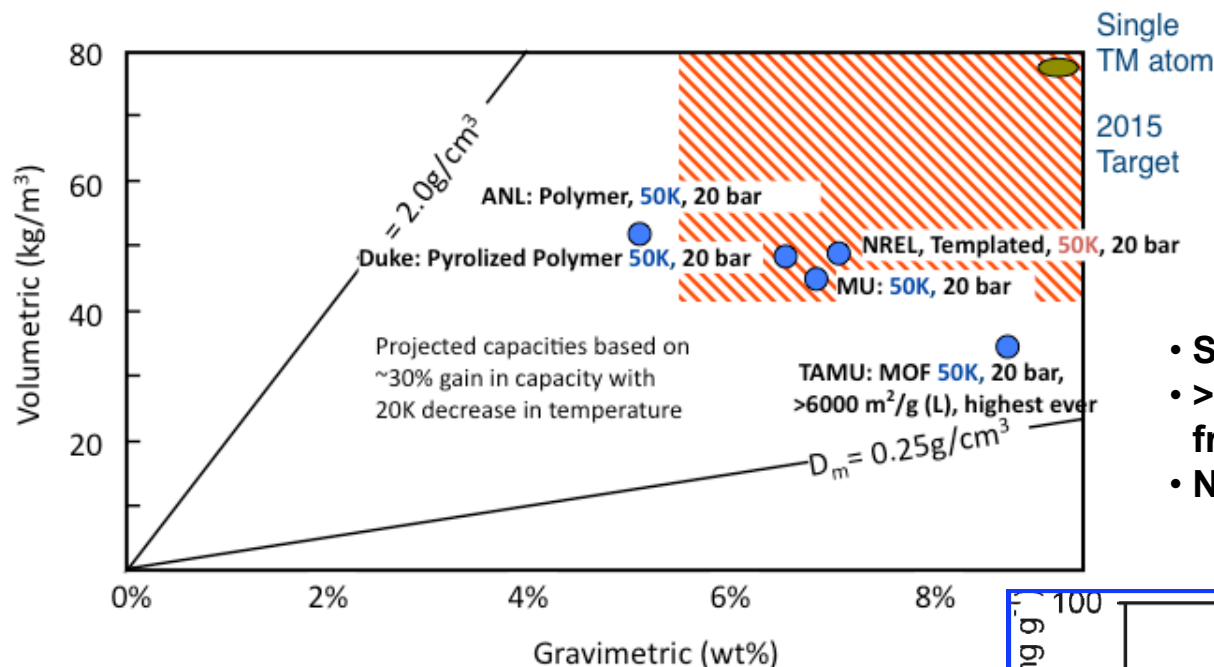
# Accomplishments Overview: Access to Optimized Sites



- Must balance high SSA with high density to achieve both high gravimetric and high volumetric capacities.
- **Optimal porosity can achieve 0.7 to ~1.4 g/ml densities; maximize volumetric capacity.**
- Ultimately achieve ~7 wt% and ~50 g/L capacities at ~80K and ~40 bar.
- **Getting close with either volumetric or gravimetric at ~80K, now need both.**
- **May meet DOE 2015 capacity targets at ~50K and ~20 bar, but need to balance system cost and efficiency**

**Storage by pure physisorption materials may meet DOE targets, but system capacities must be balanced with system costs.**

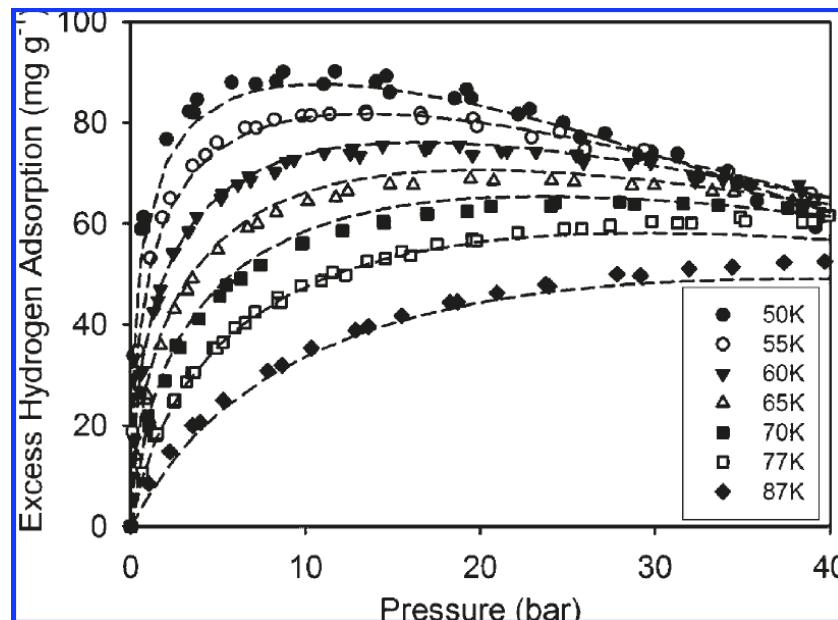
# Accomplishments Overview: Access to Optimized Sites



- Sorbents may be closest to targets
- >95% of material capacity delivered from tank
- No significant heat transport issues

**~30% increase in capacity at 50 K compared to 80 K means that sorbents may meet DOE 2015 capacity targets at ~50K and ~20 bar, but need to balance system cost and efficiency**

- Storage system costs will be significantly lower at 20 bar, compared to 350 or 700 bar.
- Well to tank efficiencies will be lower by about 10% compared to 350 bar storage.



“On the Nature of the Adsorbed Hydrogen Phase in Microporous Metal-Organic Frameworks at Supercritical Temperatures,” E. Poirier and A. Dailly, Langmuir, On-Line (2009)

# Optimum Volumetric and Gravimetric Capacity

Number of Sorption Sites per Unit Mass:

$$D_s = N_s / M = S_{SSA} / s_0$$

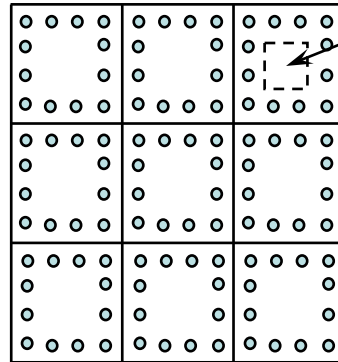
$N_s$	: Number of sorption sites
$M$	: Mass of the material
$S_{SSA}$	: Specific Surface Area
$s_0$	: Area per sorption site
$n_H$	: Number of H atoms per site
$D_M$	: Density of the material

Gravimetric Capacity:  $C_W = N_s n_H / M = D_s n_H$

$$C_V = D_s n_H D_M = C_W D_M$$

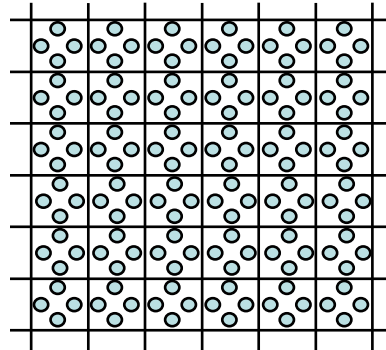
Volumetric Capacity:

- (1) Volumetric Capacity scales with gravimetric capacity through material density.
- (2) Simultaneous increase of volumetric and gravimetric capacity requires increasing both specific surface area (SSA) and material "bulk" density, which means larger voids should be removed.
- (3) For physisorption,  $H_2$  binding energy is determined by effective contact area per  $H_2$ .



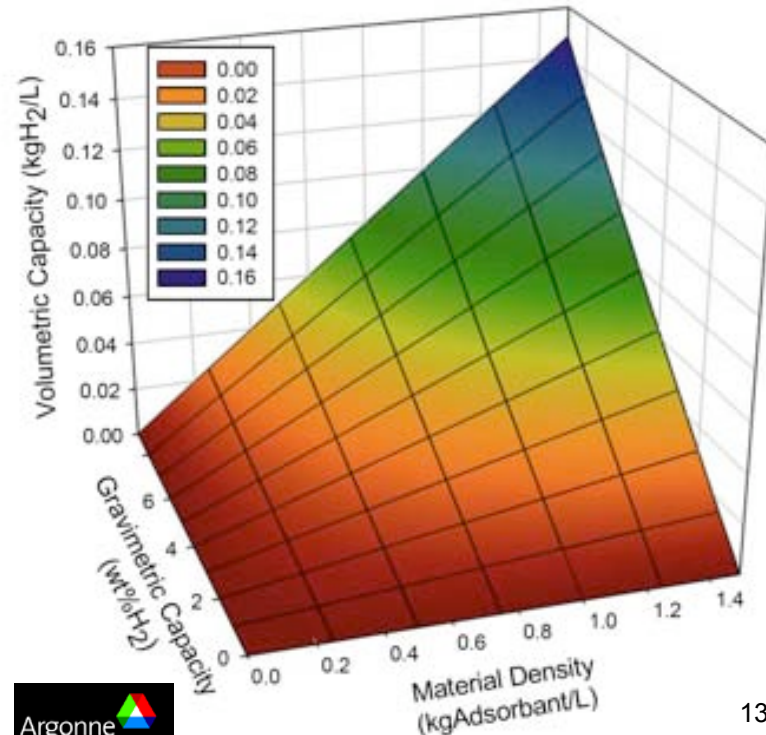
unused void

low material density,  
low volumetric



high material density,  
high volumetric

Correlations between gravimetric & volumetric capacities vs. adsorbent density

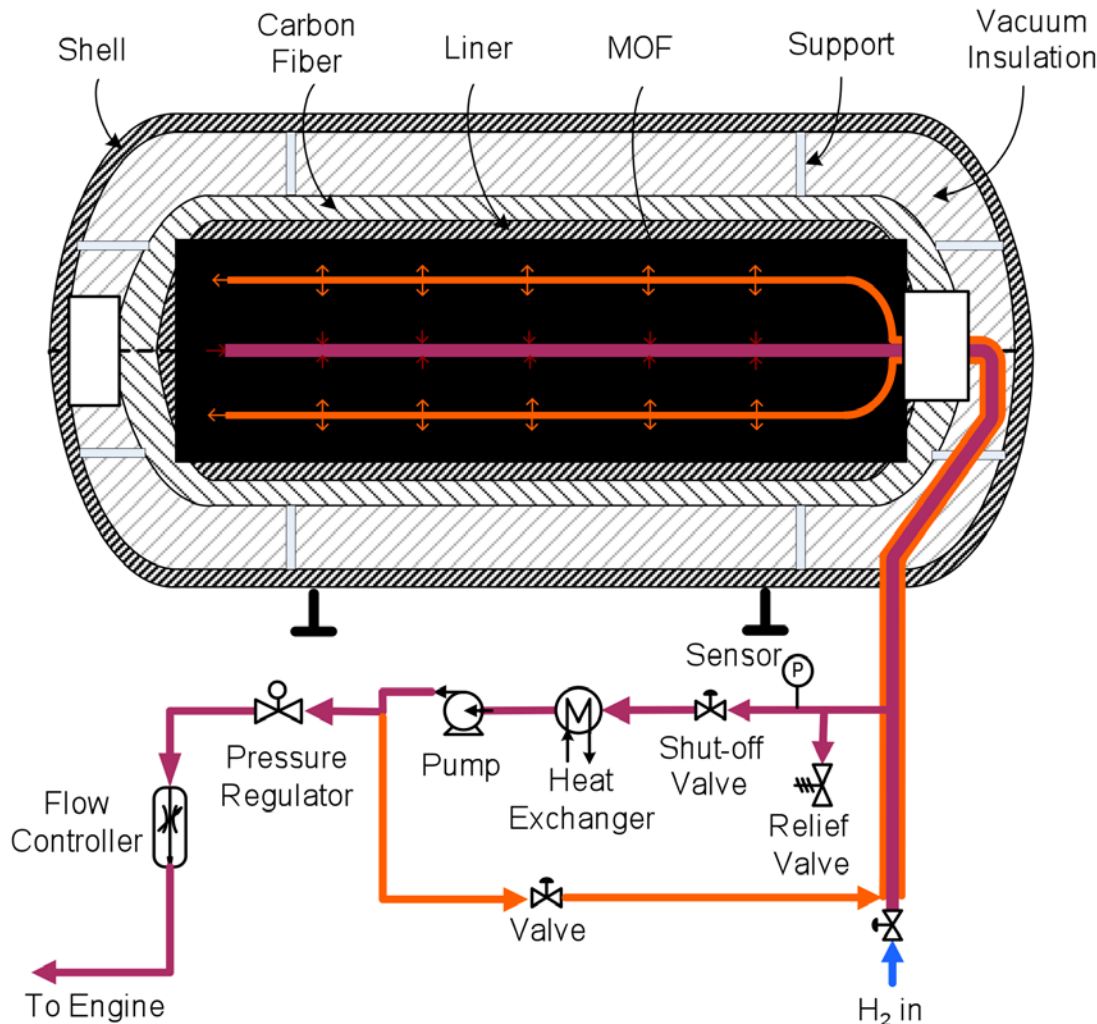


HSCoE focused on developing high-density porous materials, demonstrating materials with 0.7 to 1 g/ml bulk densities.

# Adiabatic Sorbent Storage Tank Analysis



- Sorbent system used for analysis
  - Note pump and heat exchanger included included outside



## Key System Requirements Storage Medium

- 5.6 kg recoverable H<sub>2</sub>
- 4-bar minimum delivery P
- Type-3 Containment Vessel

- 2.25 safety factor
- 5,500 P and T cycles

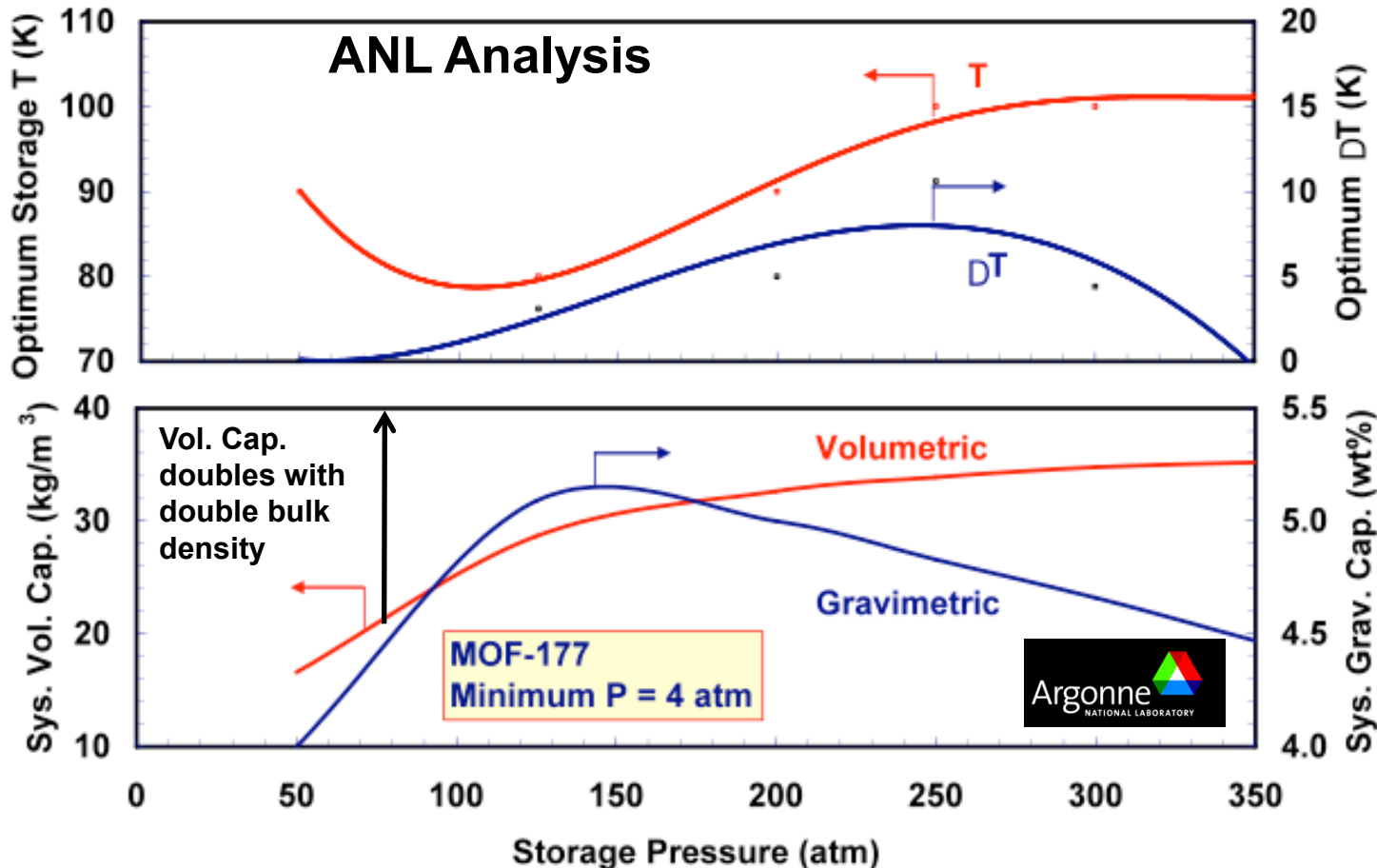
## Heat Transfer System

- 1.5 kg/min H<sub>2</sub> refueling rate
- 1.6 g/s H<sub>2</sub> min flow rate
- 1.3 W in-leakage rate through MLVSI

# Accomplishment: Optimized Sites; Sorbent Systems May Meet 2010 Capacity Targets

- Increase capacities beyond ANL MOF system by optimizing to sorbent
  - Optimized pore sizes (0.7 – 1.5nm) increases vol. capacity
  - Increase delivered capacity by operating at <80K, with  $\Delta T$
  - Decrease costs by operating @ 50 to 100 bar, may be able to meet cost targets

Analysis below indicates that with low bulk density (~0.3 g/ml) MOF-177 the storage system has to be at a higher pressure to attain higher volumetric capacities.

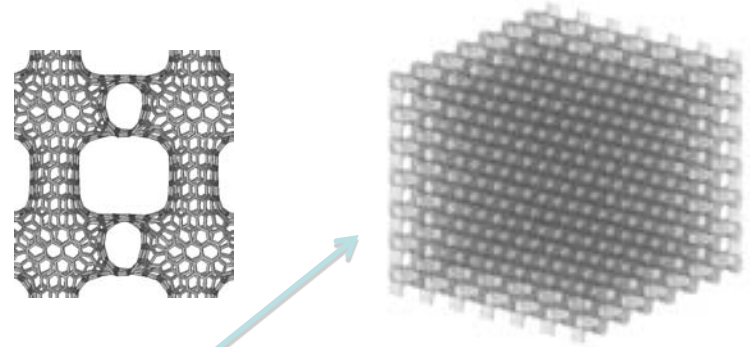


**Demonstrated materials with 0.7 to 1 g/ml bulk densities**

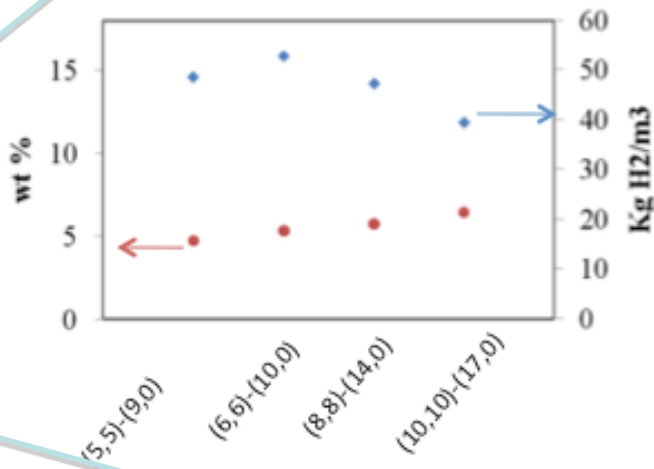
**Work with HSECoE to optimize tanks for 2015 targets**

# Accomplishment: Optimized Sites; New Carbon Structures

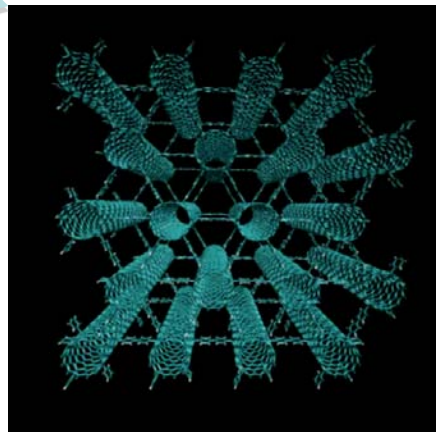
- Identified processing for high surface area carbon structures with opened van der Waals spaces and minimal wasted volume
  - Optimized spacing could increase hydrogen binding and capacity
    - Superposition of potentials can enhance sorption w/ optimum spacing
      - Patchkovskii, Tse, et al. PNAS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



Maxima of storage in foams



**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.**

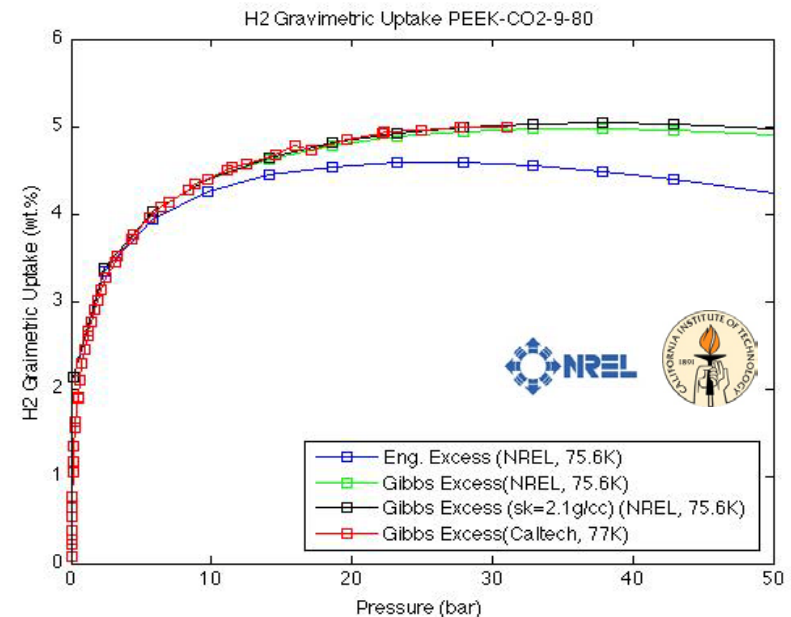
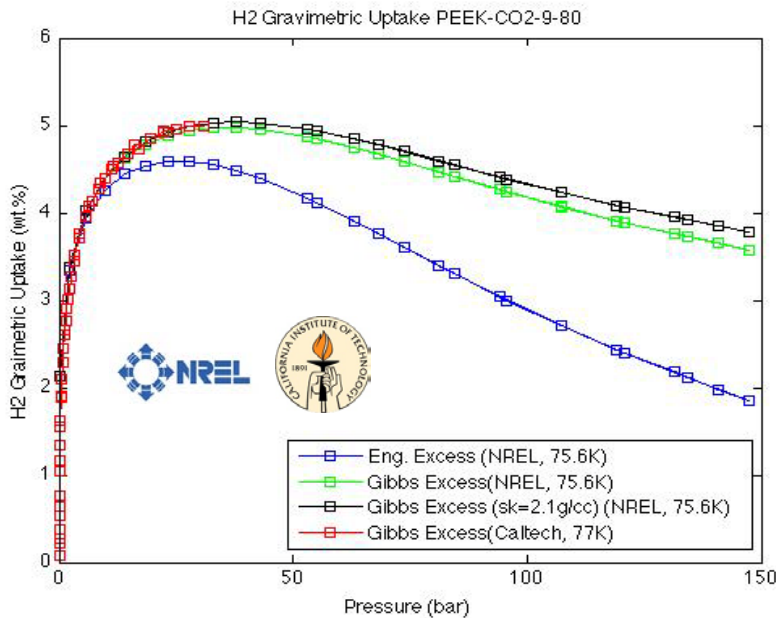
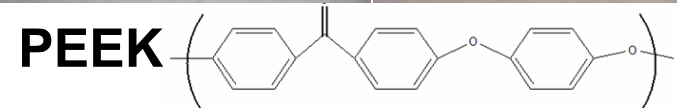




# Accomplishment: Optimized Sites; Pyrolyzed Polymer Precursors

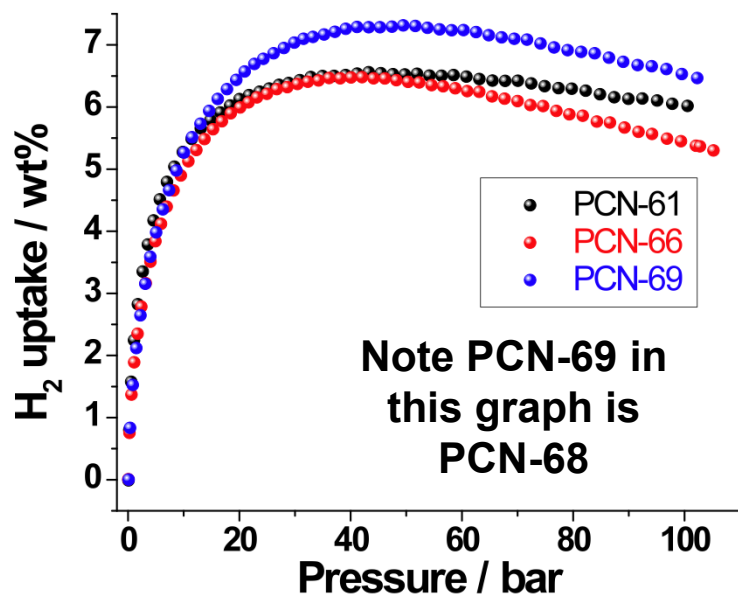
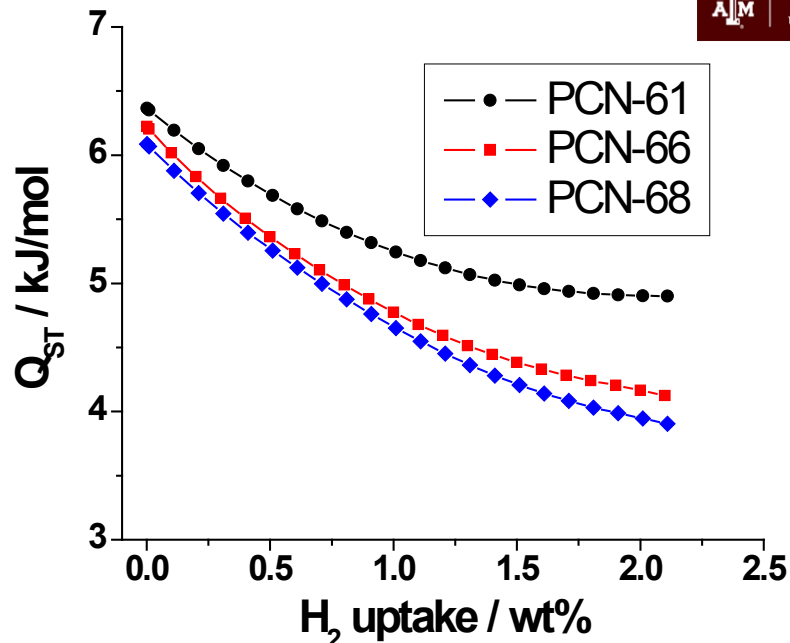
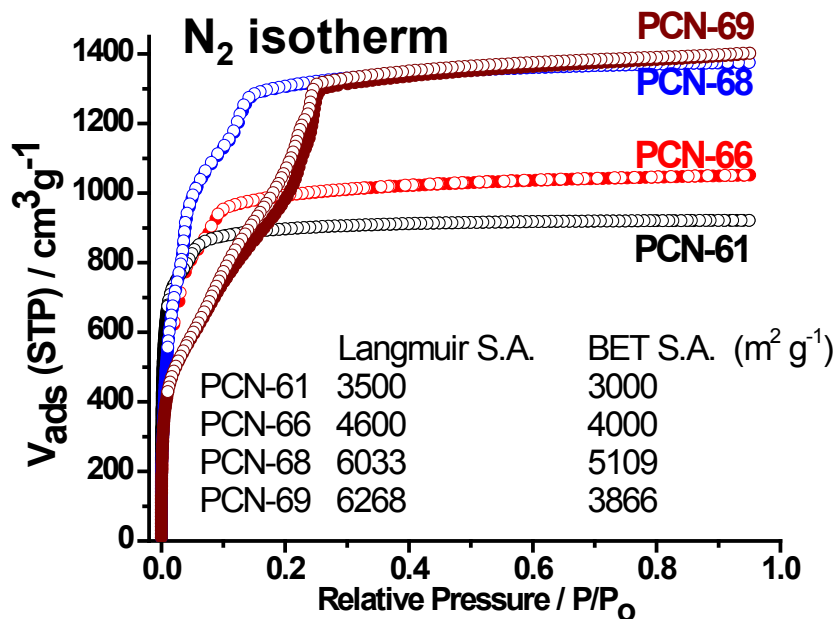


- TEM evidence suggests scalability of pore sizes, however low BET surface areas and H<sub>2</sub> NMR data suggests inaccessible micropores;
- The most promising are microporous carbons (MPC) derived from the 900°C CO<sub>2</sub> and steam treatment of Polyetheretherketone (PEEK)
- Pressed material has >0.7 g/ml bulk density



**High pressure measurement of the hydrogen uptake at both NREL and Caltech show materials can be made with >5 wt% (>35 g/L) at ~20 bar and ~77K. This inexpensive material may be used to meet DOE targets.**

# Accomplishment: Optimize Sites; MOFs with Record High Specific Surface Areas and Hydrogen Capacities



□ PCN-69: MOF with the highest Langmuir surface area 6268 m<sup>2</sup>/g (3866 m<sup>2</sup>/g BET)

□ PCN-68: 6033 m<sup>2</sup>/g Langmuir (5109 m<sup>2</sup>/g BET) and 7.2 wt% excess H<sub>2</sub> adsorption capacity. Confirmed, data from GM.

□ The excess gravimetric H<sub>2</sub> uptake is the highest (MOF-177 is ~7.0 wt%)

# Substituted Materials

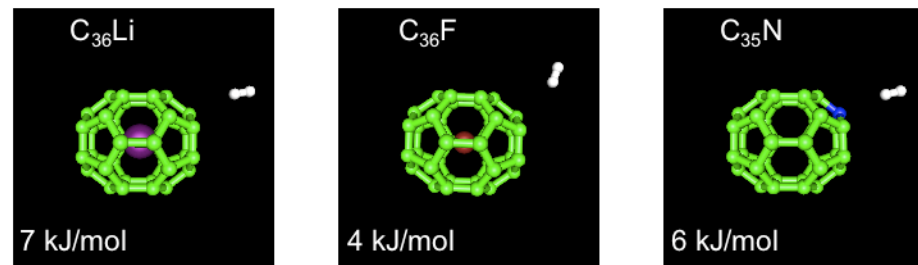
## Accomplishment Overview: Substitution Improves Storage

- Designed and developed substitutional materials with enhanced dihydrogen binding energy to increase capacities at near ambient temperatures, on a per specific surface area basis.
  - Substituted materials enhance hydrogen isosteric heats of adsorption (e.g. ~11 kJ/mol for B substituted carbon, compared to ~5 kJ/mol for pure carbon) sufficiently to increase capacities at near ambient (e.g. ~200K) temperatures. Substituted materials have the potential to meet DOE's 2015 hydrogen storage system capacity targets. Increasing storage temperatures to near ambient helps decrease system costs by reducing the amount of insulation, tank, and balance of plant costs.

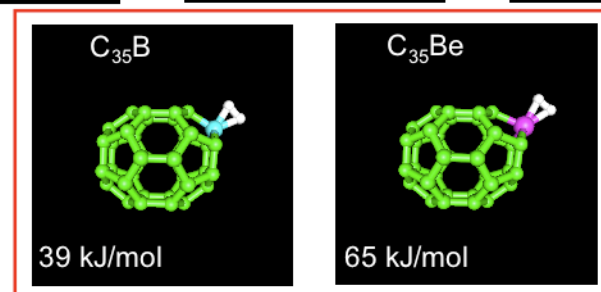
**Designed/developed substituted materials to enable higher hydrogen binding energies in porous materials. Demonstrated higher B concentration (10-15%) in carbon with higher surface area (800 m<sup>2</sup>/g). BCx could increase the storage tank temperature and capacity, thus reducing overall system costs.**

# Accomplishment: Substitution; Potential Substitutions in Carbon

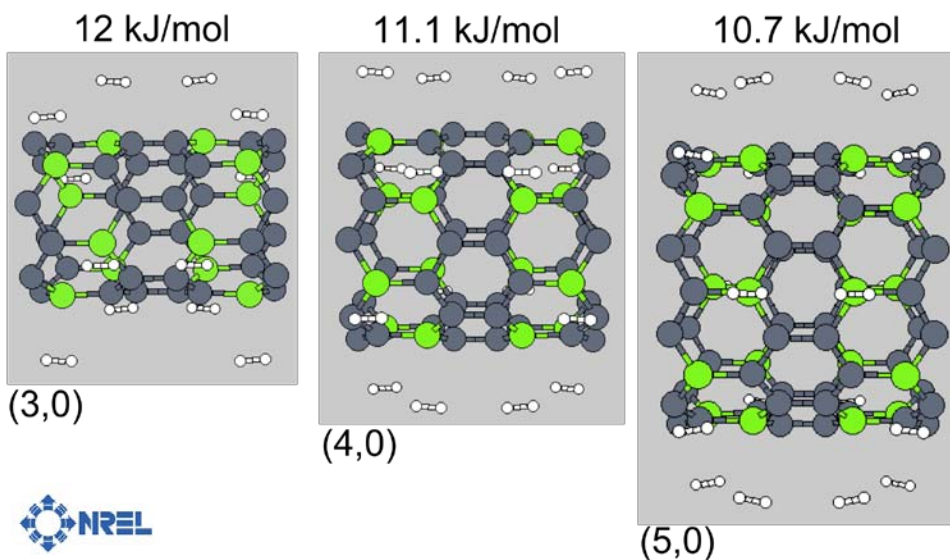
- Kim et. al., PRL 96 016102 (2006)
  - B and Be substitutions enhance H<sub>2</sub> binding
  - 3-center, 2-electron binding between H<sub>2</sub> and B site
  - H<sub>2</sub> bond lengthened (0.85 Å) vs. free H<sub>2</sub> (0.75 Å)
  - Binding decreases with number of H<sub>2</sub> adsorbed
  - Manipulation of binding by doping, charging & curvature



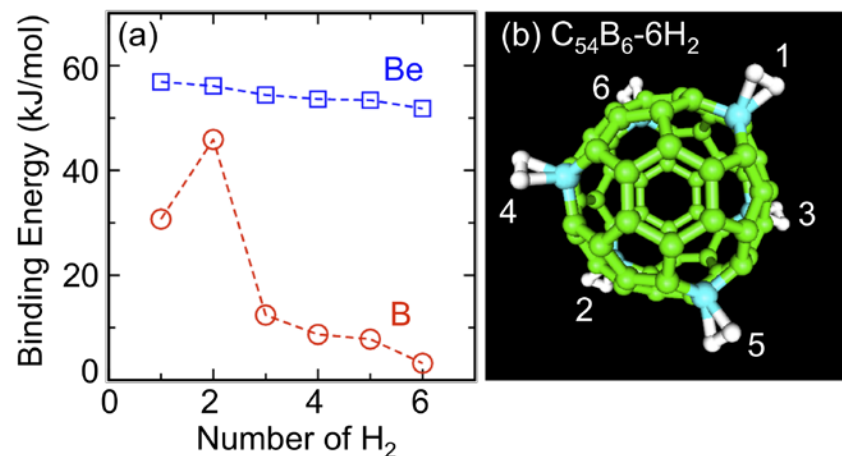
- Boron substitution also stabilizes metal atoms on the surface



Enhanced binding



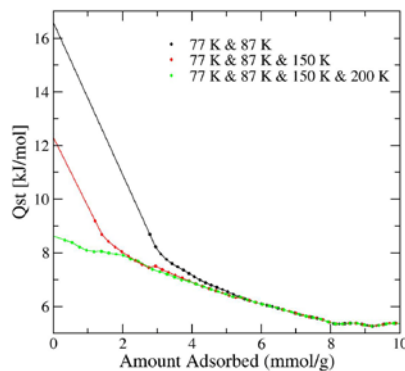
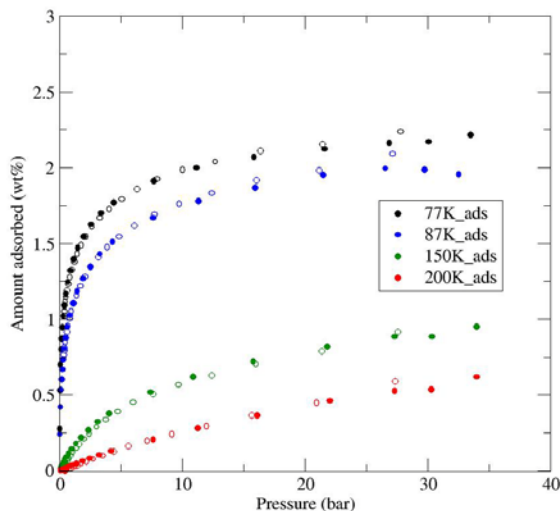
Surface curvature (sp<sup>2</sup>-sp<sup>3</sup> hybridization) affects the binding.



Calculations predict that only electronically frustrated B (i.e. sp<sup>2</sup> coordination) and Be substituted in carbon with correct coordination significantly increase H<sub>2</sub> binding (e.g. ~11 kJ/mol) and capacities at temperatures approaching ambient.

# Accomplishment: Substitution; Calculations Confirmed

## Boron substituted carbons (M. Chung, Penn State Uni.)

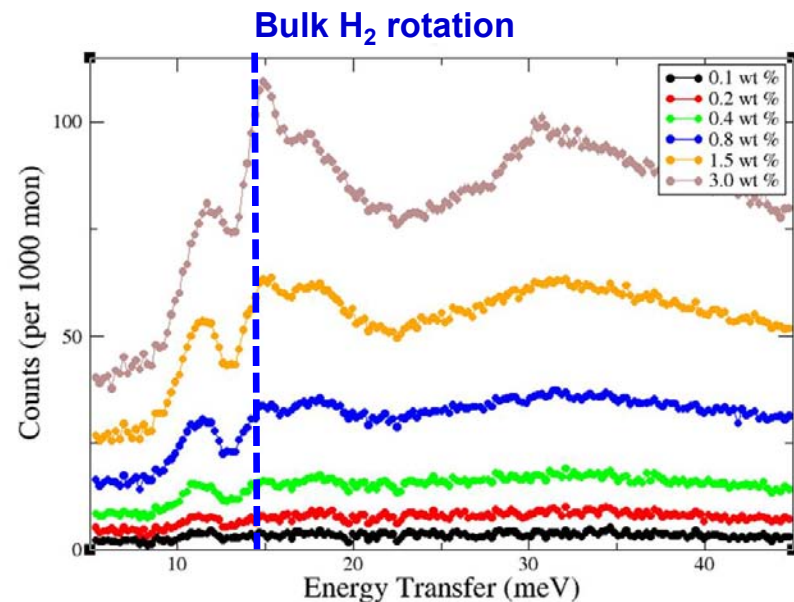


Variable temperature,  
high pressure isotherms

→ Clearly demonstrate  
the need to include  
isotherms at a range of  
temperatures to obtain  
robust  $\Delta H$  values.



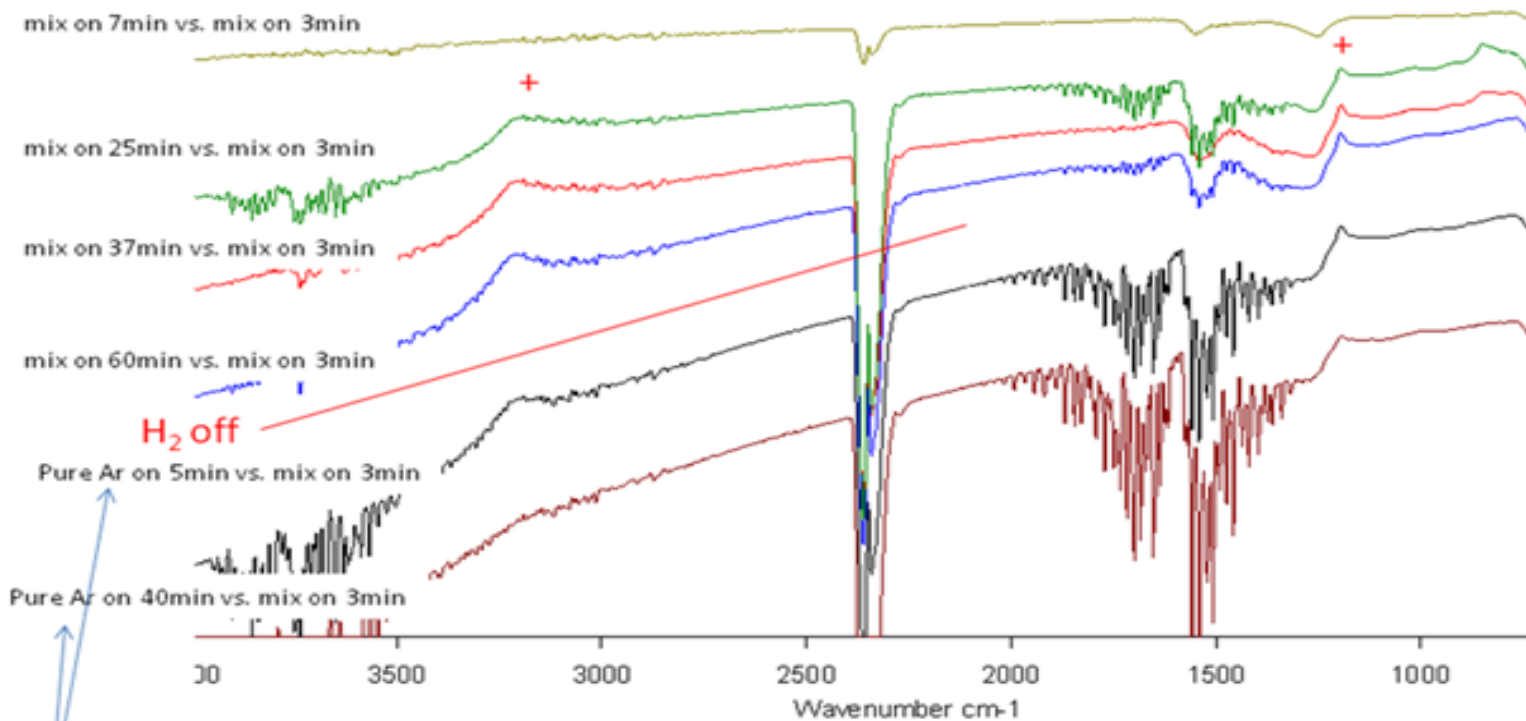
NMR indicates 6 at% B:C



Consistent with a model of hindered  $H_2$   
 $H_2$  lies II  
rotation barrier  $\sim 13$  meV

- Experimental results confirm calculations that B-C increases  $\Delta H$  values
- INS data shows, *for the first time*, a large rotational splitting indicative of enhanced  $H_2$  interactions in a substituted carbon.

# Accomplishment: Substitution; B-H Drifts Measurements



- Peaks at 3200 and 1190 cm<sup>-1</sup> appear as BC<sub>x</sub> is exposed to 5% H<sub>2</sub>/Ar gas mixture
- Peak intensity increases with time of exposure. The peaks shrink/disappear when the sample is purged with He, indicating reversible desorption of H<sub>2</sub>

• DRIFTS measurements show reversible H interaction with B:C material. Specific amounts of B-H and/or C-H binding still to be determined.

# Accomplishment: Substitution;

## Pyrolysis of B-containing polymers: $BC_x$ with 11 kJ/mol $q_{st}$

Scheme 1. Synthesis of Two Polymeric B-Containing Precursors

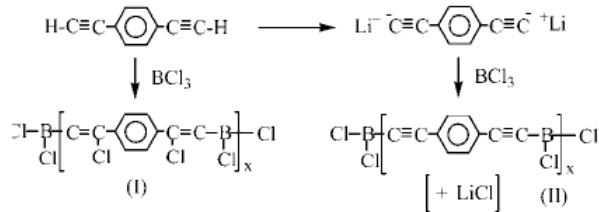


Table 1. A Summary of B/C Materials Prepared under Various Conditions

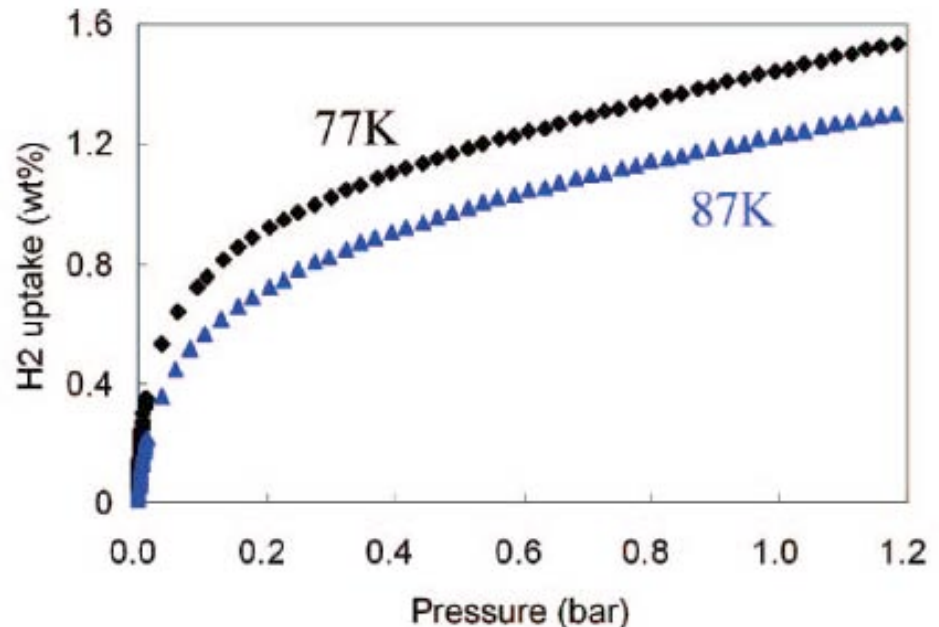
sample	precursor	pyrolysis temp (°C)	B content <sup>a</sup> (wt %)	B content <sup>b</sup> (wt %)	surface area <sup>c</sup> (m <sup>2</sup> /g)
BC-I-800	I	800	1.5	-	150
BC-I-1200	I	1200	1.2	-	35
BC-II-600	II	600	7.2	7.6	780
BC-II-800	II	800	5.7	7.1	528
BC-II-1100	II	1100	4.2	3.0	40

<sup>a</sup> B content was determined by Prompt Gamma-ray Activation Analysis.

<sup>b</sup> B content was determined by <sup>11</sup>B MAS NMR spectra. <sup>c</sup> Surface area was determined by BET method using N<sub>2</sub> gas at liquid N<sub>2</sub> temperature.

- **Isosteric heat of adsorption found to be 11 to 12 kJ/mol**
- **77 K capacity ~3.2 wt% at 2 bar for surface area of 780 m<sup>2</sup>/g**

Proposed B/C structure after pyrolysis at 1100 °C.

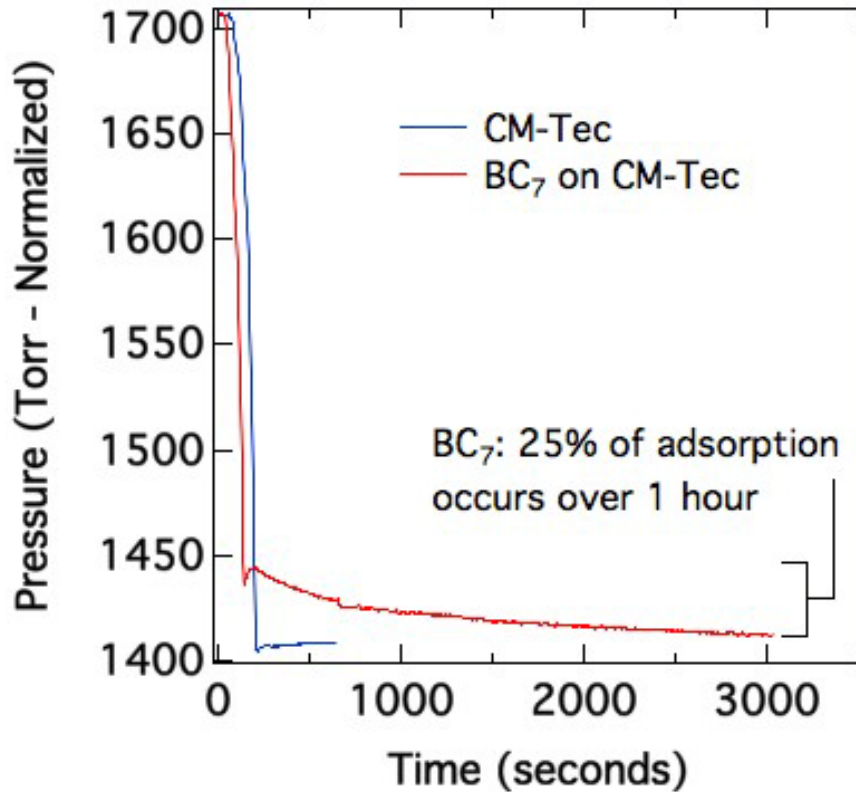


Chung et. al, J.A.C.S. 130, 6668 (2008)

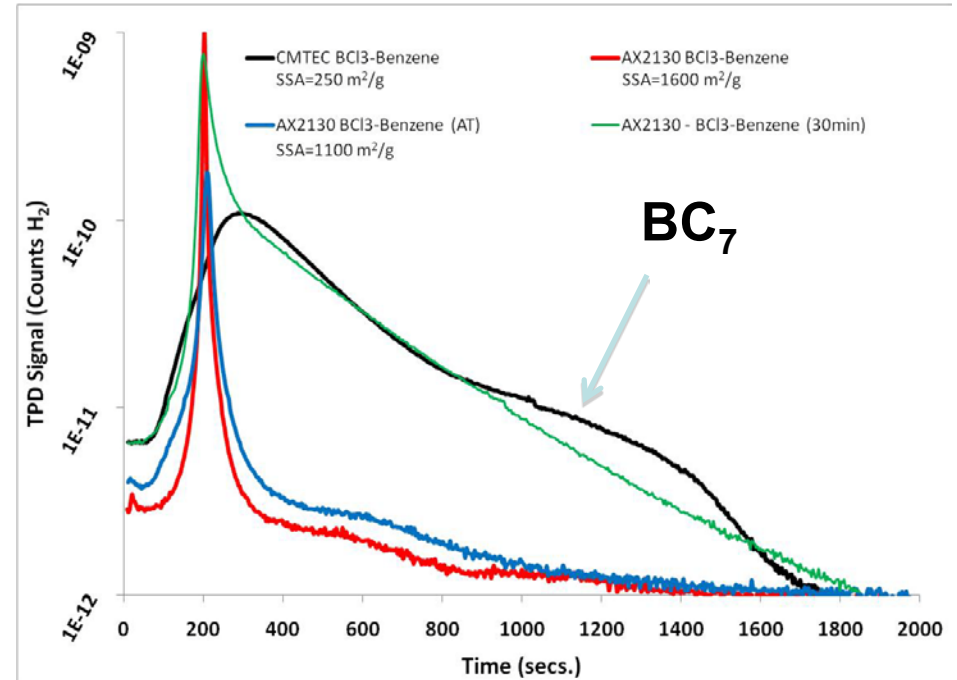
**Created high specific surface area B-C material using pyrolysis of high B content precursors.**



# Accomplishment: Templated $BC_x$ Has Slow Kinetics of Adsorption and Desorption



Sieverts – Slow Adsorption Kinetics



TPD – Slow Desorption Kinetics

**$BC_x$  Templating may have different pore structure, creating tortuous paths for hydrogen adsorption and desorption – may explain some hidden surface area effects. Because these effects are not observed with N-substituted templated carbon, this may be consistent with theory predicting a “puckered” B substitution site.**

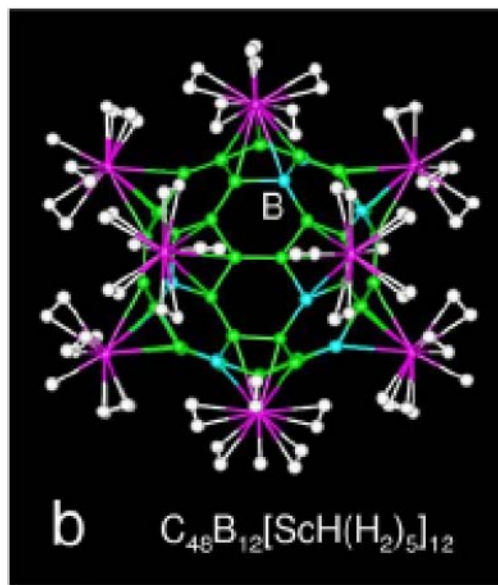
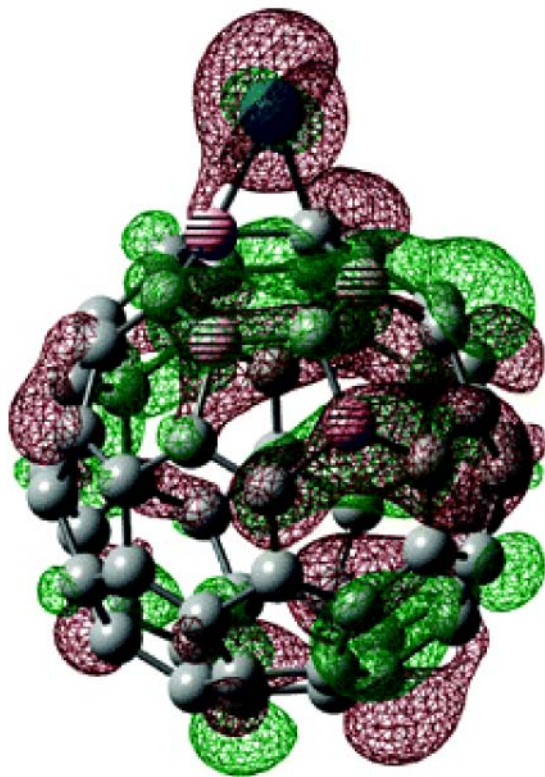
## Accomplishment: Substitution Summary

- **Four main methods to synthesize B-C** materials with high surface area using scalable/inexpensive processes
  - Created high specific surface area B-C material using **pyrolysis** of high B content precursors
    - » PSU: pyrolysis of  $BC_2-X$ ; higher B with high SSA
  - Created high specific surface area material with **templated**  $BC_x$  (NREL, PSU, Duke, APCI)
  - 6% B in **graphene through chemical self-assembly** routes (Rice: ~10% P & ~30% N substitution, too)
  - Replacement: Missouri- **ion irradiation** of pyrolyzed corncobs
- **Still have issues with higher B only with lower SSA**
  - **Must balance processing conditions to optimize SSA & B;** Best so far is ~12% B & ~800 m<sup>2</sup>/g
  - **BC<sub>x</sub> helps bind metals and improves spillover**
- **F based material systems (APCI) did not demonstrate enhancements**
- **BC<sub>x</sub> may have unique properties to be a spillover material (APCI)**

# Accomplishment: Substitution; B Sites Anchor Metal Atoms for Strong Binding of H<sub>2</sub>

Acharya, J.P.C.B. 2006, 110, 17706

(d) LUMO – Pt<sub>1</sub> on C<sub>56</sub>B<sub>4</sub> fullerene



Zhao, P.R.L. 94, 155504



- Transition metal d electrons transferred to B sites; empty d orbitals accept electron density from H<sub>2</sub> σ bond

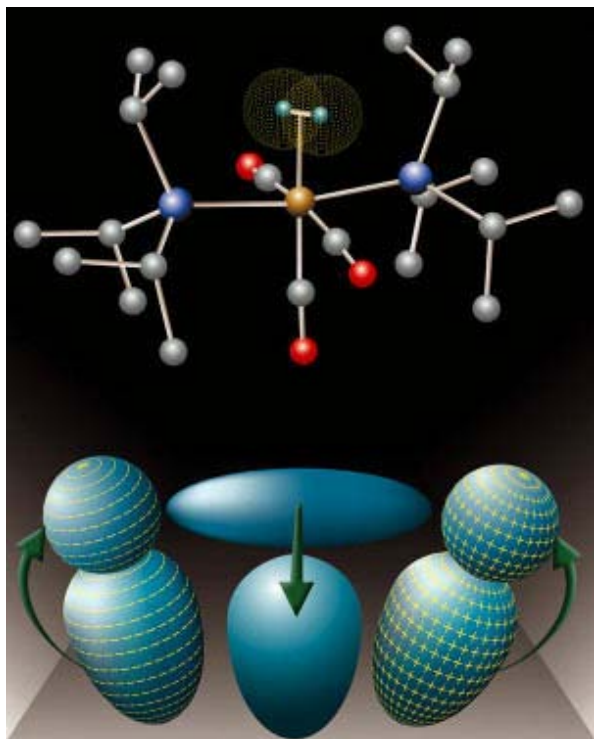
# Strong and Multiple H<sub>2</sub> Binding

# HSCoE Accomplishments: Strong/Multiple Binding of H<sub>2</sub>

- **Discovered & championed entire class of viable materials that uses lightweight (e.g. 3d metals) metal centers to enhance H<sub>2</sub> isosteric heats of adsorption and enable multiple H<sub>2</sub> binding on each metal site.**
  - Initial theoretical work demonstrating **multiple molecular hydrogen (H<sub>2</sub>) binding to electronically unsaturated 3d metals (30 kJ/mol – H<sub>2</sub>) was first performed by HSCoE at NREL.** These studies **initiated hundreds of subsequent** theoretical and experimental **studies** in the research area of strong/multiple H<sub>2</sub> binding. The original paper (Zhao et. al. PRL 94, 155504 (2005)) has been **cited nearly 200 times**. This work paves the way to **meet DOE's ultimate storage targets at ambient Temperatures.**

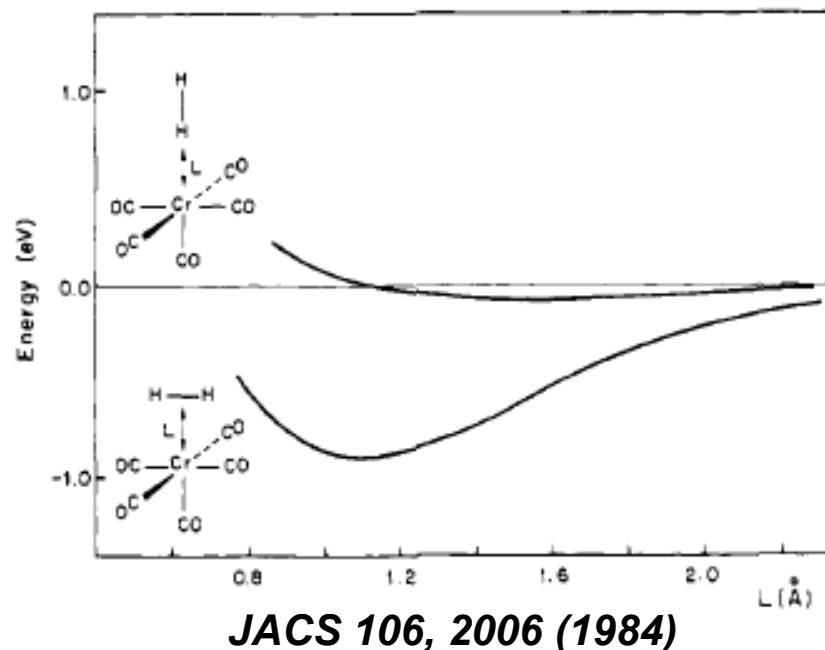
# Strong/Multiple H<sub>2</sub> Binding: A Historic Perspective

- In 1984, Kubas experimentally demonstrated H<sub>2</sub> adsorption on  $W(CO)_3(P-i-Pr_3)_2$



JACS 106, 451 (1984)

- In the same year, Saillard & Hoffmann suggested by extended Hückel calculation H<sub>2</sub> adsorption on  $Cr(CO)_5$  &  $Rh(CO)_4^+$

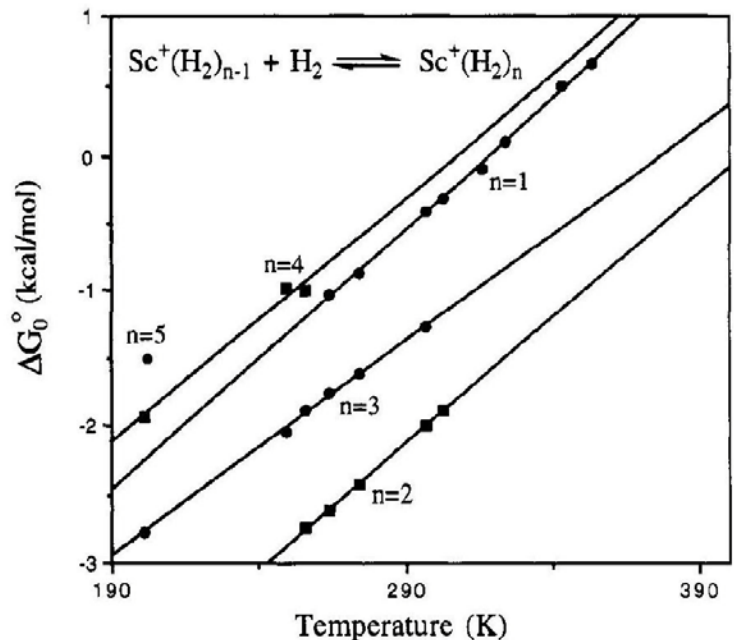


JACS 106, 2006 (1984)

**Leveraged known materials to develop/optimize routes to stabilize multiple di-hydrogen ligands on a transition or simple metal atom that exhibit moderate H<sub>2</sub> binding energies in order to meet DOE targets.**

# Strong/Multiple H<sub>2</sub> Binding: A Historic Perspective

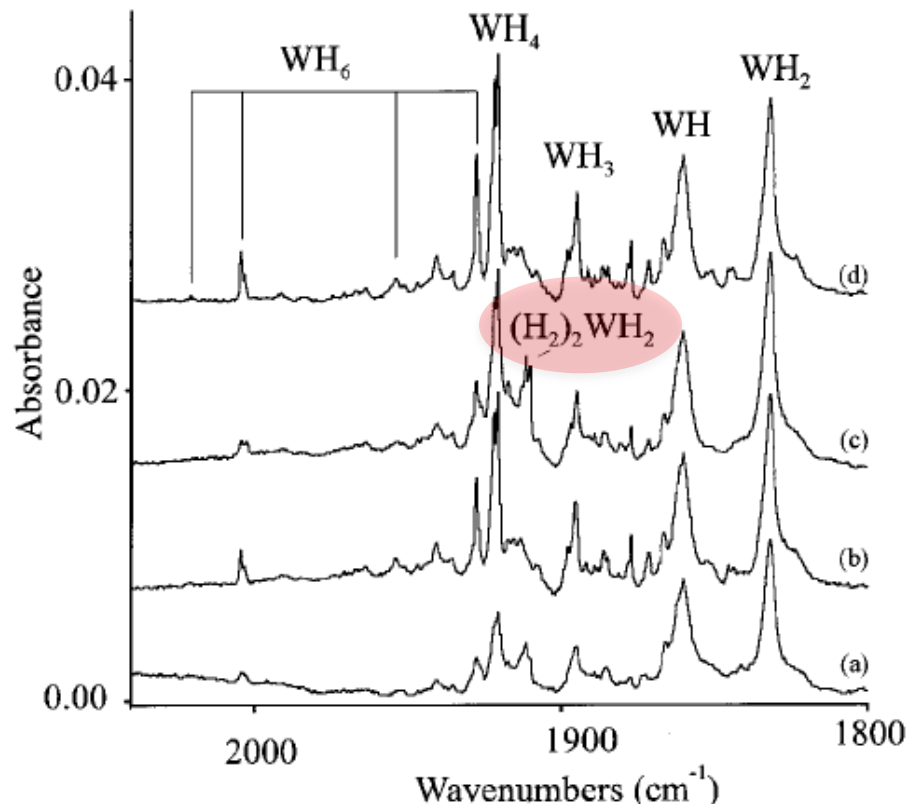
Measured H<sub>2</sub> binding Energy in Sc<sup>+</sup>(H<sub>2</sub>)<sub>n</sub>



n	1	2	3	4	5
kJ/mol	23.0	28.8	22.6	20.9	18.8

Bushnell et. al., *JACS* 116, 9710 (1994); Bowers, *Acc. Chem. Res.* 27, 324 (1994). 7 H<sub>2</sub> observed with Co, Zr and Nb

Infrared absorption of (WH<sub>x</sub>)(H<sub>2</sub>)<sub>y</sub>

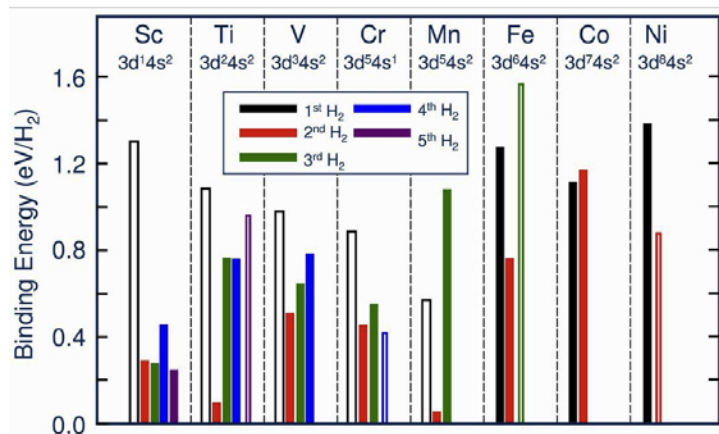


Wang & Andrews *JACS* 124, 5636 (2002), Also see Niu, et al., *PRL* 68, 2277 (1992), *PRB* 51, 4475 (1995)

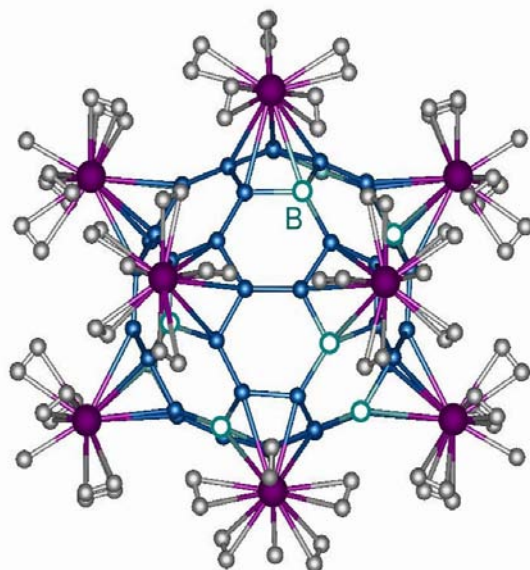
There are few experimental examples of stable metal complexes that can bind multiple H<sub>2</sub>. A rational synthesis of sorbents that can bind multiple H<sub>2</sub> must include a lightweight metal (1<sup>st</sup> row transition metal or alkali/alkaline metal).

Individual transition metal atoms have been experimentally observed to adsorb 4-7 H<sub>2</sub> molecules. The key is to stably coordinate the metal atoms so that the H<sub>2</sub> molecules can reversibly adsorb/desorb in a hydrogen storage system.

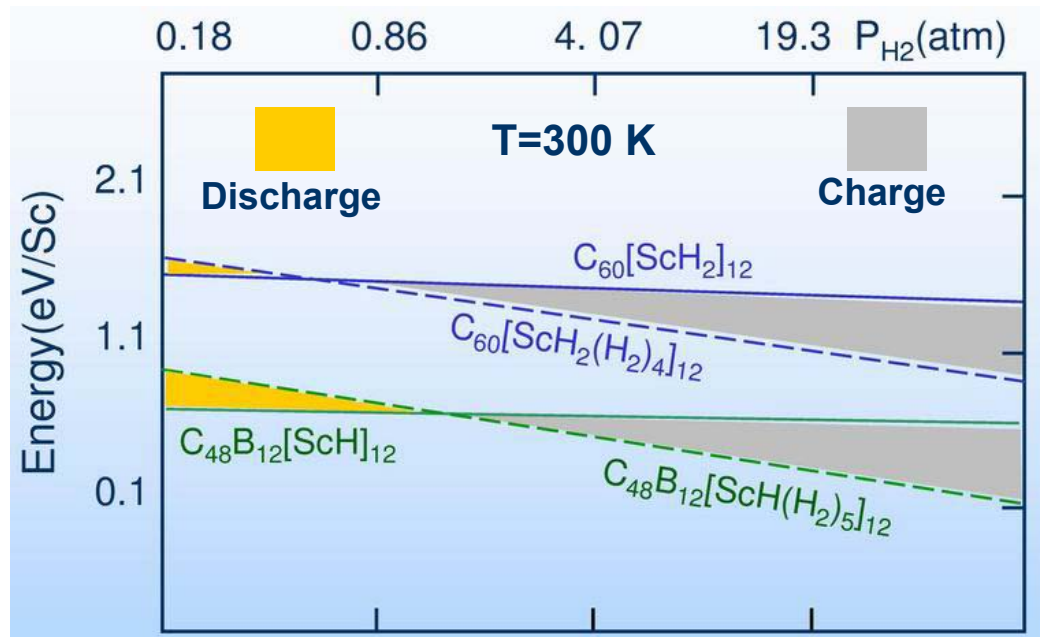
# Accomplishment: Strong/Multiple Binding; Original Work



1. H<sub>2</sub> Binding Strength Depends on the TM



2. Dispersion of Sc Metal Atoms on Boron Doped Carbon Cage (9 wt% H<sub>2</sub>)



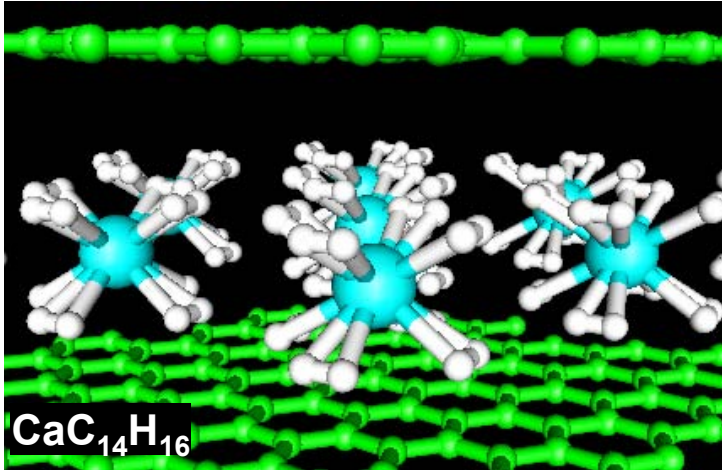
3. Charge/discharge is switched at ~ 1 atm, T=300K.

Initial theoretical work demonstrating multiple molecular hydrogen (H<sub>2</sub>) binding to electronically unsaturated metal sites (30 kJ/mol – H<sub>2</sub>) was first performed by NREL. These studies initiated many subsequent theoretical and experimental studies in the research area of strong H<sub>2</sub> binding.

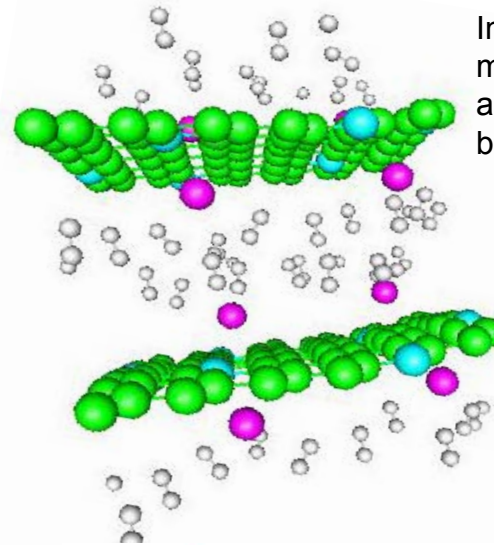
The ideal binding energy (E<sub>b</sub>) for storing H<sub>2</sub> reversibly at near ambient conditions is 15-30 kJ/mol – H<sub>2</sub>, thereby enabling fast-kinetics and high energy efficiency.



# Accomplishment: Strong/Multiple Binding; Designed Synthetically More Attainable Systems



1.  $\text{H}_2$  storage in Ca intercalated graphite



Initial experiments have validated many of the predictions, including ability to co-intercalate and enhanced binding only with Li and B present.

C ●

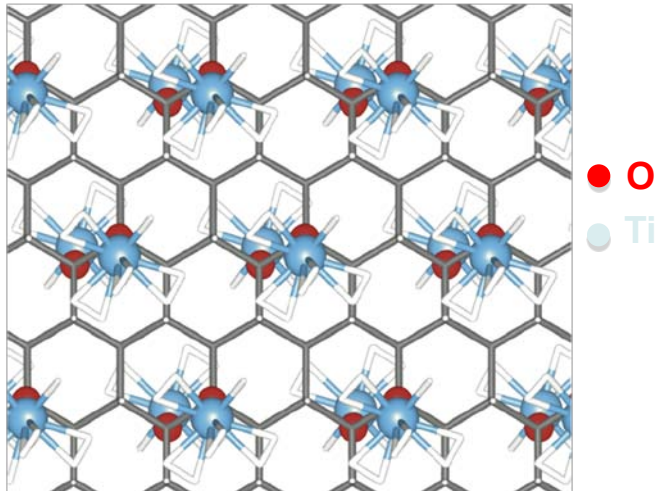
B ●

Li ●

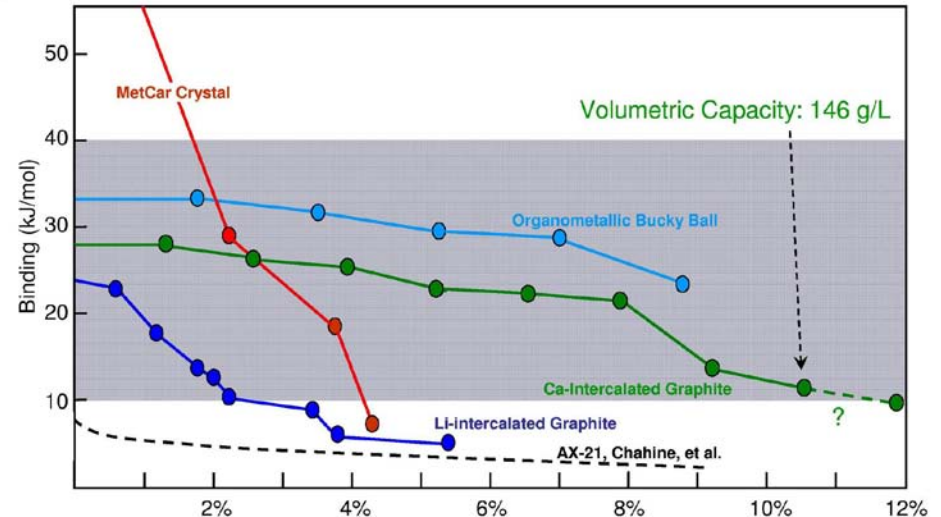
H ●



3.  $\text{H}_2$  storage in Li intercalated  $\text{BC}_x$  graphite



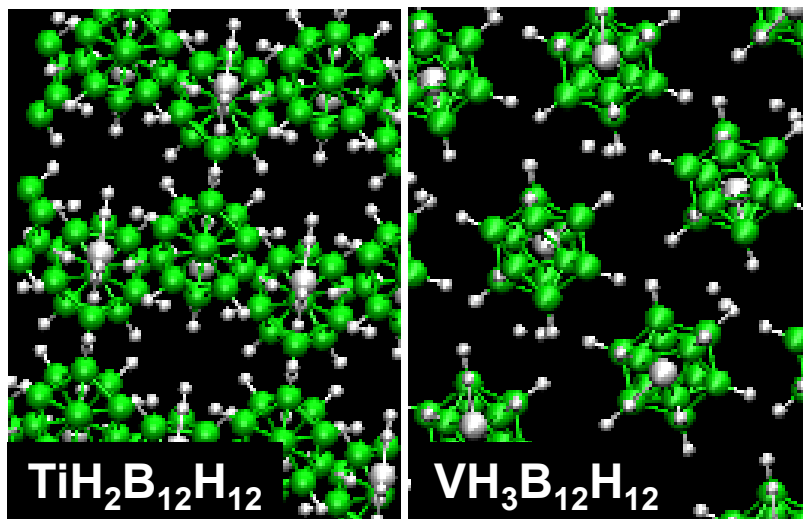
2.  $\text{H}_2$  binding to Ti on graphene oxide



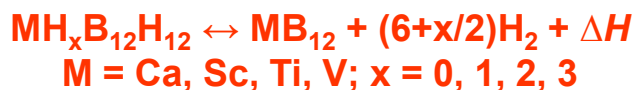
4. Summary of storage behavior for all materials

Designed materials in close collaboration with experiment to be energetically stable and reversibly store  $\text{H}_2$  ideally with binding energies ( $E_b$ ) between 15-30 kJ/mol –  $\text{H}_2$ ; enabling near-ambient temperature storage with fast-kinetics and high energy efficiency.

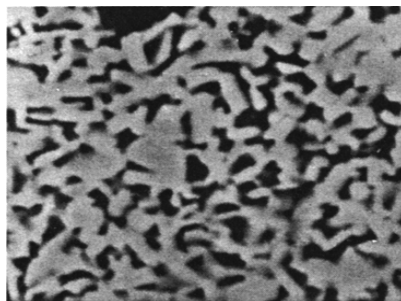
# Accomplishments: Strong/Multiple Binding; **Synthesizable Materials**



H-rich compounds derived from CaB<sub>12</sub>H<sub>12</sub>



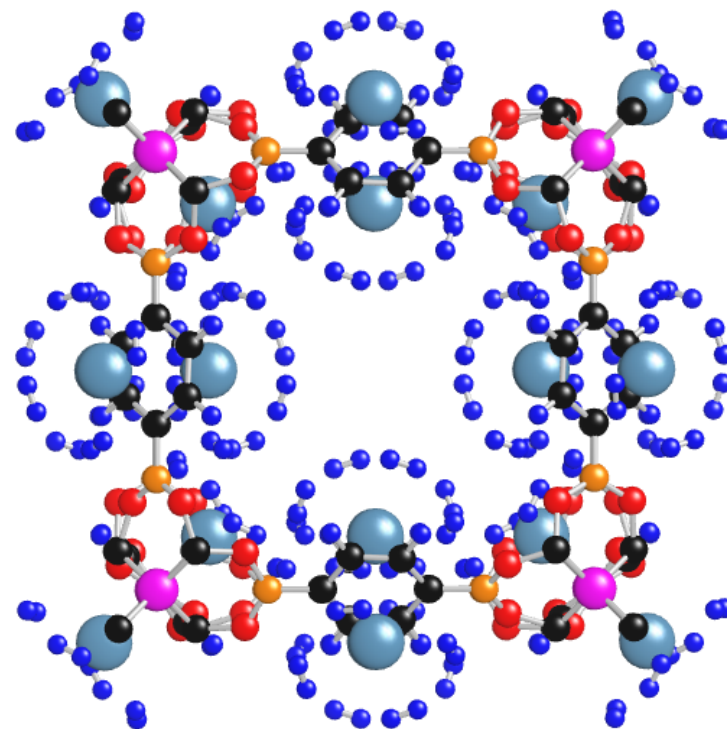
$\Delta H = 160 \sim 200 \text{ kJ/mol-H}_2$  for Ca  
 $35 \sim 50 \text{ kJ/mol-H}_2$  for Ti, V



Synthesized TiB<sub>12</sub>

Lepakova et al.,  
*Inorganic Materials*  
36, 568 (2000)

Tuning H binding energy in MB<sub>12</sub>H<sub>12</sub> : a new receptor for hydrogen spillover?



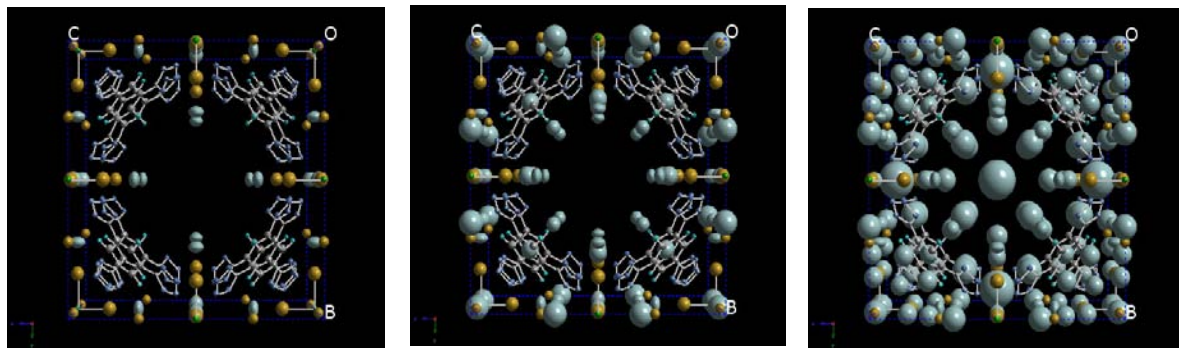
## Ca-Decorated COF-T for H<sub>2</sub> Storage

### Key Findings:

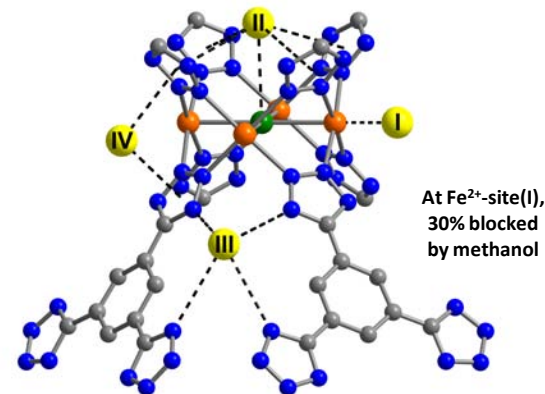
- 5.6 wt% and 44 g/L
- Average binding energy 0.15 eV/H<sub>2</sub>
- Strong Ca-linker binding & metal clustering is no longer an issue.

# Accomplishment: Strong Binding; MOFs

Effect on transition metal on H<sub>2</sub>-M interactions (Long U.C. Berkeley)



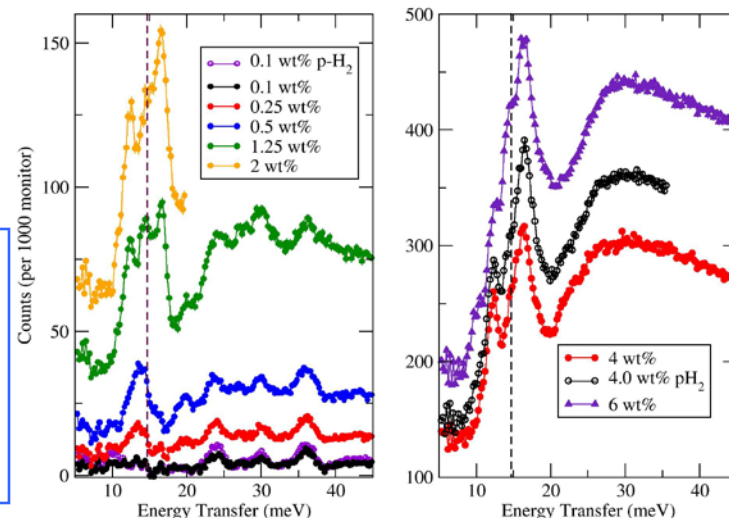
Neutron diffraction allows identification of adsorption sites with H<sub>2</sub> loading



INS: H<sub>2</sub> rotational spectra

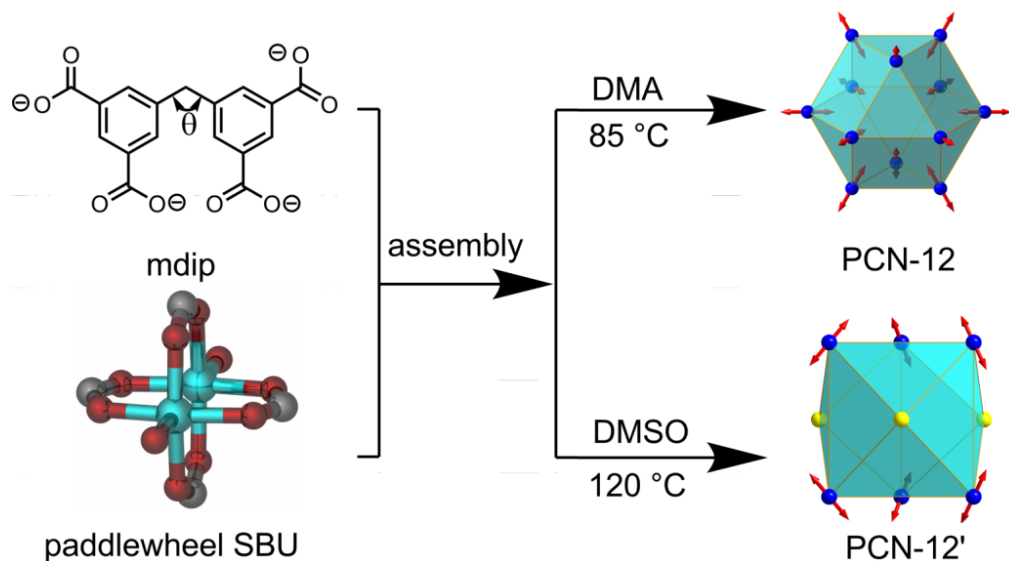
Correlation of **adsorption strength: Fe<sup>2+</sup> > Mn<sup>2+</sup> > Cu<sup>2+</sup>**  
 with **TM-H<sub>2</sub> distance: Fe<sup>2+</sup> < Mn<sup>2+</sup> < Cu<sup>2+</sup>**  
 [2.17(5) < 2.27 < 2.47 Å]  
 but not **ionic radius\* : Mn<sup>2+</sup> > Fe<sup>2+</sup> > Cu<sup>2+</sup>**

- **Primary adsorption sites @TM have highest enthalpy**
  - Shortest TM-D<sub>2</sub> distance found so-far is in Fe-BTT
- **INS consistent with strong H<sub>2</sub>:Fe interaction at low loading**
- **Fe<sup>2+</sup> site catalyzes hydrogen conversion to para-H<sub>2</sub> (complete at low loading, partially at high loading)**



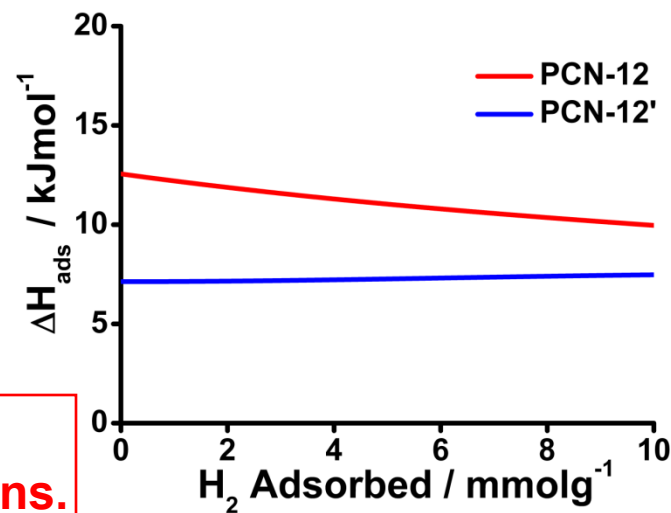
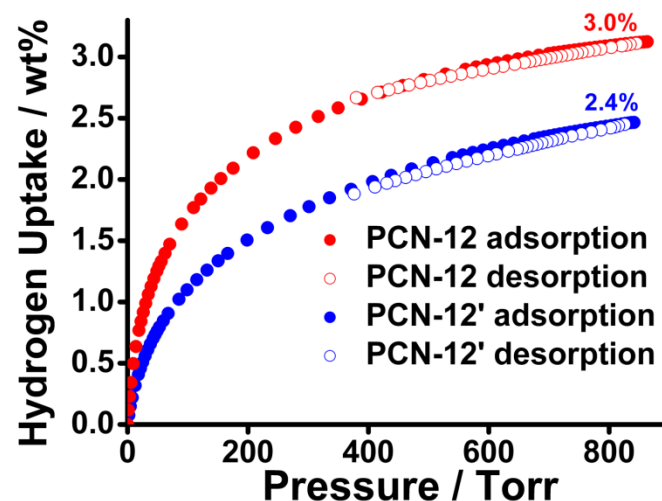
- **The binding energy of the TM center in MOFs to H<sub>2</sub> can be tuned in a range of about 10 to 50 kJ/mol (NREL: Sun et. al., JACS 129, 12606, 2007). Spin polarization effects may need to be included to accurately predict the binding energy for a specific TM in a MOF.**
- **\*MOF-74 isostructural series has been predicted by NIST to have ΔH (TM-H<sub>2</sub>) distance varying ~PROPORTIONAL (INVERSE) with ionic radius. Zhou, Wu and Yildirim JACS, 130, 15268, 2008.**

# Accomplishments: Strong/Multiple Binding; Alignment in MOFs



The isosteric heat of adsorption of PCN-12' is 7.13 kJ/mol at lower coverage. However, the H<sub>2</sub> adsorption heat of PCN-12 can reach as high as 12.5 kJ/mol at low coverage, higher than those of other reported MOFs such as MIL-100 (10 kJ/mol), PCN-9 (10.1 kJ/mol), a manganese MOF (10.1 kJ/mol), and NiSIP (10.4 kJ/mol).

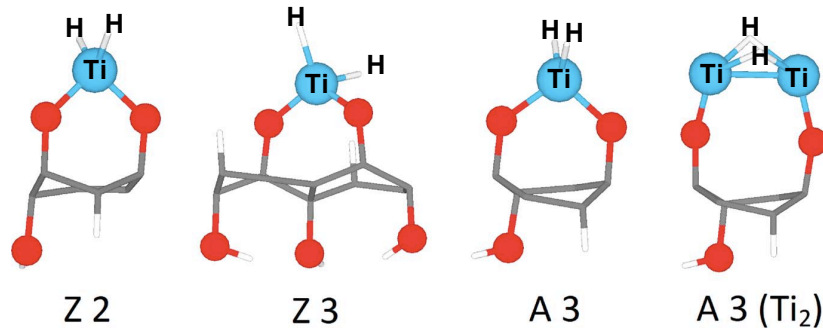
**Designed materials with higher binding energies based on initial principles identified by calculations.**



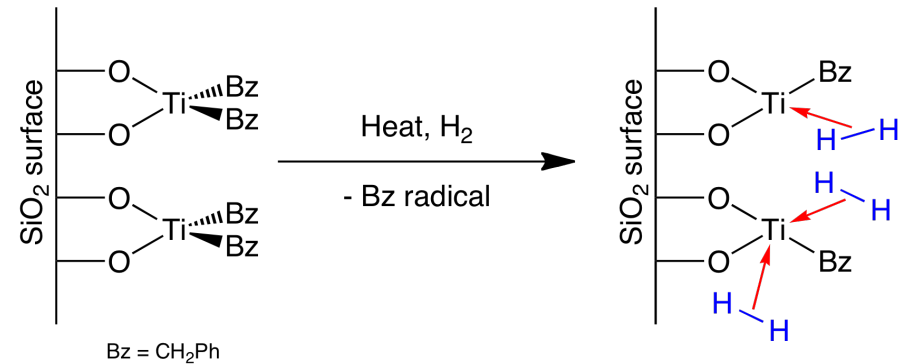
# Demonstrated H<sub>2</sub> Binding to a Single Metal Atom via Solution-Phase Routes

## Graphene Oxide as Ideal H<sub>2</sub> Storage Material: Literature Precedent

1) Zhang; et al. *ACS Nano* 2009, 3, 2995



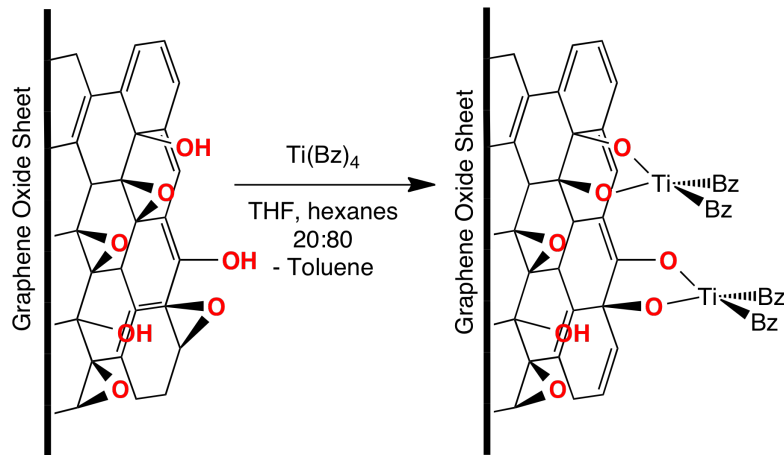
2) Antonelli; et al. *J. Am. Chem. Soc.* 2008, 130, 6992



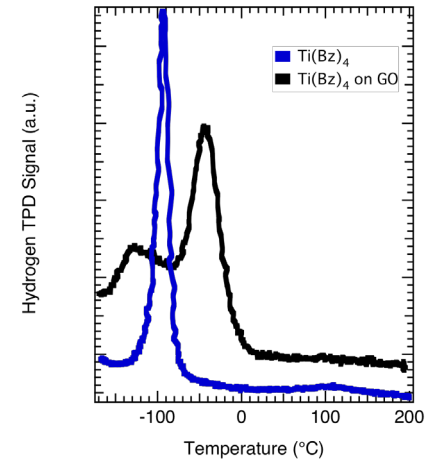
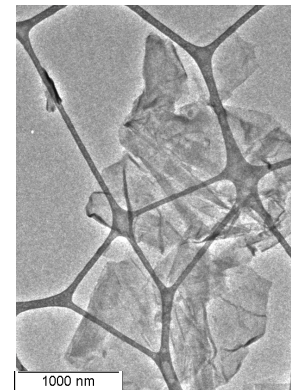
Ti-silanol: ~2.7 H<sub>2</sub> -Ti @ ~22 kJ/mol-H<sub>2</sub>

NREL/RPI theory 2.4 H<sub>2</sub> stored/Ti @ ~30 kJ/Mol-H<sub>2</sub>

## Experimental Scheme



## TEM Micrograph of Degased GO



**Ti-silanol: theory and experiment agree, more than 2 H<sub>2</sub> per Ti.  
Successfully combined Ti with GO sheets using solution phase chemistries.  
Ti binds strongly to the hydrogenated GO surface (481 kJ/mol), similar to Ti grafted mesoporous silica. TPD measurements reveal evidence for energetically favorable H<sub>2</sub> binding sites.**

## HSCoE Accomplishments: Strong/Multiple Binding of H<sub>2</sub> (1 of 2)

- **Calculations in quantitative agreement (binding energy and capacity) with all known 3-d metal based hydrogen storage materials. Also, calculations appear to be good for alkali and alkaline earth metals.**
  - **Calculations-experiments also agree: Cp-M, C-M and X-M-H<sub>2</sub> binding**
  - Individual transition metal atoms have been experimentally observed to adsorb 4-8 H<sub>2</sub> molecules (Niu, et al., PRL 68, 2277 (1992), PRB 51, 4475 (1995)). The key is to stably coordinate the metal atoms so that the H<sub>2</sub> molecules can reversibly adsorb/desorb in a hydrogen storage system.
- Designed materials in close collaboration with experiment to be energetically stable and reversibly store H<sub>2</sub> ideally with binding energies ( $E_b$ ) between 15-30 kJ/mol – H<sub>2</sub>; enabling near-ambient temperature storage with fast-kinetics and high energy efficiency.
  - **Ca may be a special element** that with appropriate coordination may enable 8 to 10 dihydrogens to be reversibly adsorbed and desorbed all with binding energies between ~ 10 and 30 kJ/mol (**>10 wt% & >100 g/L > liq. H<sub>2</sub> density but at ambient Ts**)
- Calculations in quantitative agreement (binding energy and capacity) with coordinated metal centers in MOF structures.
  - e.g. H<sub>2</sub>-Mn-MOF: experiment 10 kJ/mol, theory 8.4 kJ/mol (Sun, Kim, Zhang, JACS 129, 12606 (2007)), NIST work
  - Binding mechanism similar to metal decorated C60

# HSCoE Accomplishments: Strong/Multiple Binding of H<sub>2</sub> (2 of 2)

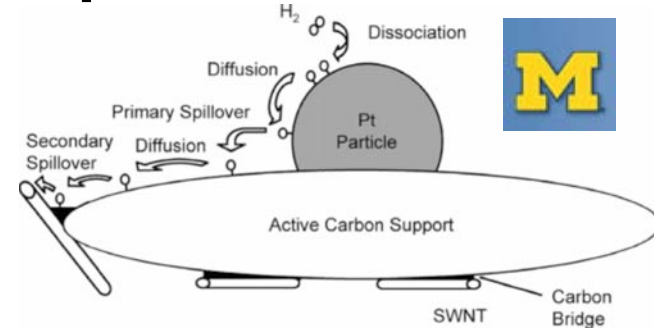
- **Synthetically challenging to avoid metal agglomeration (clustering) on pure elemental surfaces. Metal atoms need to be coordinated to well-defined higher binding energy sites.**
  - **Currently, there is only limited experimental evidence supporting theories that a pure carbon substrate can coordinate a metal atom sufficiently to serve as a high-capacity hydrogen storage material. e.g. two H<sub>2</sub>'s with Fe or Co on activated carbon (NREL)**
  - Successfully deposited organometallic Ti fragments on graphene oxide (GO) sheets using solution phase chemistries. Determined that Ti binds strongly to the hydrogenated GO surface (481 kJ/mol), comparable to Ti grafted mesoporous silica (Ti-silanol: ~2.7 H<sub>2</sub> -Ti @ ~22 kJ/mol-H<sub>2</sub> (Hamaed, JACS 2008), NREL/RPI theory 2.4 H<sub>2</sub> stored/Ti @ ~30 kJ/Mol-H<sub>2</sub>). Demonstrated H<sub>2</sub> binding to a single metal atom via temperature programmed desorption (TPD). Measurements revealed evidence for energetically favorable H<sub>2</sub> binding sites.
  - Successfully **dispersed Li metal atoms on a supported BC<sub>6</sub>** activated carbon material. TPD measurements are consistent with theoretical results (NREL Predictive Theory, Zhao). **The B sites provide well-defined Li metal binding sites; enables reversible enhanced H<sub>2</sub> binding.** BC<sub>6</sub>-Li very stable, enabling reversible desorption of H<sub>2</sub> even after *exposure* to O<sub>2</sub> and H<sub>2</sub>O.
  - Measured a uniform H<sub>2</sub>-adsorption heat for a metal-organic framework (MOF, PCN-12) that reached as high as 12.5 kJ/mol at low coverage. This value is higher than those of other reported MOFs such as MIL-100 (10 kJ/mol), PCN-9 (10.1 kJ/mol), a manganese MOF (10.1 kJ/mol), and NiSIP (10.4 kJ/mol).
  - Confirmed the presence of three H<sub>2</sub> adsorption sites in KC24 graphite intercalated compound via neutron diffraction and incoherent inelastic neutron scattering. Measured constant hydrogen binding enthalpies as high as 14.9 kJ/mol for CsC24. The interlayer H<sub>2</sub> adsorption in the graphite intercalation compounds was reversible at low temperatures (< 150 K) and H<sub>2</sub> reacted chemically at higher temperatures (~195 K).

# Weak Chemisorption



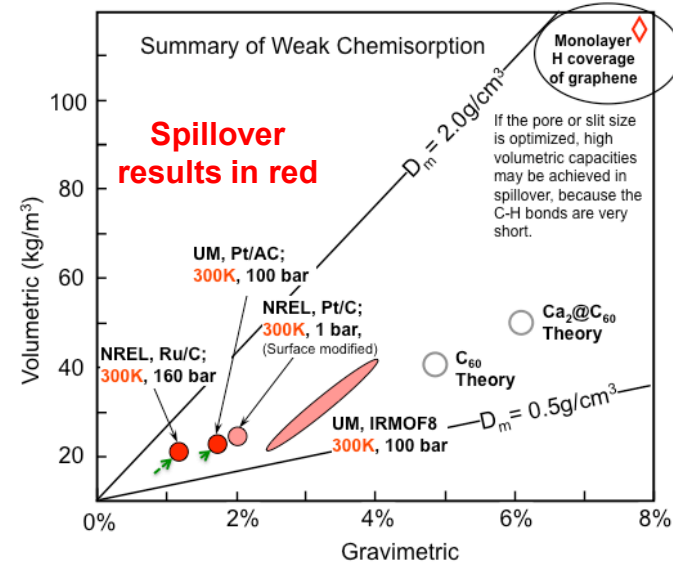
# Accomplishments Overview: Improved Spillover Materials

- Designed and developed reversible sorbents via ambient temperature hydrogenation techniques that have over 4 wt% storage capacities with isosteric heats of adsorption of 10 - 30 kJ/mol.



- Pioneered the development of materials that have relatively low chemical binding of hydrogen, potentially allowing efficient reversible on-vehicle refueling. This class of materials enables hydrogen storage system designs with more than 75% of the volumetric and gravimetric capacities of the materials and substantially reduces system costs and complexity.

- Spillover observed on numerous materials
  - Over 1.8 wt% spillover demonstrated on pure carbon @ RT
  - Over 4 wt% spillover demonstrated with Pt/AC bridged MOF
  - 10-30 kJ/mol isosteric heats of adsorption measured

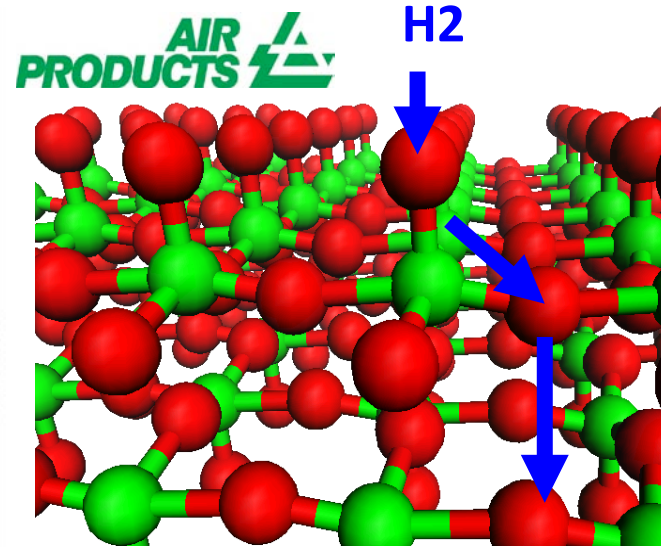
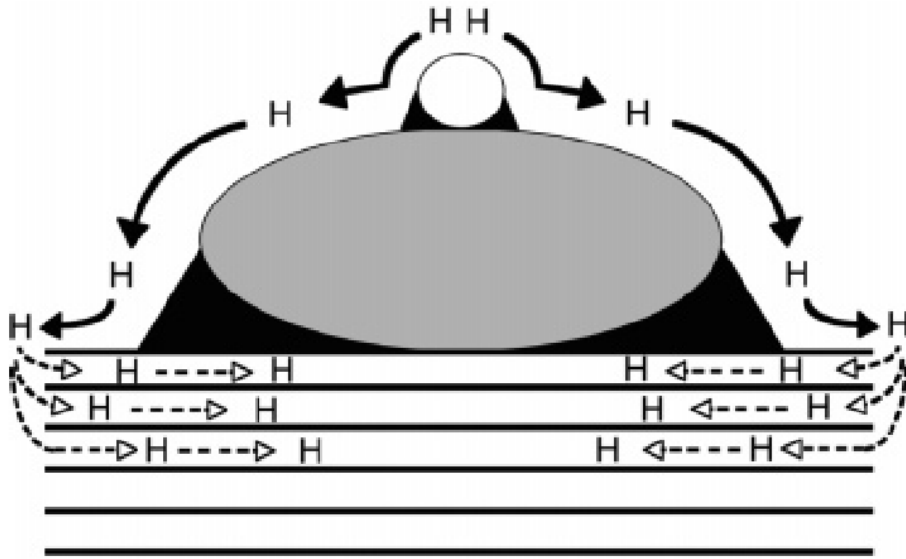


SSWAG analysis: ~3 wt% H storage if IRMOF 4 wt% spillover material used.

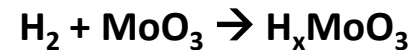
- ~8wt% spillover material could meet the DOE 5.5 wt% and 40 g/L 2015 hydrogen storage targets.

**Spillover has been demonstrated experimentally to be a viable mechanism that may be able to meet DOE hydrogen storage targets.**

# Hydrogen Spillover Known for Decades



APCI models validated using “hyd. bronze”, a known spillover material





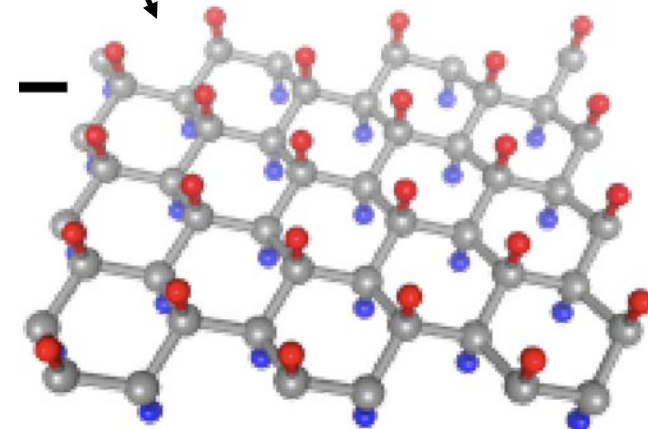
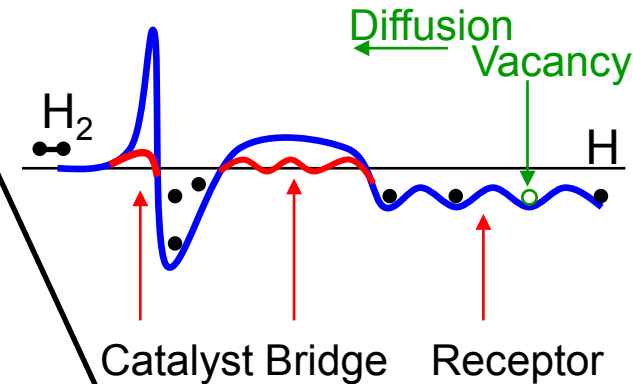
Spillover demonstrated experimentally and proven thermodynamically

- Observed on numerous materials for decades
  - e.g. Conner Jr. and Falconer, Chem. Rev. 95, 759. Srinivas and Rao J. Catal. 148, 470, 1994
  - Previous to HSCoE spillover observed at the ~0.01 wt% level
  - Initial thermodynamic models validated with known spillover materials
    - e.g. “Hydrogen Bronze”
- Main Issues:
  - Increasing capacities and rates
  - Developing a better theoretical foundation to understand the experimental processes involved
  - Stability

# Accomplishments Overview: Understanding Spillover

Confirmed experiments, consensus thermodynamics allowed

- Rice: First principles models identified H nucleation as a viable phase with  $\sim 20$  kJ/mol effective binding energies
  - H on both sides required, H vacancy migration energies too high
  - Catalysts saturation/transport to receptor agree with experiment
  - Metal saturation and catalyst-receptor transport are viable
- APCI: Calibrated models with known  $\text{MoO}_3$  system
  - Propose H physisorption as transport mechanism 
  - $\text{BC}_3$  in appropriate configuration may catalyze spillover
- NREL: Previously developed models for hydrogenating endohedral fullerenes and metcars are applicable
  - Prehydrogenation of the receptors may be required 
  - Upper spillover capacity is one H per carbon (i.e.  $\sim 8$  wt%, 60 g/l)
    - e.g. 7.5 wt% hydrogenation demonstrated at ambient T & P
    - Determined by  $\text{sp}^2$ - $\text{sp}^3$  rehybridization in carbon
    - Sensitive to the structure of the receptor and subjected to the relationship between H binding energy and coverage.
      - For  $\text{C}_{60}$  and CNTs, capacities up to 5 wt% through tuning the behavior of H binding energy versus coverage.
- Main issue is how H moves along lattice (kinetics)
  - NREL & RPI investigated mechanisms for kinetic enhancement of spillover, i.e., surface-mediated H migration and hole-mediated H diffusion.



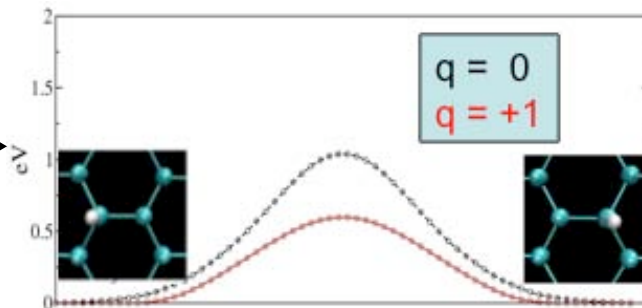
**Thermodynamics of spillover well understood. Calculations indicate that 7-8 wt% (50-60 g/L) capacities at ambient temperature are possible. Hydrogenation experiments have demonstrated 7.5 wt% on carbon samples.**

# Accomplishments Overview: Understanding Spillover

## Identified potential mechanisms for improving kinetics

- NREL: identified potential structural and electronic mechanisms that enable H transport on sorbent surfaces
  - H migration in nanoscale carbon materials mediated by a neighboring surface that approaches to  $\sim 3.4 \text{ \AA}$ 
    - i.e. **hopping between surfaces** faster than diffusion on surface
  - NREL/RPI: **Holes in valence band (e.g. doping or defects)** lowers energetics & enables H transport. Agrees w/ observed charge transfer.
    - Improve with optimal structures and doped/functionalized materials
- APCI/Rice/NREL: **B may help spillover migration**

Hopping between closely spaced surfaces decreases the diffusion barrier by  $\sim 40 \text{ kJ/mol}$

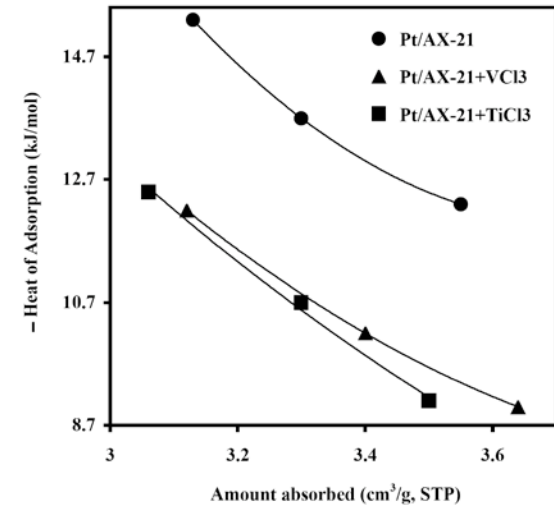
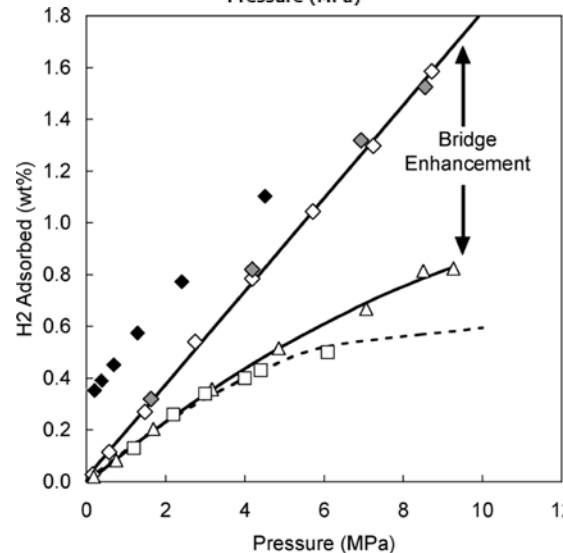
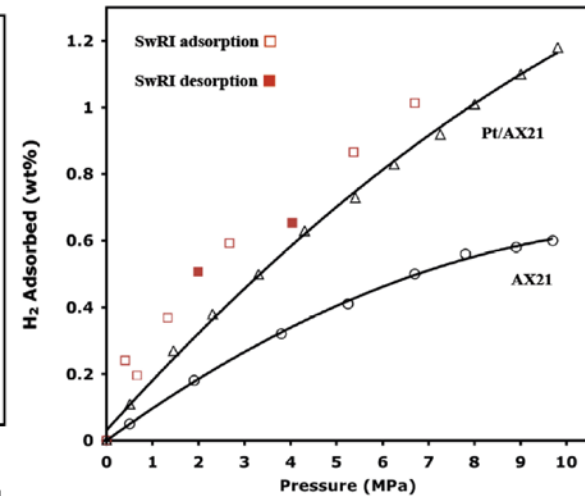
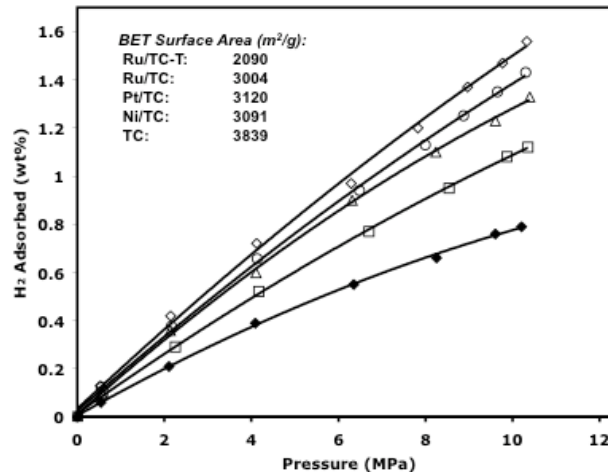


**First principle calculations indicate that spillover is thermodynamically viable, with binding in agreement with observed measurements. Improved spillover kinetics understanding needed to enable materials to be designed with higher capacities and sorption rates that can meet DOE 2015 targets.**

# Accomplishment: Spillover; U-Michigan, Activated Carbon

- Spillover demonstrated on many activated or high surface area carbons.
- Spillover results on AX-21 validated at SwRI®
- H<sub>2</sub> isotherms at 298 K on TC (templated carbon) & 6wt% metal-doped (ultrasound assisted) M/TC. All M/TC were H<sub>2</sub>-reduced at 300°C except Ru/TC-T where spillover was improved by thermally reduced (in N<sub>2</sub>) at 900°C (1 hr) (Metal particle size: 2 - 4 nm)
- Storage on nanostructured carbons is far from reaching theoretical limit: >2wt% per 1000 m<sup>2</sup>/g.
- Recent NREL result demonstrate spillover continues well past 100 bar

UM developed phenomenological model of spillover. Diffusion on carbon matrix is the limiting factor, not dissociation. Phenomenological spillover schematics



High-pressure hydrogen isotherms at 298 K for AX-21 receptor.

- △, AX-21/Pd-C physical mixture (9:1); □, AX-21.
- ◇, AX-21/Pd-C/Carbon Bridge (8:1:1) First Adsorption;
- ◆, AX-21/Pd-C/Carbon Bridge (8:1:1) Desorption;
- grey ◇, AX-21/Pd-C/Carbon Bridge (8:1:1) Second Adsorption.

Plot of delta ΔH for spillover on AC



# Accomplishment: Spillover; U-Michigan, Bridged MOFs



Over 4 wt% on Bridged MOF Spillover demonstrated experimentally and thermodynamically

- Issues: Loss of spillover activation and Stability of MOFs in spillover

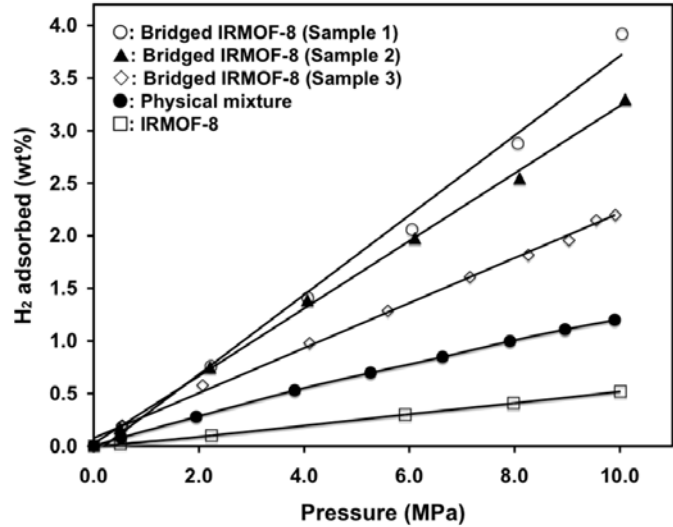
• Integration of catalysts directly with MOFs difficult and usual collapse MOF structure

• Carbon bridges between MOFs and Pt/AC produces substantial increases in spillover

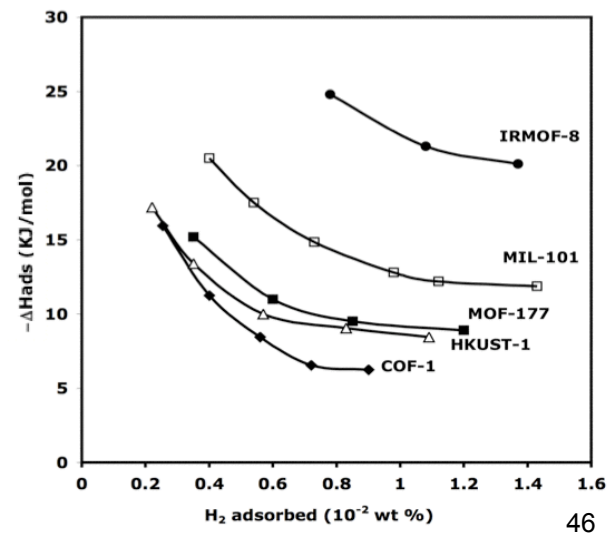
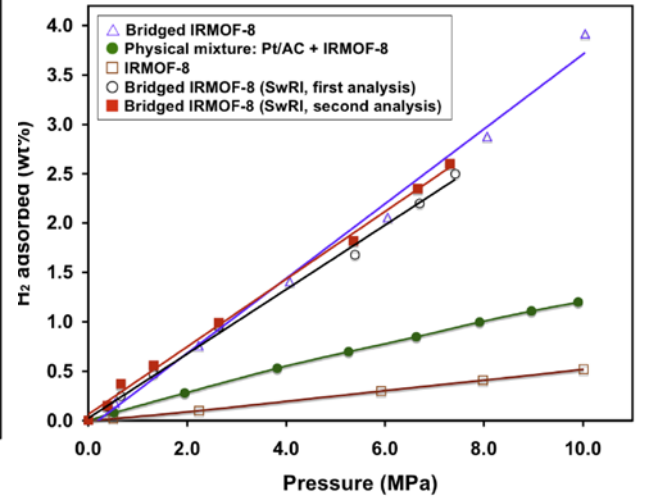
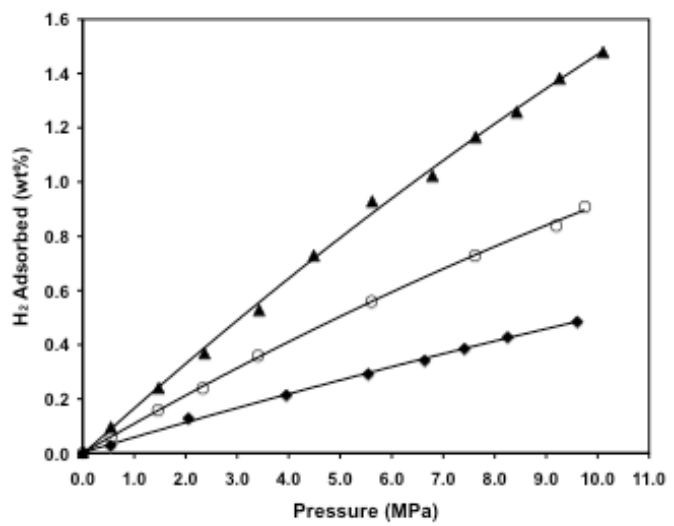
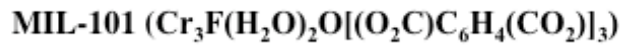
• MOF spillover results independently validated at SwRI<sup>®</sup> with Tiawan sample

• Spillover capacities with MOFs directly related to  $\Delta H$

• IRMOF-8 has highest capacity and  $\Delta H$  so far

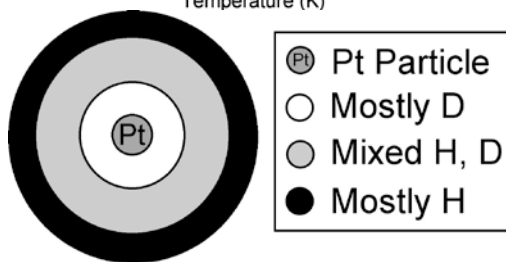
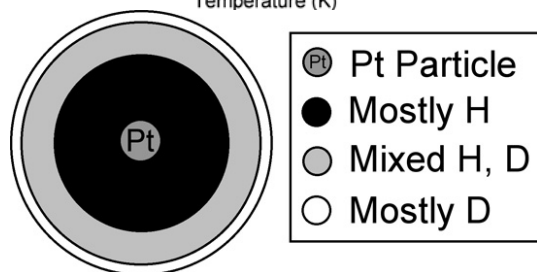
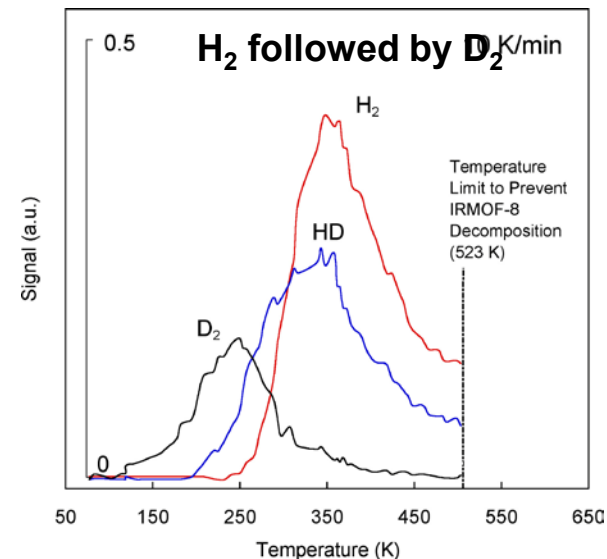
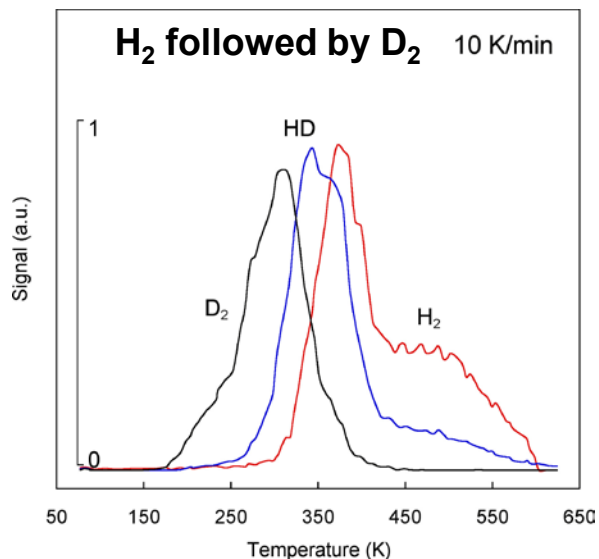
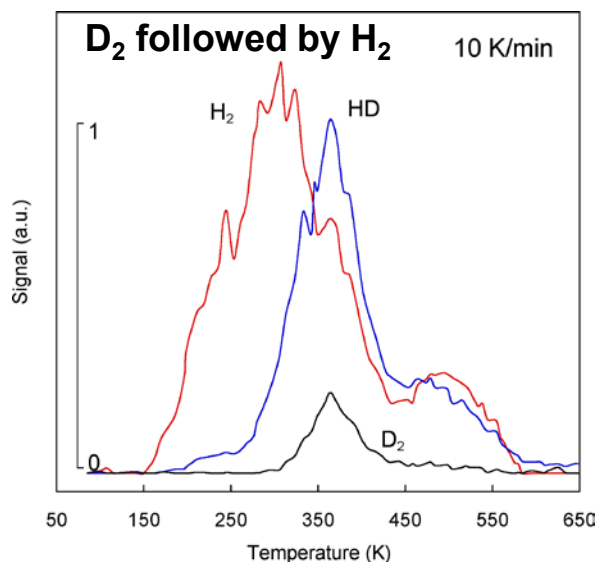


Li et al. JACS 128, 8136 (2006)



# Accomplishment: Spillover; Dissociation Demonstrated

TPD Result for 6 wt% Pt on Templated Carbon (3400 m<sup>2</sup>/g) and IRMOF-8 bridged to 5 wt% Pt/C after dosing with 0.4 atm H<sub>2</sub> or D<sub>2</sub> at 298 K for 5 min (followed by quench, gas phase removal and TPD)



- The formation of HD is clear evidence for the dissociation-spillover mechanism.
- The desorption is basically the reverse order of the adsorption.
- If the H and D did not adsorb, then the TPD would have both H<sub>2</sub> and D<sub>2</sub> coming off at the same time

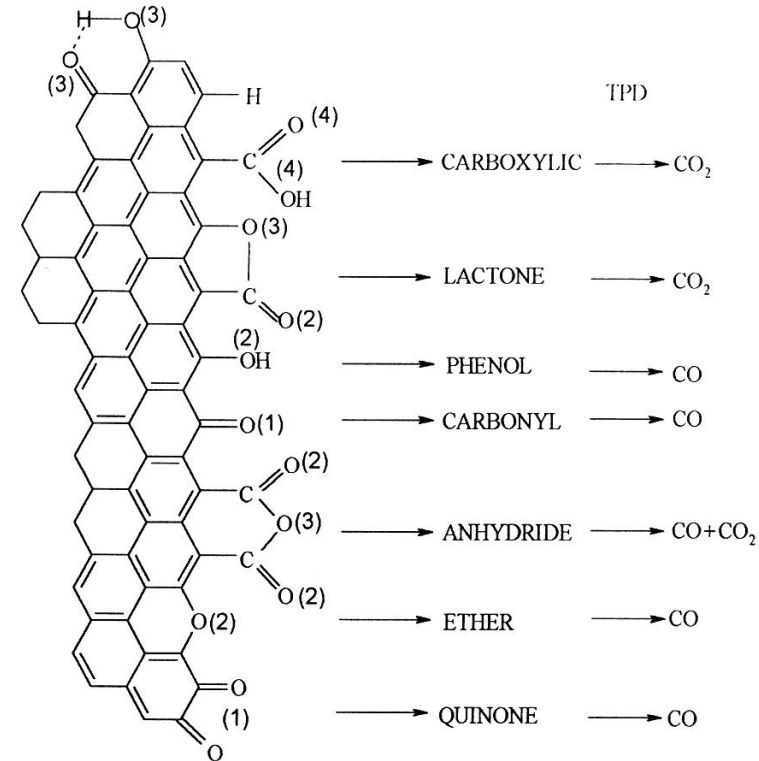
# Accomplishment: Spillover; Effects of Surface Functional Groups

## Surface composition important for H diffusion

- Reactions with surface moieties can inhibit or promote spillover mechanism
- TPD analysis of desorbed gases from spillover samples indicate that reductions sometimes occur

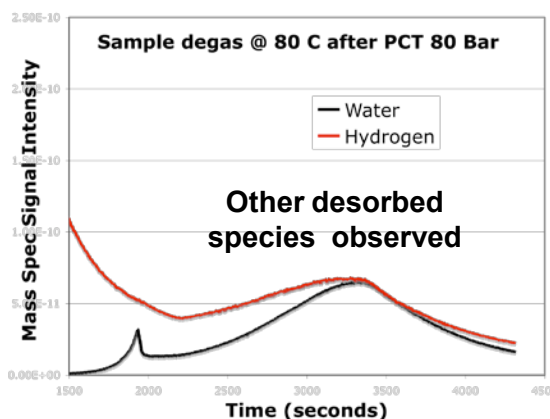
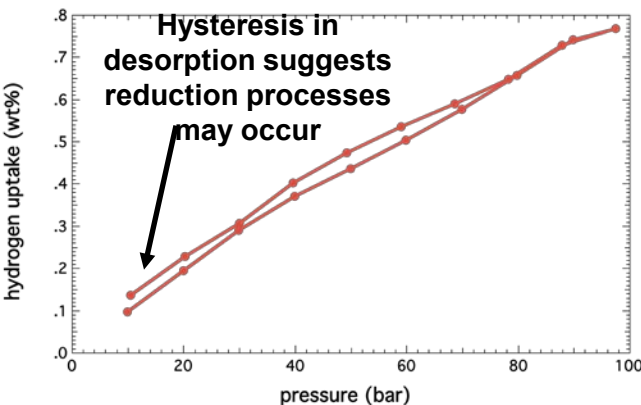


- Water, CO<sub>2</sub>, CO, CH<sub>4</sub>, and other hydro-carbons found
- Suggests some functional groups reacting with H
  - Produces some irreversibility, i.e. hysteresis in desorption
  - Removed by higher temperature degassing
  - Typically the higher the O the more water produced
- Must perform species specific characterization
  - TPD, IR, Raman, neutron scattering, and NMR
  - Define surface species that enhance H diffusion
    - e.g. UM CH<sub>4</sub> and some O<sub>2</sub> increase capacities 15%
      - TiCl and VCl increased sorption rates
    - e.g. NREL: No O surface groups, no spillover (see backup slides)
    - Catalyst connection to receptor also important (see backup slides)



J.L. Figueiredo et al., *Modification of the surface chemistry of activated carbons* Carbon 37 (1999) 1379–1389  
 Jing-Hong Zhou et al, *Characterization of surface oxygen complexes on carbon nanofibers by TPD, XPS and FT-IR* Carbon, 45, (2007), 785-796

**NREL identified potential issues that produce irreversibilities and cause irreproducible hydrogen sorption measurements. Improved understanding of surface functionalization will enhance spillover capacity and sorption rates.**

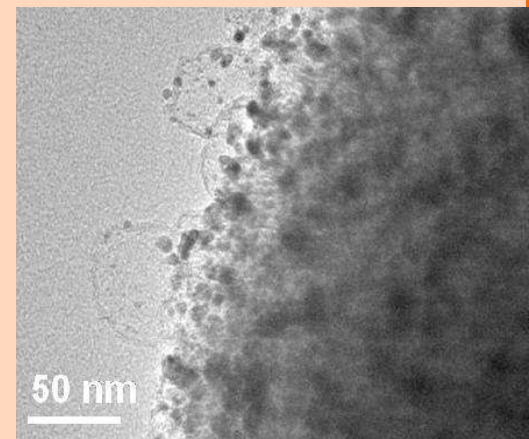
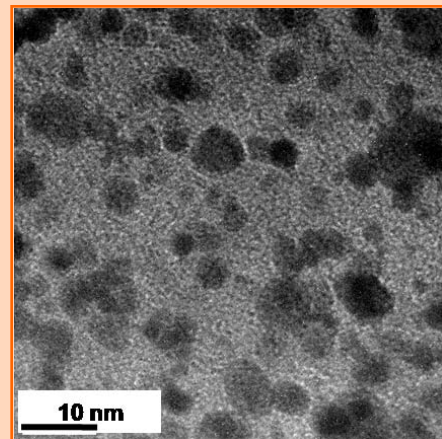
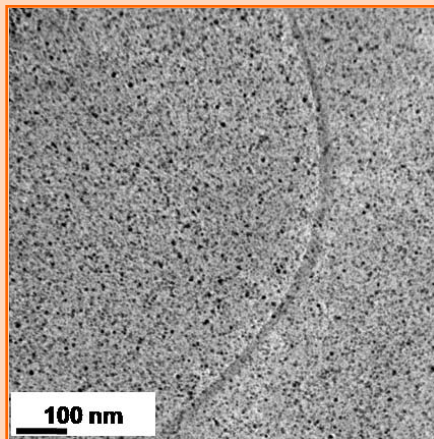
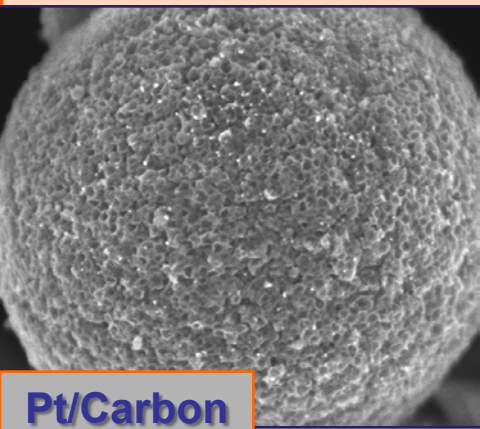




# Accomplishment: Spillover; Receptor Properties

Receptor material surface functionalization very important

- Dopants and functional groups must be adjusted for optimum spillover
- 10% Pt on Nanoporous Silica Templated Carbon from Infused Sucrose
  - **O and/or OH groups of receptor substantially enhances spillover**

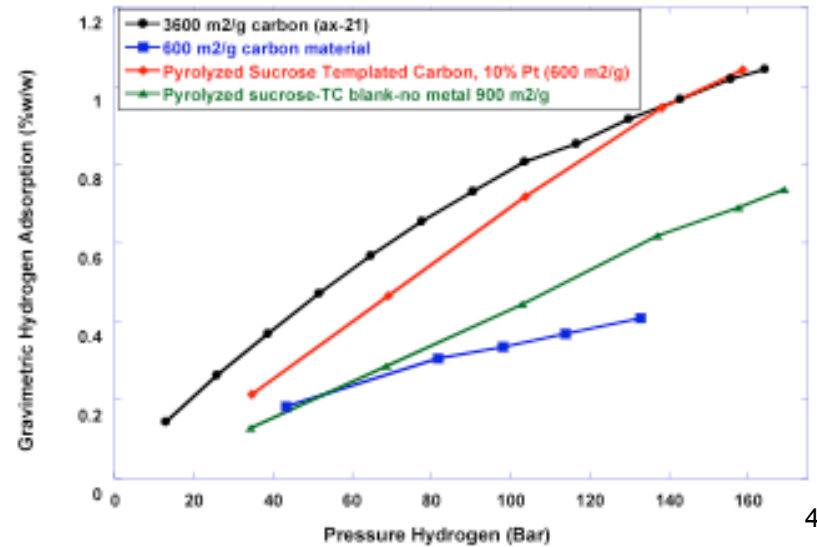


Pt/Carbon  
SEM

600 m<sup>2</sup>/g, Pt content controlled. (10%w/w)

Carbon templated materials from sucrose

- **5x faster than Ru/MSC-30 samples**
- **Larger capacity enhancement (~3x) suggest their may be "hidden" pore structure**
- **Demonstrates unique features of pyrolyzed sucrose that is used for "bridging" to MOFs**
- **May be able to improve more with higher surface areas and improved catalyst processing**

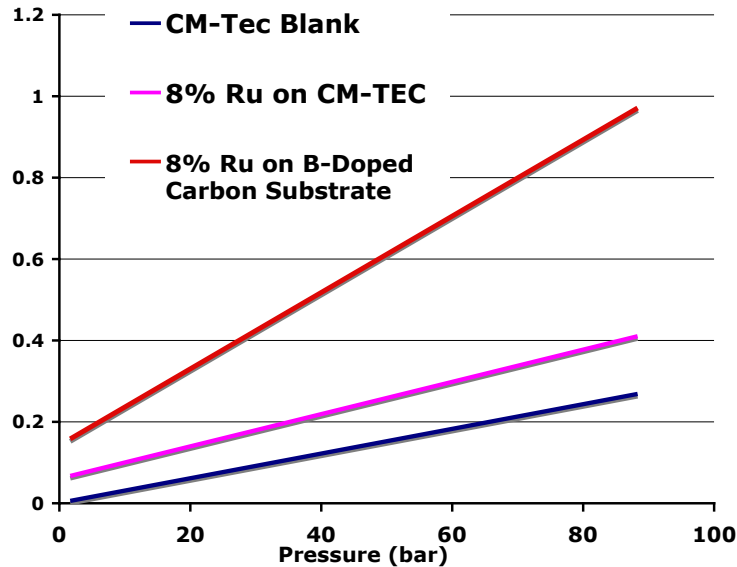
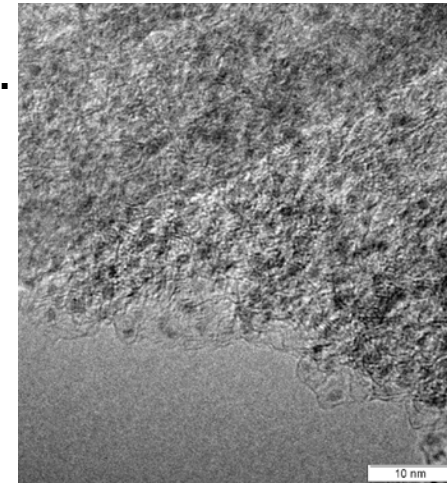


Templated Platinum/Carbon Oxygen Reduction Fuel Cell Electrocatalysts, S. Pylypenko, T. S. Olson, N. J. Carroll, D. N. Petsev and P. Atanassov, J. Phys. Chem C., in press

## Boron Substitution In Carbon Enhances Spillover

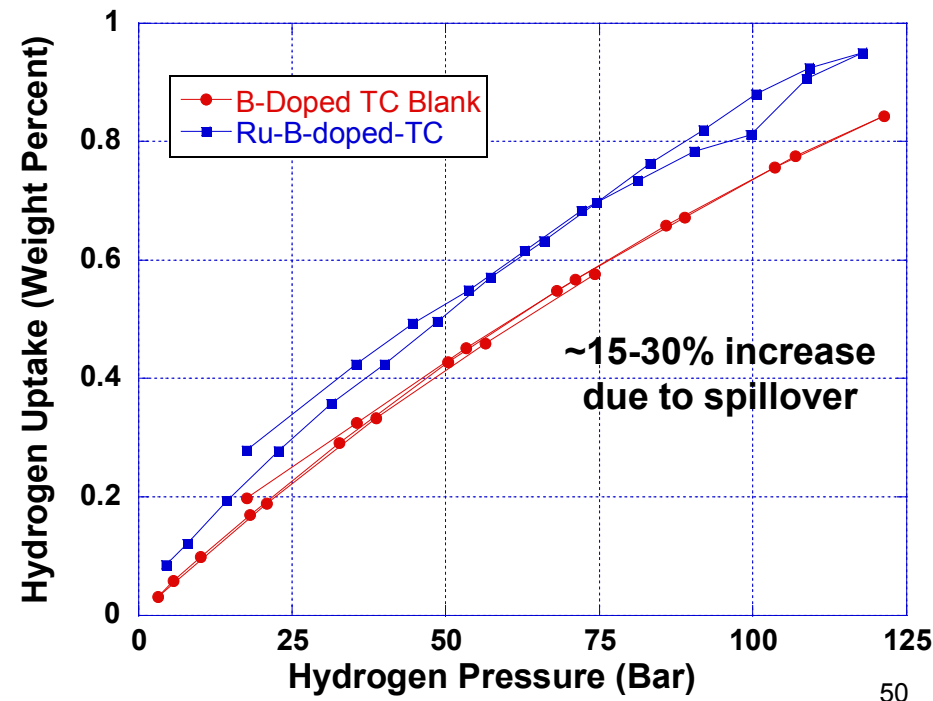
Initially speculated that spillover on BCx Materials at  $\sim 200 \text{ m}^2/\text{g}$  could have  $\sim 1 \text{ wt}\%$  @  $1000 \text{ m}^2/\text{g}$

Synthesized B-substituted carbon coated AX-21,  **$750 \text{ m}^2/\text{g}$** .  $>2 \text{ nm}$  dia., 8 wt% Ruthenium. Transient occurred at every step. Improved kinetics with max adsorption achieved approx 25x faster than similar carbon materials. (10 minutes versus 4-6 hours)



**Demonstrated experimentally in agreement with calculations that BCx materials improves spillover/adsorption**

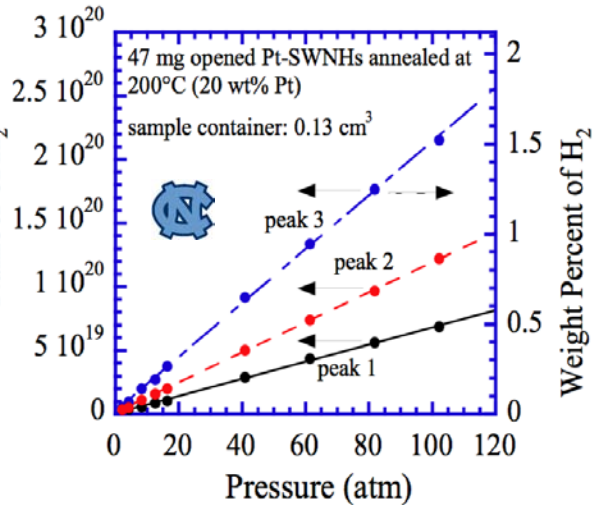
- Rates substantially faster, 10 min. adsorption
- Per SSA,  $\sim 300\%$  higher capacities
- Initial results: direct correlation between capacity and SSA. Must increase SSA.
- Specific processes involved to be determined



# Accomplishment: Spillover; Measurements

## Pt-SWNHs (ORNL) – Spillover and Enhanced Binding Energies

### NMR measurements by UNC



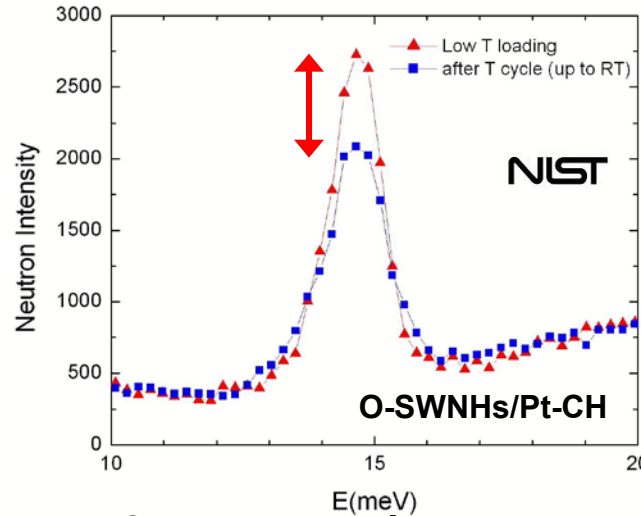
Room temperature adsorption / confinement increases linearly to 1.5 wt% at 100 atm.

**Spillover effects observed with NMR, INS, and TPD.**

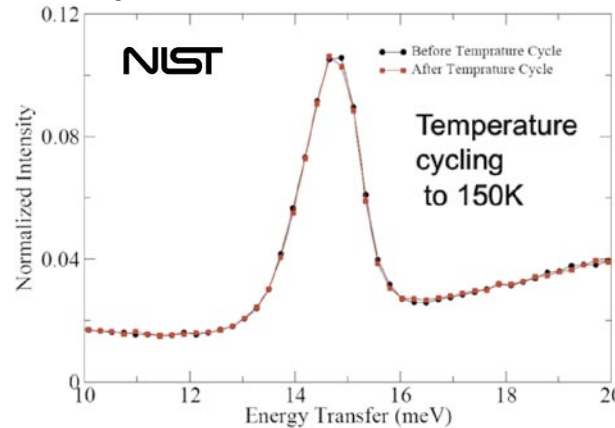
Other Results include:

- Desorption rates meet DOE H<sub>2</sub> delivery rate targets
- Smaller better connected catalysts increase uptake/rate
- Charging rates increased with charging pressures.

### Neutron scattering measurements by NIST

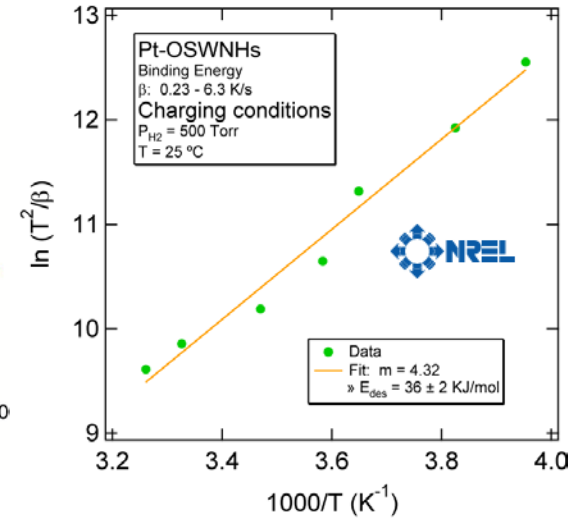


INS Pressure drop → correlates to 0.08 wt% of H<sub>2</sub> spillover at room temperature and ~5 bar

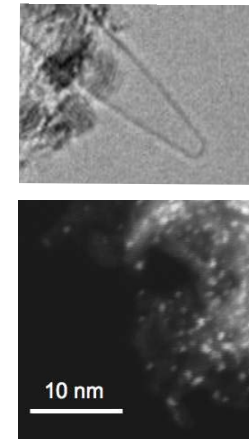


“Spillover” measurements confirm that Pt-decorated SWNHs dissociate H<sub>2</sub> with an onset temperature between 150K < T < 298K.

### Temperature programmed desorption measurements



Kissinger plot shows the desorption barrier energy  
E<sub>des</sub> = 36 ± 2 kJ/mol



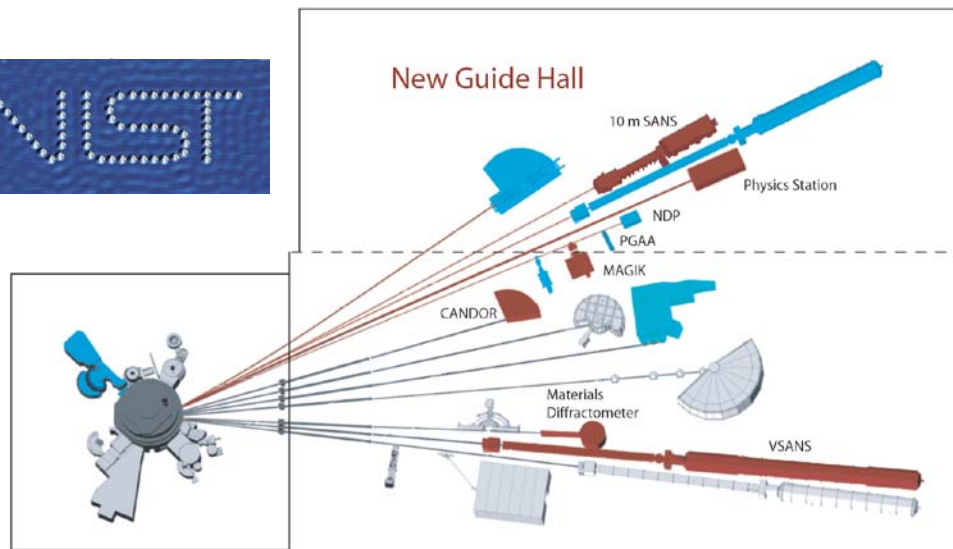
TEMs of “Long” opened SWNHs and Pt-decorated SWNHs. The Pt-SWNHs show RT hydrogen uptake, “spillover”, and increased H<sub>2</sub> binding energy

# Accomplishments: Unique Measurements

- Developed unique measurement capabilities to accurately and reliably characterize hydrogen storage properties.

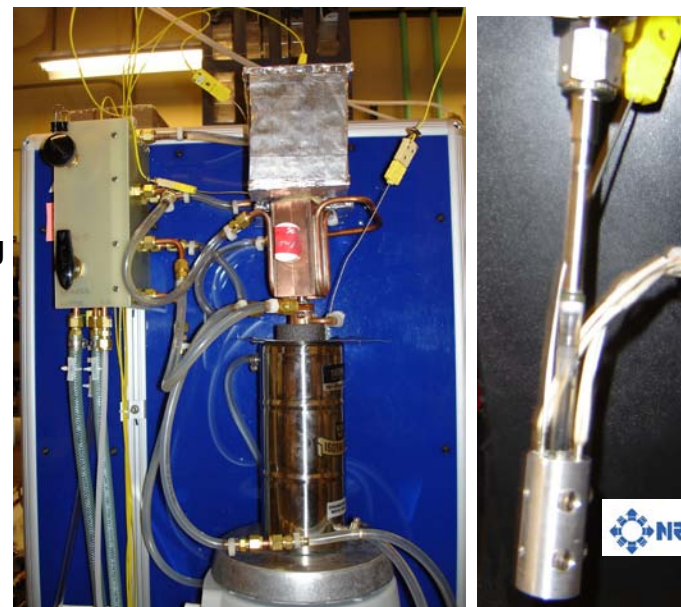
- Neutron Scattering
- High pressure H<sub>2</sub> NMR
- H storage properties with small laboratory scale (1-100 mg) samples

- Enables high throughput and rapid screening analysis
- Accurate H storage property measurements a major problem in the community for decades.
  - Partly due to only having small quantities of “laboratory scale materials” to characterize.
  - Developed protocols and measurements capable of accurate results from small amounts of sample
    - » Substantially enhanced throughput by eliminating need to develop larger scale synthetic methods or repeating synthesis processes numerous times to make enough material.



NIST Center for Neutron Research

**NREL improved the temp. control of sample holders to enable more accurate measurements using external port configurations for higher throughput.**



**Constructed and used unique materials measurements capabilities to accelerate sorbent development.**

# HSCoE Recommendation: Materials

- The Center recommends that development efforts for specific material classes be continued where viable routes exist for synthesizing sorbents that can be used to meet the appropriate set of targets.
  - The specific selection criteria for future efforts should focus on the DOE 2015 and the Ultimate Full-Fleet hydrogen storage targets.
- Numerous Materials Recommended for No Further R&D
- Develop materials for hydrogen storage by weak-chemisorption.
  - **Ambient-temperature storage** via catalytic hydrogen dissociation and transfer to high-specific-surface-area receptor materials (e.g., spillover) demonstrate 10 to 30 kJ/mol reversible hydrogen binding energies, which enable ambient-temperature storage.
  - **Minimizes Thermal Management and reduces overall storage system cost**
  - Need to improve understanding of atomic H transport to increase rates/capacities and enhance reproducibility and durability
  - Weak chemisorption enables ambient temperature storage with systems having more than 75% of the material capacities at moderate (~100 bar) pressures.
- Develop materials for multiple H<sub>2</sub> storage on designated sites.
  - Maybe only route that enables materials to be developed to meet DOE Ultimate System Targets; especially for on-vehicle refueling
  - **Inexpensive material systems identified to meet ultimate targets**
  - Meeting DOE's Ultimate targets will enable hydrogen to become a viable energy carrier for transportation and other important renewable energy applications.
- Develop substituted/heterogeneous materials that have demonstrated hydrogen binding energies in the range 10 – 25 kJ/mol.
  - **Enables near-ambient-temperature (150–250K) hydrogen storage.**
  - These heterogeneous materials also demonstrate substantial stabilization of single-metal centers and other absorbed species that improve hydrogen storage.

# HSCoE Recommendations and Remaining Issues

- Limit development of materials in which the storage mechanism is physisorption to only those with optimized structures.
  - To meet the DOE 2015 targets, the only physisorption materials that should be considered for development are those that can have specific-surface areas greater than **~3,000 m<sup>2</sup>/g**, optimized uniform **pore sizes** in the range of **~0.7 to ~1.5 nm**, and excess material hydrogen storage capacities **greater than 50 g/L and 7 wt% at cryogenic temperatures (~80–200 K)** and moderate pressures (less than 100 bar).
- Remaining Issues
  1. Develop robust, reproducible, and scalable synthetic methods that create materials where all the adsorption sites are accessible to the hydrogen.
  2. Improve computational methods to more accurately predict the ability to synthesize designed materials and the hydrogen storage capacity as a function of temperature and pressure.
  3. Develop a better understanding of atomic hydrogen transport on receptor materials.
  4. Develop a better understanding of metal center coordination and its effect on hydrogen adsorption.
  5. Develop materials in concert with designs for hydrogen storage systems.
  6. Develop Sorbent Material Measurements Standards and Certifications.

# HSCoE Collaborations and Leadership

- Center had 100's of joint projects and >100 joint publications
  - Leveraged unique partner capabilities to accelerated materials development while closely coordinating activities to minimize duplication
  - **Theory actively coordinated** by steering committee and groups to ensure efforts worked closely with experiment to maximize materials development
- **Partners work with > 50 groups around the world**
  - Lead efforts in hydrogen storage measurements and instrumentation
  - Part of IEA and IPHE working groups
  - Worked with DOE, other storage centers, & BES/NSF/DoD projects.
- **Partners organize conferences around the world**
  - e.g. MRS, ECS, APS, ACS
- Published **100's of papers** and gave **100's of presentations**

- **Actively managed unique partner capabilities and overall resources to accelerate hydrogen storage materials development.**
- **Hundreds of collaborative interactions that are openly discussed, evaluated, and redirected during face-to-face and other meetings.**
- **Instrumental in accelerating hydrogen storage materials development; as seen by huge surge in publications and technical conference participation.**

# Future Hydrogen Sorbent Development Efforts

- Write Center Final Report (Complete by end of FY2010)
  - Partner contributions to report collected and draft report should be available in June 2010 for review
  - Work with partners to get data base populated
- **Continue working the the sorbent community to develop new materials**
  - **Continue to characterize and qualify sorbents with unique capabilities developed by the Center**
    - e.g. NREL will continue performing measurements on small laboratory scale samples to help characterize materials and validate measurements
  - **Develop Sorbents Working Group**
    - Help replace some of the benefits of working in close collaboration with partners in the Center
- **Support the Hydrogen Storage Engineering Center of Excellence (HSECoE)**
  - Work with HSECoE to select potential materials and provide their intrinsic hydrogen storage properties needed for system engineering design, analysis, and perhaps demonstration.
    - Sorbent materials approach DOE 2010 targets: In general, sorbents meet almost all of the DOE hydrogen storage targets.
    - Sorbents may greatly improve volumetric capacities, and the HSCoE has developed several materials that may meet DOE's 2010 (and possibly the 2015) onboard refueling targets.

More Details in Back-up slides and in partner presentations.



# Back-up Slides

# DOE HSCoE Accomplishments Summary

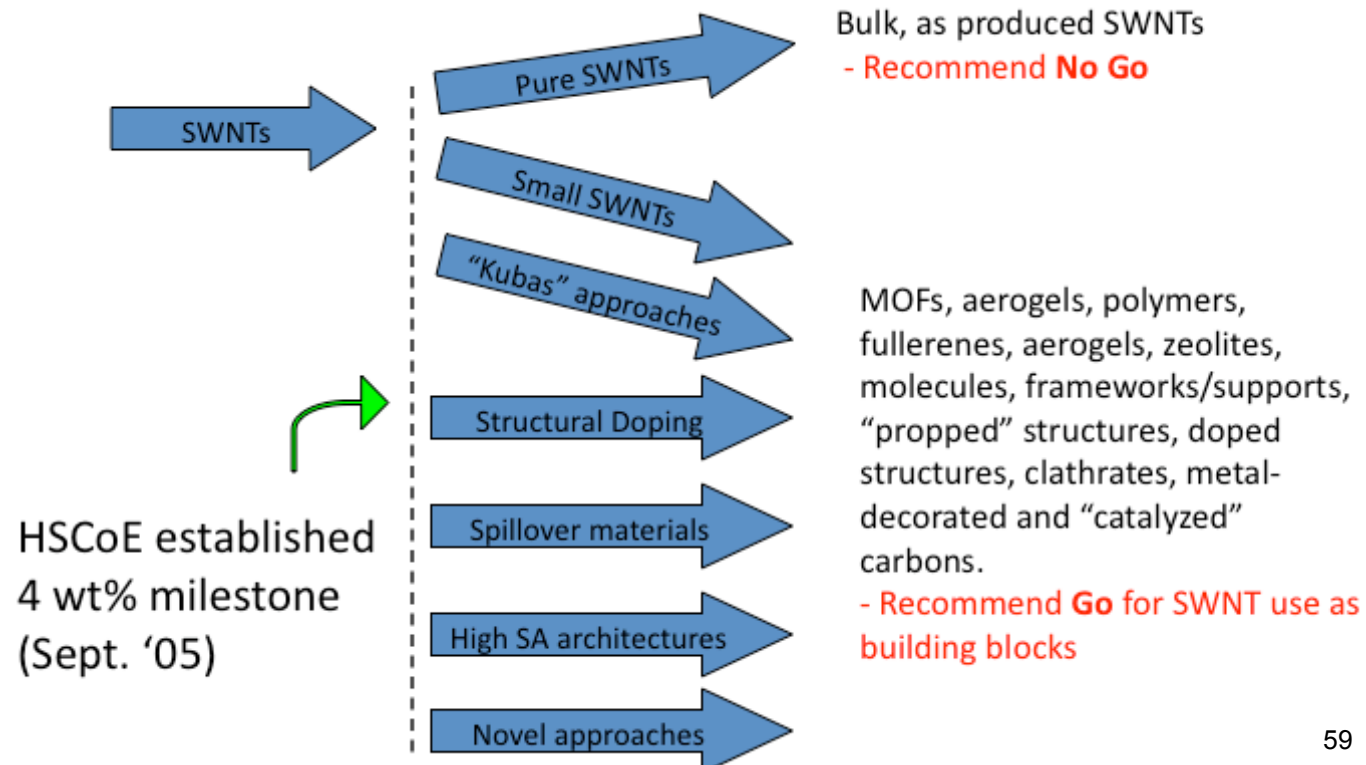
1. The Center discovered and demonstrated coordinated, unsaturated metal centers as a new class of hydrogen storage materials that could meet DOE targets. Several systems have been demonstrated and specific synthetic paths based on known materials have been identified.
2. Designed and developed reversible high capacity sorbents via ambient temperature hydrogenation techniques that demonstrated over 4 wt% storage capacities.
3. Developed new materials that increased the gravimetric (~40%, e.g. from ~5 to >7 wt % at 77K) and volumetric (~150%, e.g. from ~15 to >35 g/L at 77K) hydrogen storage by physisorption onto high specific surface area (SAA) sorbents by optimizing pore sizes (0.7 to 1.5 nm) to increase SAA and packing density.
4. Designed and developed substitutional materials with enhanced dihydrogen binding energy to increase capacities at near ambient temperatures, on a per specific surface area basis.
5. The Center developed unique measurement capabilities to accurately and reliably characterize hydrogen storage properties of small laboratory scale (1-100 mg) samples to enhance high throughput and rapid screening analysis (Isotherms, specific surface area, pore size distribution, isosteric heats of adsorption, temperature programmed desorption, nuclear magnetic resonance).
6. The Center has confirmed that standard physisorption based dihydrogen adsorption scales with specific surface area. To date, no validated experimental evidence exists that any substantial capacity enhancements occurs due to “special” geometric configurations.

# Accomplishment: Optimized Sites; Go/No-Go Carbon Nanotubes

At the outset of the Center, numerous publications had reported extraordinary results for carbon nanotubes where the enhanced capacities were potentially a result of novel geometries or structures.

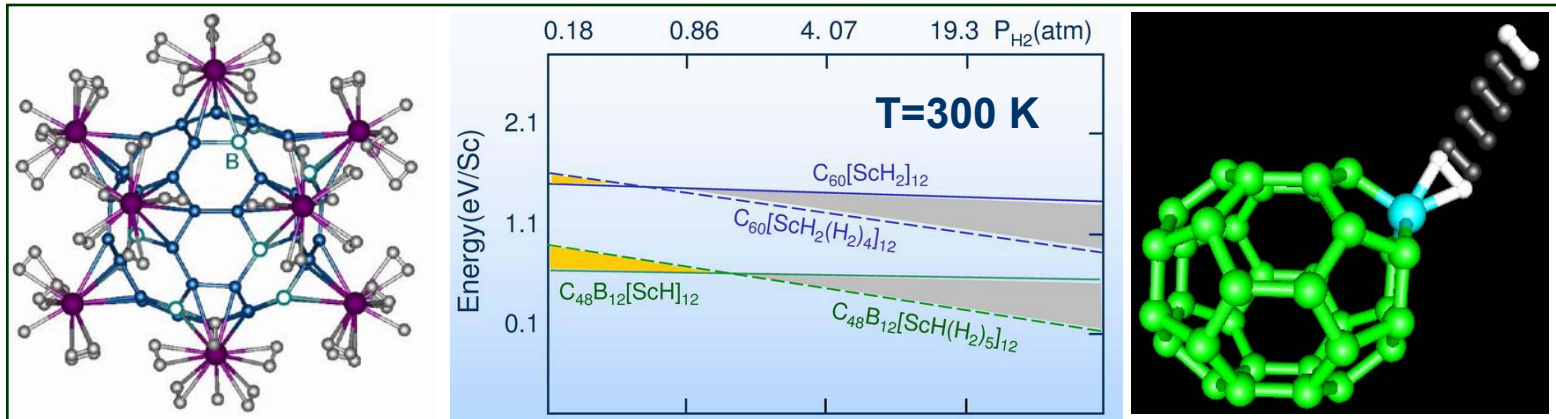
- The Center did not validate any single element material or any materials with unexceptional electronic states including carbon nanotubes that have substantially higher hydrogen storage capacities beyond what is expected based on the specific surface area and specific storage conditions
  - Recommended “No Go” for work on pure SWNT to meet room temperature 6 wt% goal.
  - Recommended “Go” for nanotubes under other storage conditions
  - **With these recommendations, the Center reallocated resources to develop other sorbents**

In general, no high specific surface area material that uses only pure physisorption binding identified to date will be able to meet DOE capacity targets at ambient temperature. However, they may still meet DOE capacity targets at lower temperatures (e.g. 50 K)

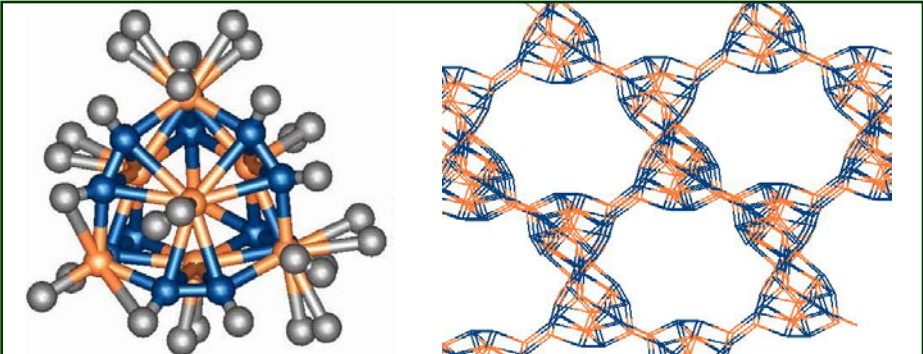


# Accomplishment: Strong/Multiple Binding; Key Results Since the Center Started

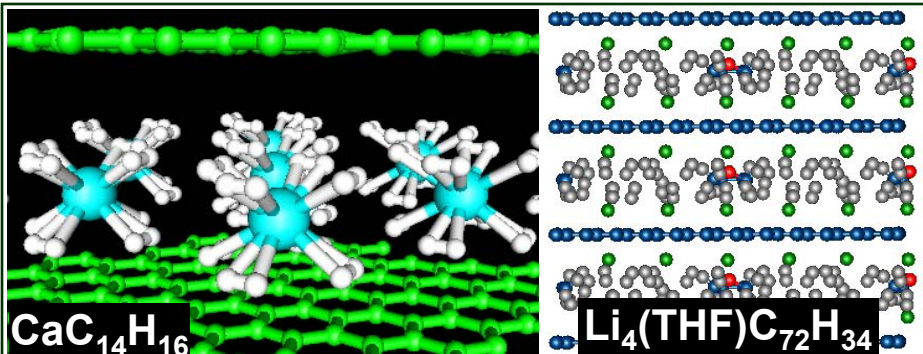
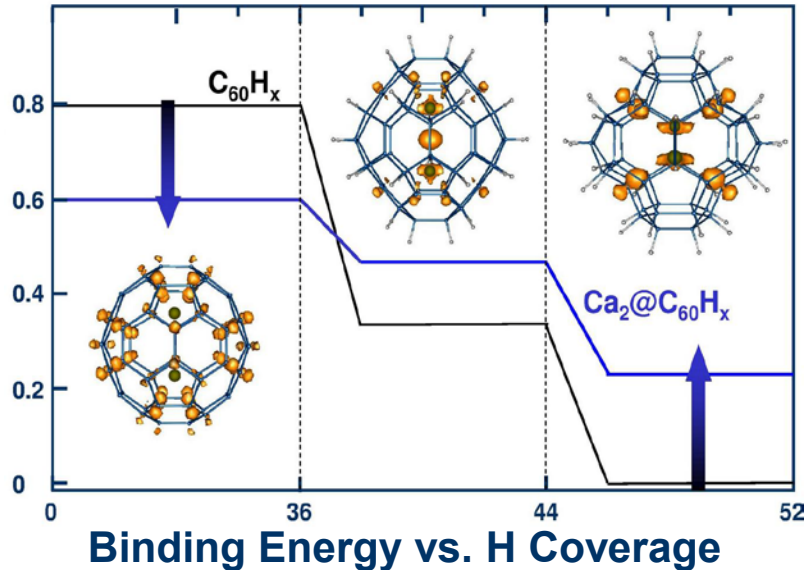
1. Propose the concept of Strong Binding



2. Test the concept in MetCar.



3. Tune binding of atomic H with metal.



4. Enhanced  $H_2$  binding with simple metal.

# Accomplishment: Strong/Multiple Binding; M- Intercalation Compounds

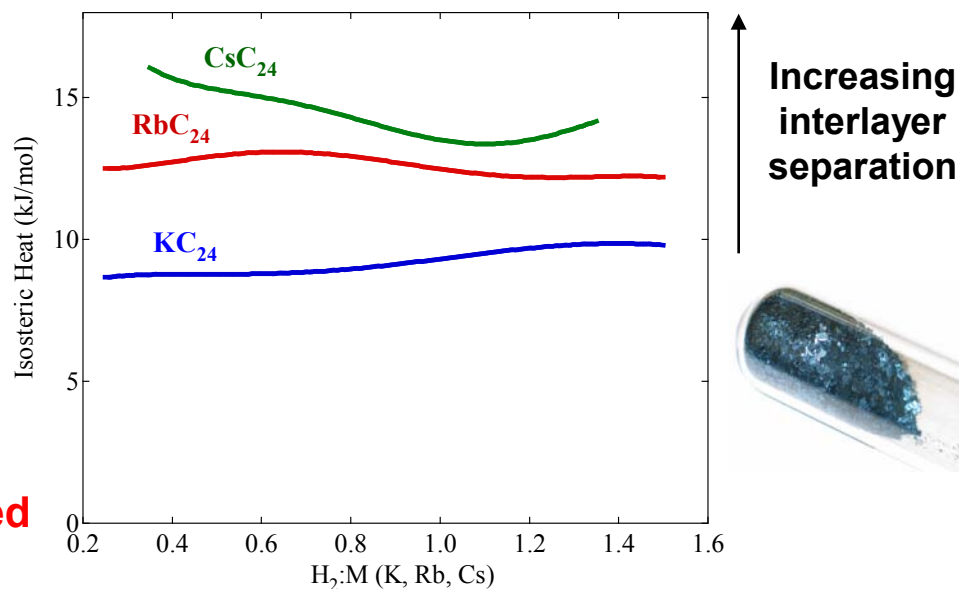
## Problem

- Graphene slit-pore structure **not stable**
- Need a “spacer molecule” to prop open layers

## Strategy

- Vapor-phase intercalation of alkali-metal (AM) atoms between graphite layers
- Nomenclature: “Graphite intercalation compounds”
- Pore-width controlled by size of AM atom
- Confirmed the presence of three H<sub>2</sub> adsorption sites in KC<sub>24</sub> graphite intercalated compound via neutron scattering.**
- Measured hydrogen binding enthalpies as high as 14.9 kJ/mol for CsC<sub>24</sub>.**
- The interlayer H<sub>2</sub> adsorption in the graphite intercalation compounds was reversible at low temperatures (< 150 K) and H<sub>2</sub> reacted chemically at higher temperatures (~195 K).**

Graphite Intercalation Compounds	Isosteric Heat <sub>ave</sub> (kJ/mol)	Adsorption <sub>max</sub> (77 K, wt%)
KC <sub>24</sub> (H <sub>2</sub> ) <sub>x</sub>	9.2	1.24
RbC <sub>24</sub> (H <sub>2</sub> ) <sub>x</sub>	12.6	1.03
CsC <sub>24</sub> (H <sub>2</sub> ) <sub>x</sub>	14.9	0.85

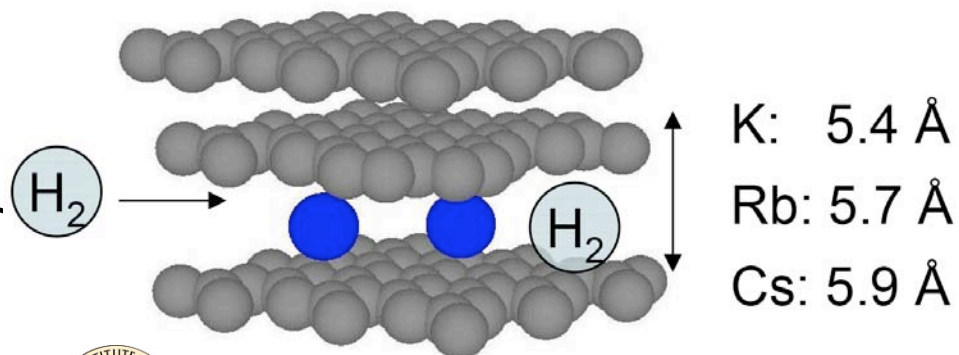


- Correlation between interlayer spacing and H<sub>2</sub> adsorption enthalpy
- H<sub>2</sub> adsorption reversible at low temperatures (< 150 K); H<sub>2</sub> reacted chemically at higher temperatures (~195 K).

# Accomplishments: Materials Down-Selections

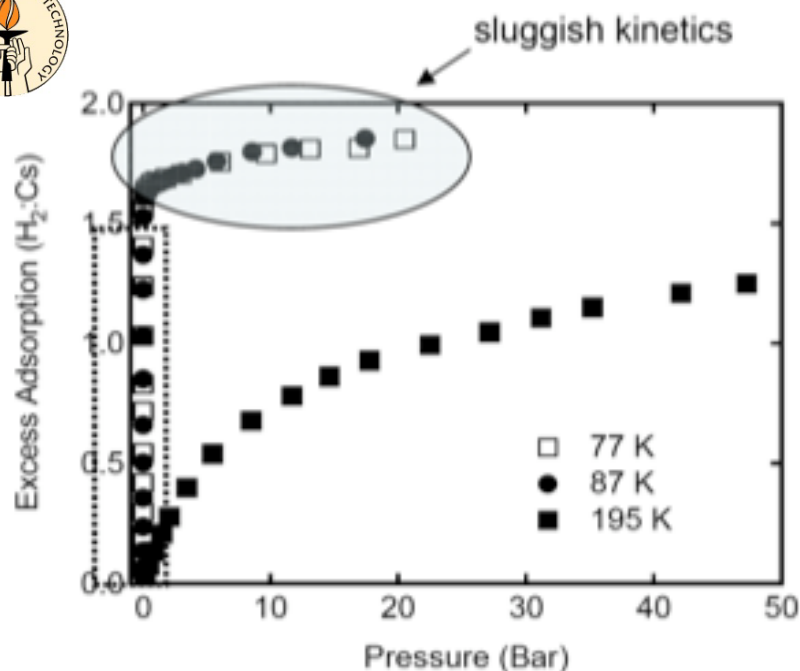
## • Materials Down-Selections

- Performed hundreds of systematic investigations, in which the ultimate conclusion for dozens of specific materials and/or processes were that they should not be investigated further for vehicular hydrogen storage applications.



## • Example of down-select

- Multiple wall enhanced binding, e.g. K, Cs and Rb intercalated graphene
  - Provides good model systems for studying effects of higher binding and very small pores, but will never have the capacity
    - See backup slides



**Identification of paths, processes, and/or materials that should no longer be investigated provides DOE and the hydrogen storage community with valuable information that can be used to better define and identify future efforts.**

# Accomplishment: Spillover; Catalyst Integration with Carbon

**Pt catalyst deposited with drop wise integration of H<sub>2</sub>PtCl<sub>6</sub> solution with AX-21 in acetone**

- **Catalysts must be ~2 nm diameter and uniformly distributed**

- e.g. J. Phys. Chem. Lett. 2010, 1, 1060–1063

- **Requires very slow integration of catalysts**

- **Faster integration decreases spillover capacities**

- **Catalyst activation critical to spillover**

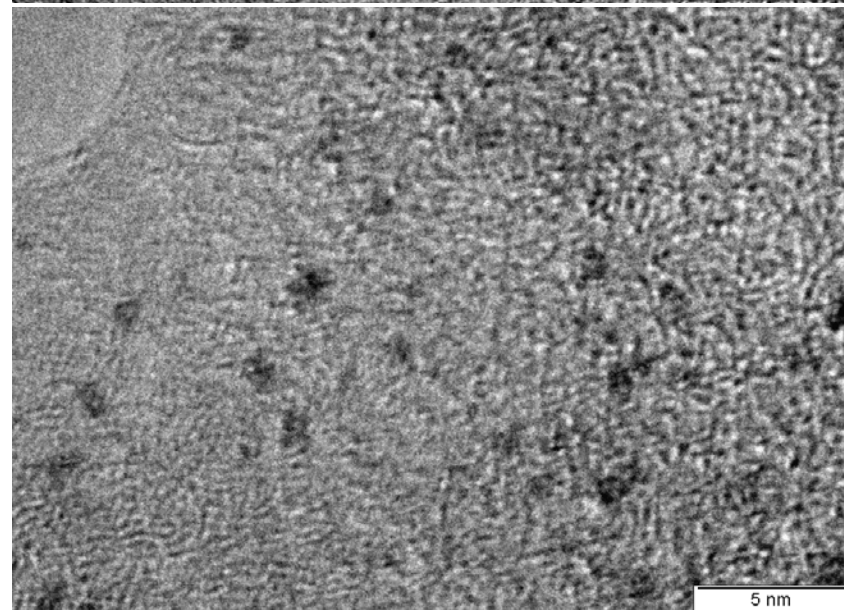
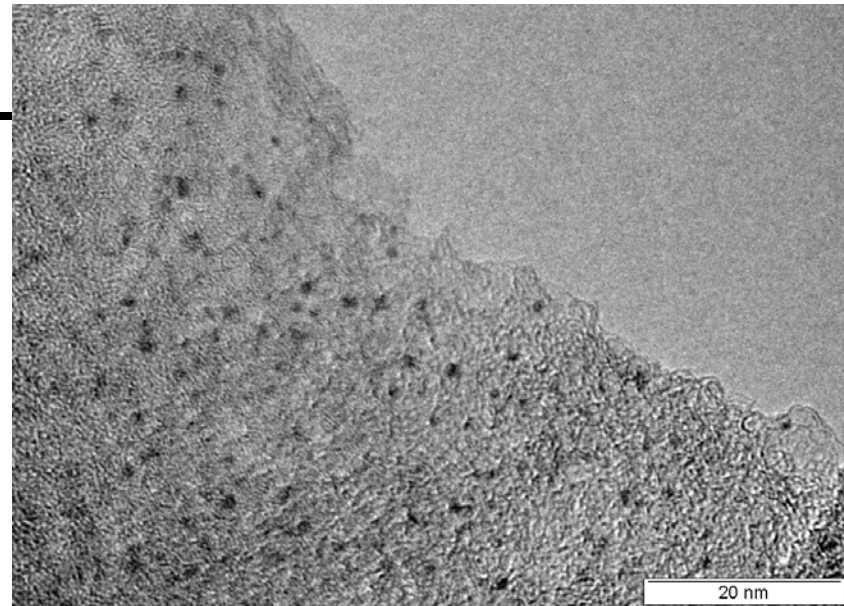
- e.g. J. Phys. Chem. Lett. 2010, 1, 1060–1063

- **High hydrogen activation or degassing temperatures creates catalyst clusters that decrease spillover**

- **Pt/AX-21 spillover enhancements observed at SwRI<sup>®</sup> and NREL**

- **Reproducibility issues related to synthetic processes**

- **see backup slides**

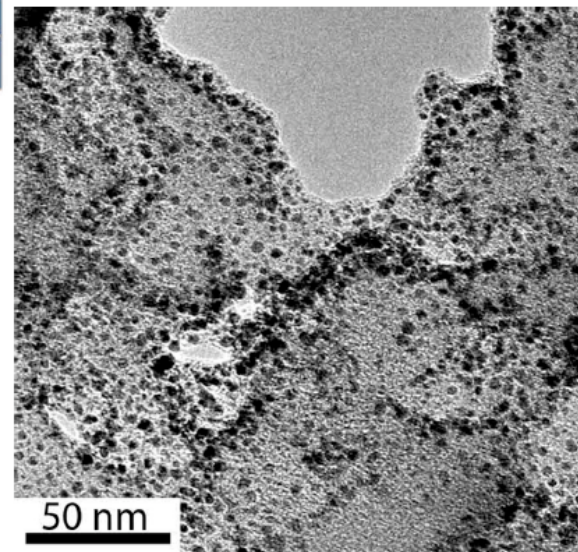


*TEM of 1-2 nm diameter Pt nanoparticles deposited on MSC-30 showing even dispersion.*

# Accomplishment: Spillover Catalysts; Catalyst Deposition

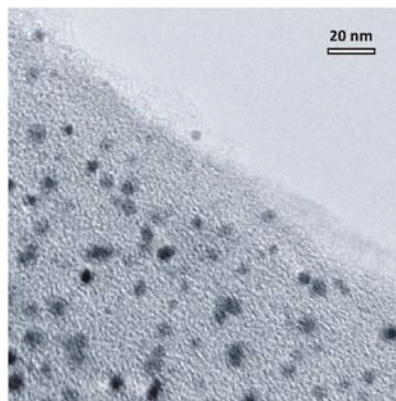
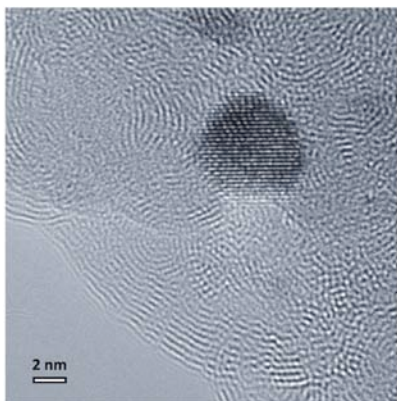
Different processes used to deposit catalysts on different materials

- e.g. atomic layer deposition (ALD) resulted in catalytically-active Pt nanoparticles on high surface area carbon aerogel supports<sup>1</sup>
  - Uniform particles size necessary but not sufficient
  - Uniform distribution may be needed over all surfaces, not just on outside of receptor particles
    - Depth of penetration suggest that this ALD process did not provide as uniform a distribution as possible of catalysts
    - Larger ALD precursors may have difficulty getting into the smaller pores
- Rapid integration (5 min.) using solution chemistry results in catalysts that may be too large and not in all the pores
- None of the materials demonstrated spillover

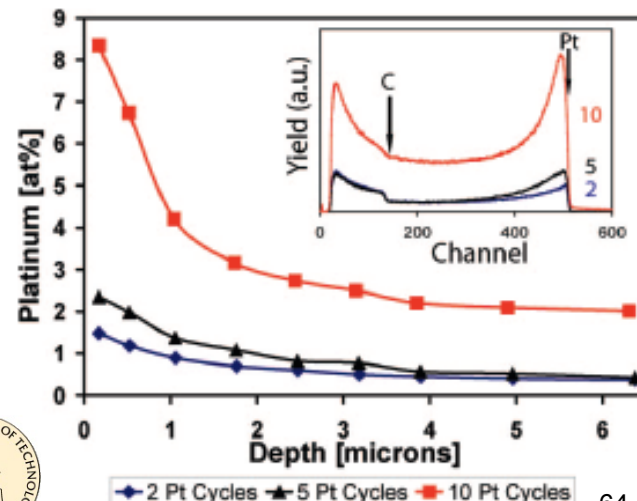


ALD deposited Pt nanoparticles on carbon aerogels.

<sup>1</sup>Nano Lett., 2008, 8(8), 2405-9.



Pt nanoparticles deposited on MSC-30 using solution processes produced 6 to 10 nm diameter particles, instead of the desired ~2 nm.





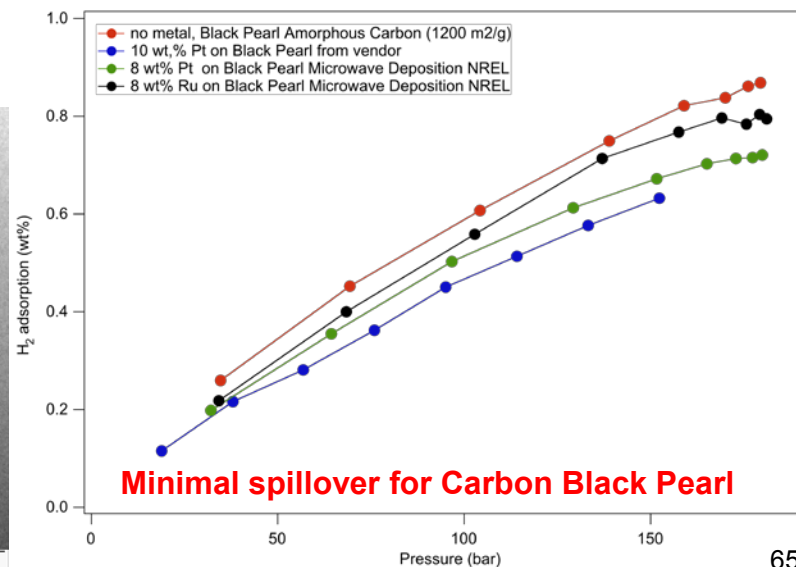
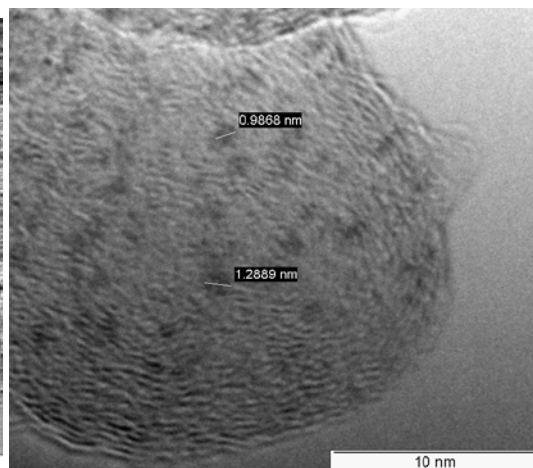
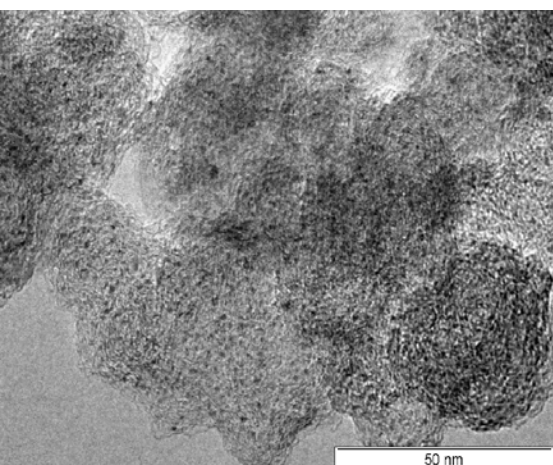
# Accomplishment: Spillover; Receptor Properties Carbon Black



Receptor material surface functionalization very important

- Dopants and functional groups must be adjusted for optimum spillover
- **Demonstrated that receptor oxygen groups are important for spillover**
  - Ru particle dispersion on 1200 m<sup>2</sup>/g amorphous carbon black
  - While all indications are good that catalyst integration was done appropriately, no significant amount of spillover was detected with Carbon Black.
    - This may be due to the complete lack of oxygen groups associated with this material

**TEMs showing appropriate catalyst size and dispersion on Carbon Black Pearl materials. This material has no oxygen surface groups.**

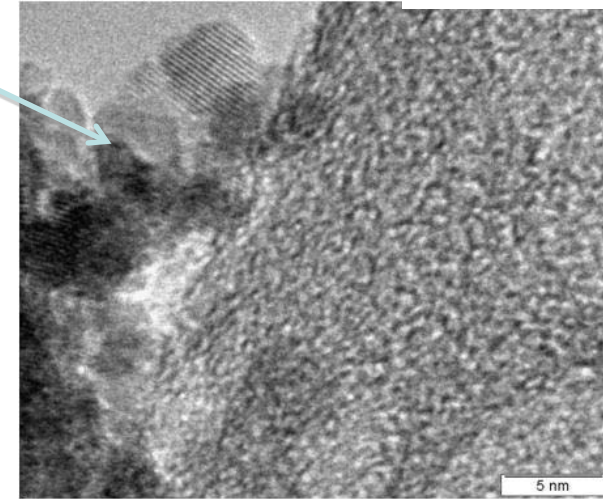


# Accomplishment: Spillover; Catalyst-Receptor Interface

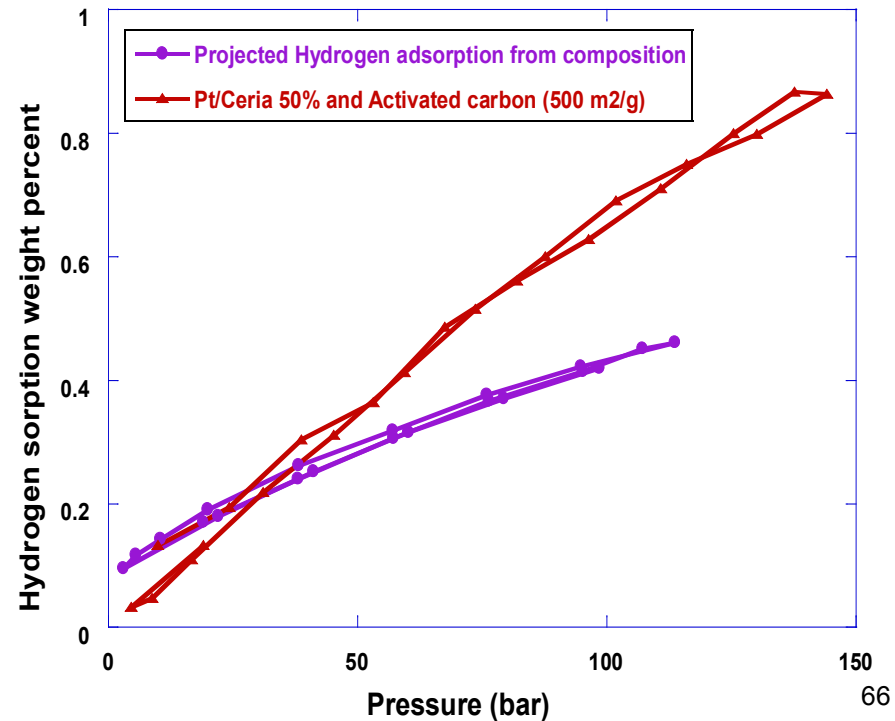
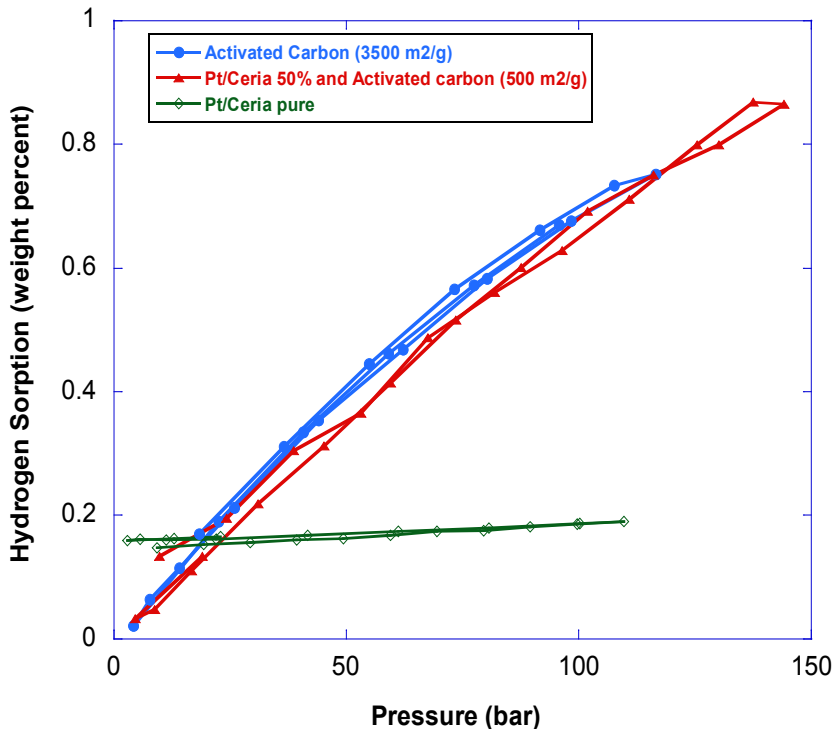
## Pt-Ceria Core Shell 5nm particles on AX-21



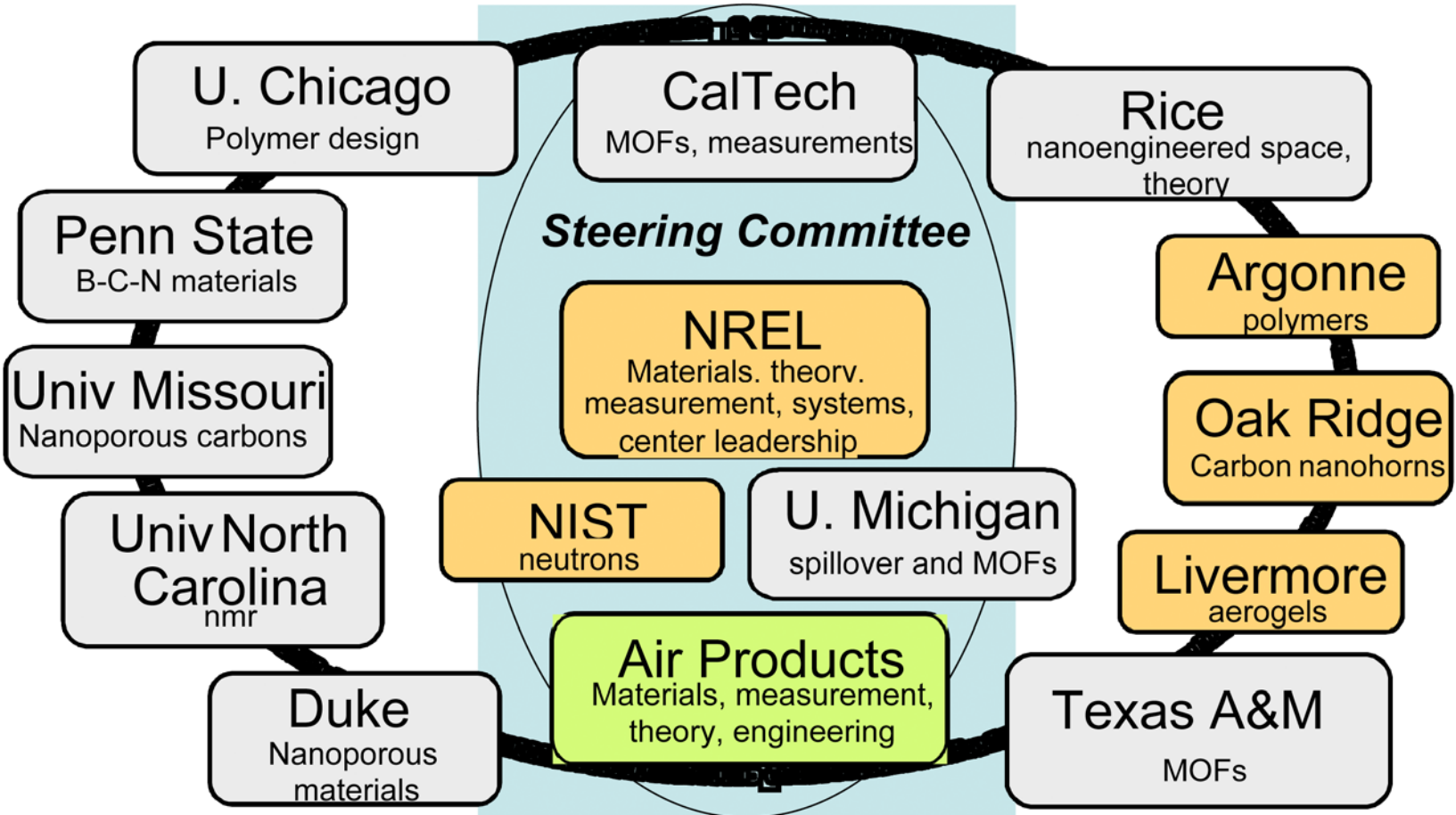
Typically, the isolated core-shell nanoparticles were on the order of 3 – 5 nanometers. The hydrogen sorption properties of the resultant materials were evaluated via low to high pressure volumetric adsorption at room temperature from 1 – 140 bar. Representative TEM Images of Pt/Ceria via microemulsion technique. (Dark areas contain platinum nanoparticles)



- **The total gravimetric hydrogen adsorption is almost double that expected from the mixture if there was no synergistic/catalytic effect.**
- **Improving the catalyst/receptor interface via integration with Ceria appears to enhance spillover.**



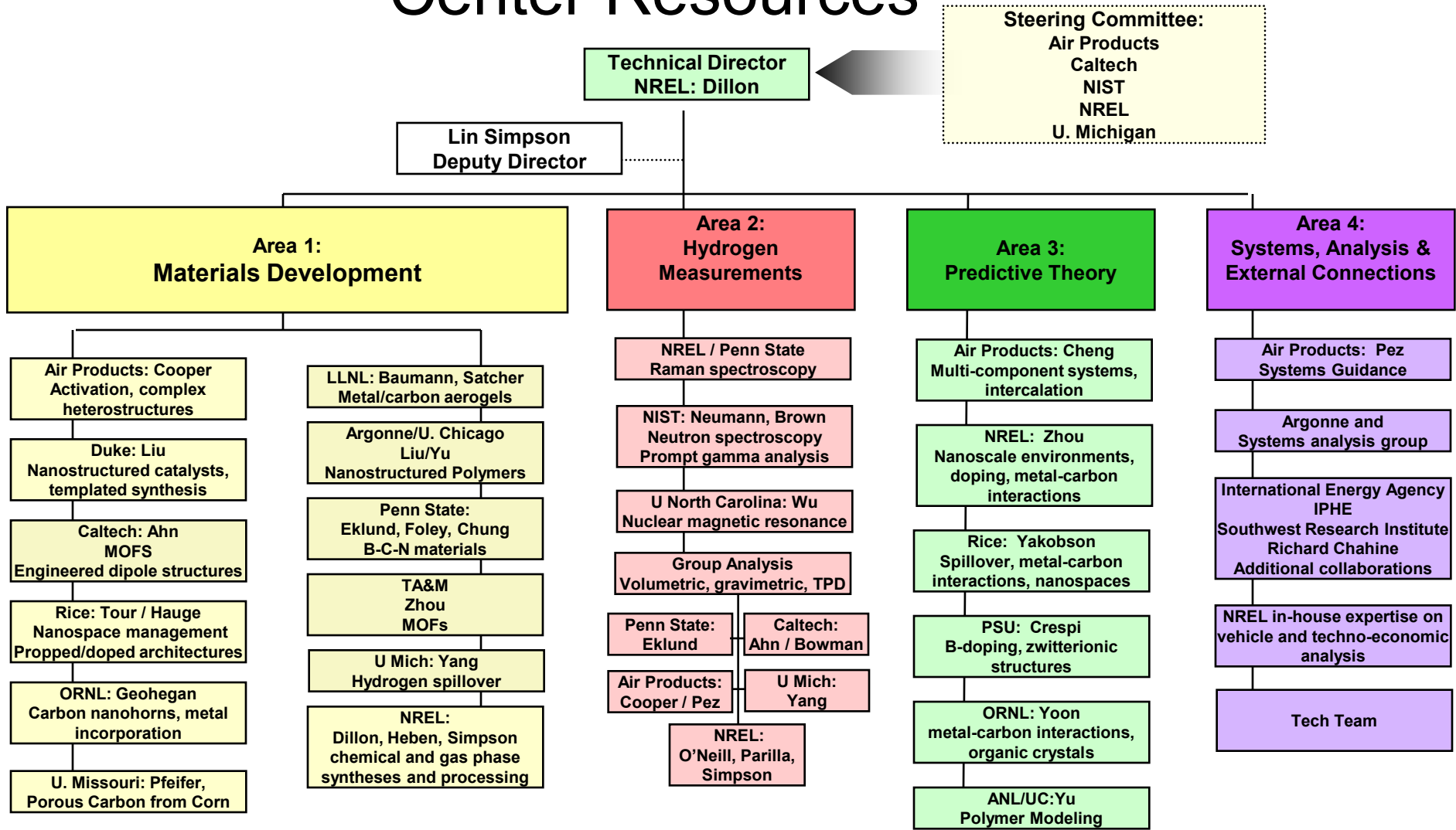
# DOE Hydrogen Sorption CoE



□ University      □ Industry      □ Federal Lab

*9 universities, 5 government labs, 1 industrial partner*

# Center Resources

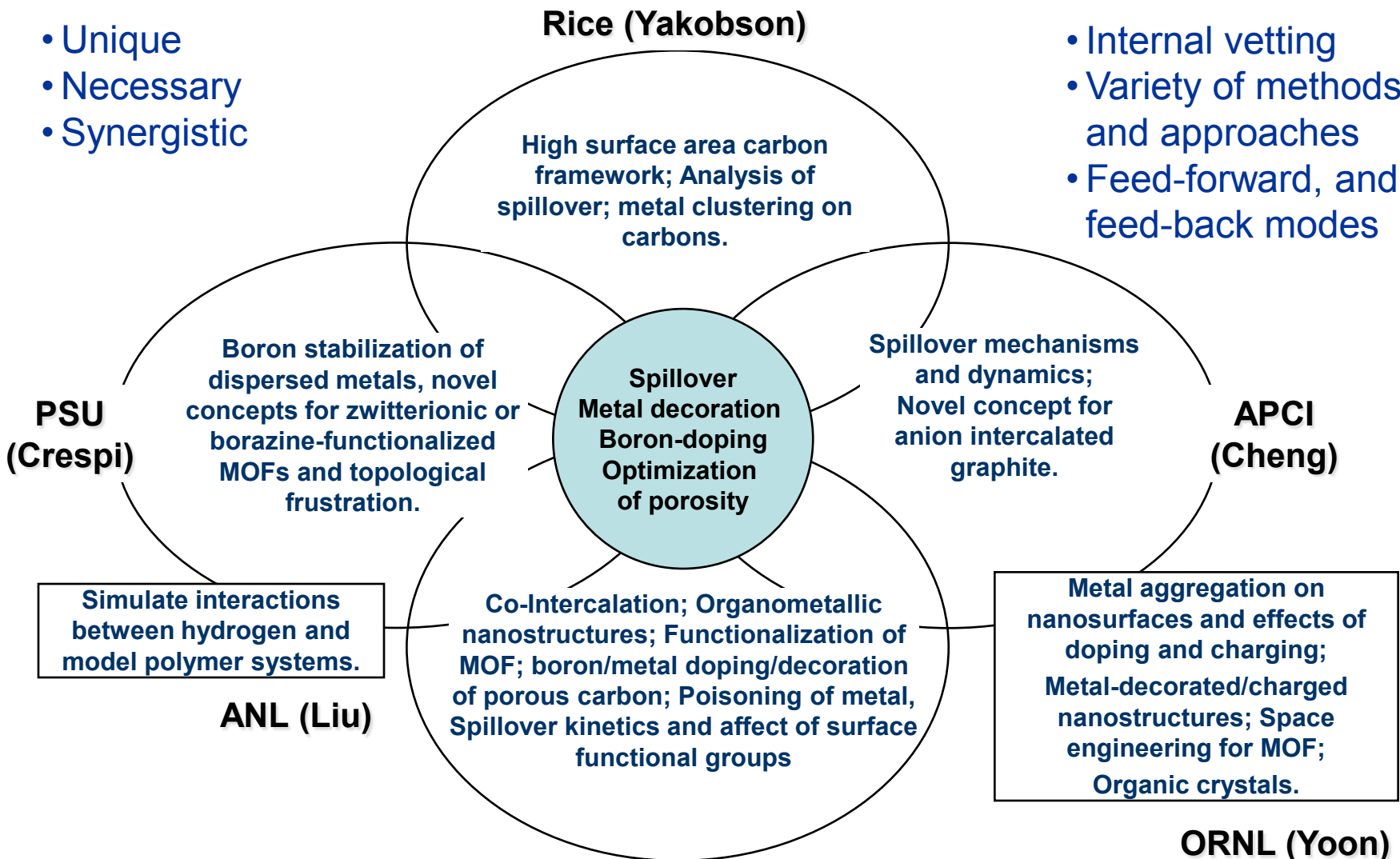


- Level of effort in Materials >> Measurements > Theory (~4:~1.5:~1)
- No significant effort in producing 1 kg system in agreement with new DOE goals

# Theory is Coordinated Across the RCs

- Unique
- Necessary
- Synergistic

- Internal vetting
- Variety of methods and approaches
- Feed-forward, and feed-back modes



NREL/CoE Theory Coordinator: Zhao

# Down Select Criteria for Each RC

## Down-Select Criteria for Engineered Nanospace:

1. The material's gravimetric storage capacity should be approximately 0.03 kgH<sub>2</sub>/kg with a volumetric storage capacity of approximately 0.03 kg H<sub>2</sub>/L with a possible temperature range of 77 - 200 K and a pressure range of 30 - 100 bar, with a *clear potential* for further improvement.
2. The high-pressure adsorption isotherm should be >80% reversible, i.e., at least 80% of the stored hydrogen is desorbed or discharged between 77 - 200 K, at nominal fuel cell operating pressures.
3. The desorption or discharge rate at 77 - 200 K should meet or be within 90% of the DOE discharge rate target of 0.02 g/s/kW.
4. The charge rate at 77 - 200 K should meet or be within 90% of the DOE target of 3 minutes for 5 kg H<sub>2</sub>.
5. Material cost projections should be <0.5 system cost targets

## Down-select Criteria for Substitution:

1. The initial binding energy should be in the range of 10-25 kJ/mol, and the material should operate within a temperature range of 77 - 353 K and pressure range of 30 - 100 bar. There should be a *clear potential* for gravimetric and volumetric capacity optimization.
2. The high-pressure adsorption isotherm should be >80% reversible, i.e., at least 80% of the stored hydrogen is desorbed or discharged between 77 - 353 K, for nominal fuel cell operating pressures.
3. The desorption or discharge rate at 77 - 353 K should meet or be within 90% of the DOE discharge rate target of 0.02 g/s/kW.
4. The charge rate at 77 - 353 K should meet or be within 90% of the DOE target of 3 minutes for 5 kg H<sub>2</sub>.
5. Material cost projections should be <0.5 system cost targets

## Down-select Criteria for Strong Binding:

1. The initial binding energy should be in the range of 10-25 kJ/mol, and the material should operate within a temperature range of 77 - 353 K and pressure range of 30 - 100 bar. There should be a *clear potential* for gravimetric and volumetric capacity optimization.
2. The high-pressure adsorption isotherm should be >80% reversible, i.e., at least 80% of the stored hydrogen is desorbed or discharged between 77 - 353 K, for nominal fuel cell operating pressures.
3. The desorption or discharge rate at 77 - 353 K should meet or be within 90% of the DOE discharge rate target of 0.02 g/s/kW.
4. The charge rate at 77 - 353 K should meet or be within 90% of the DOE target of 3 minutes for 5 kg H<sub>2</sub>.
5. Materials cost projections should be <0.75 system cost targets

## Down-select Criteria for Spillover:

1. The material's gravimetric storage capacity should be approximately 0.01 kgH<sub>2</sub>/kg with a volumetric storage capacity of approximately 0.01 kg H<sub>2</sub>/L with a possible temperature range between 298 - 353 K at 100 bar, with a *clear potential* for further improvement.
2. The high-pressure adsorption isotherm should be >80% reversible, i.e., at least 80% of the stored hydrogen is desorbed or discharged with a temperature that does not exceed 353 K, for a nominal fuel cell operating pressure.
3. The desorption or discharge rate at 298 - 353 K should meet or be within 80% of the DOE discharge rate target of 0.02 g/s/kW.
4. The charge rate at 298 - 353 K should not exceed 10 hours for a full charge of 5 kg H<sub>2</sub>.
5. Materials cost projections should be <0.75 system cost targets