Overview of the DOE Hydrogen Sorption Center of Excellence

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ST15

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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:	60%

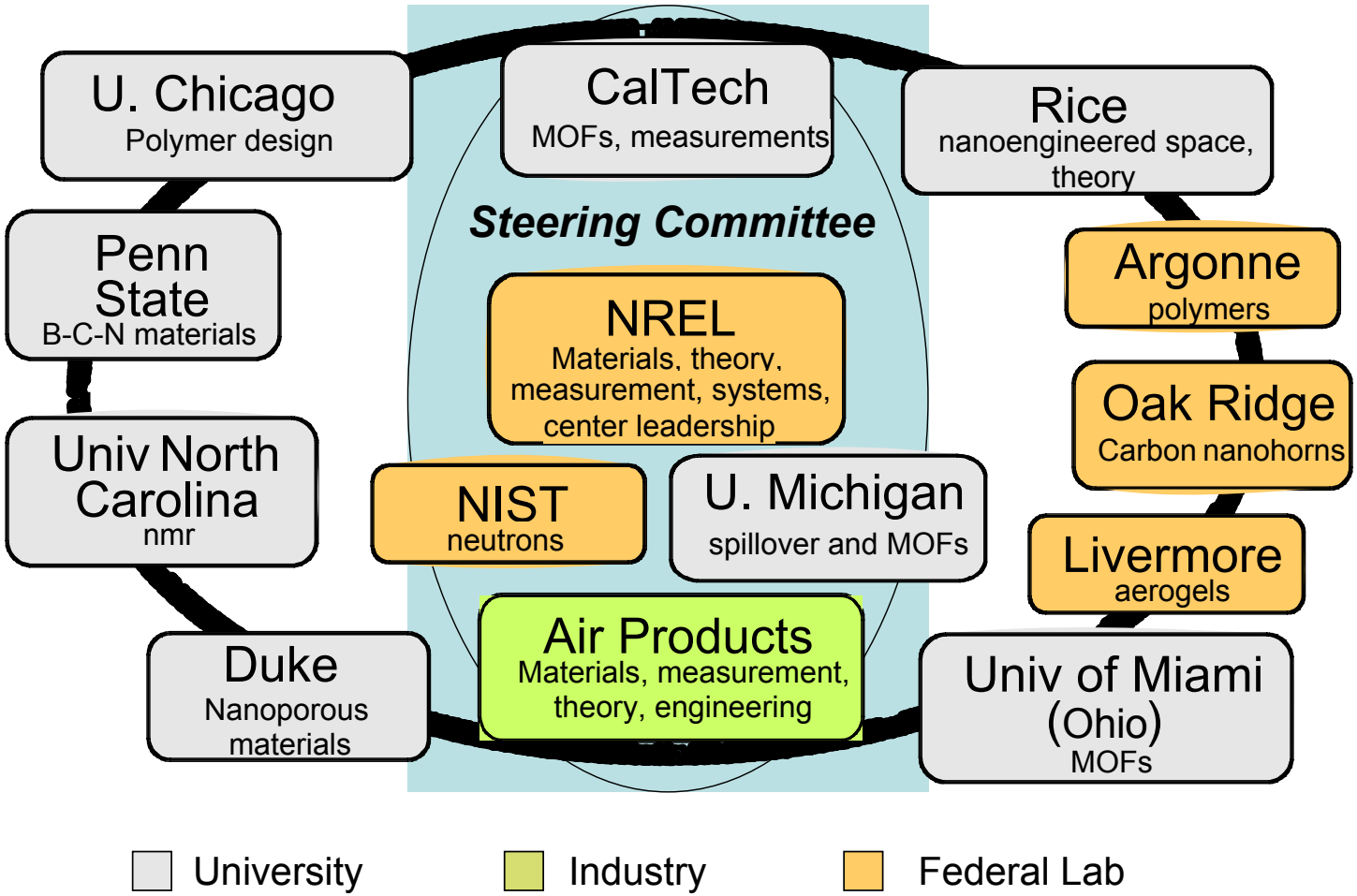
Budget: Center Management - $350K

Partners: 8 universities, 5 government labs, 1 company

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

DOE Hydrogen Sorption CoE

Steering Committee was reformulated in July 2007 to reflect new focus



8 universities, 5 government labs, 1 industrial partner

Objectives

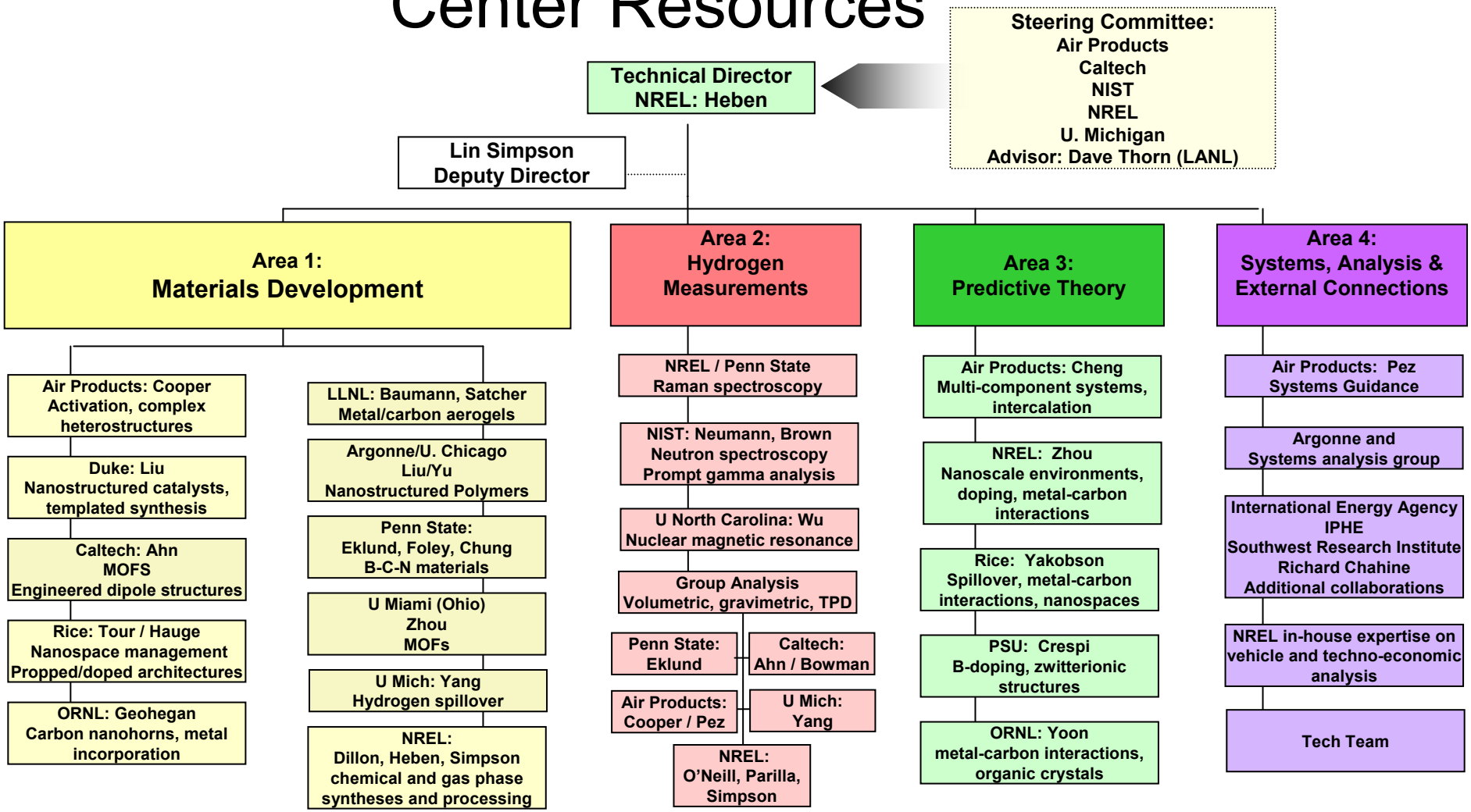
Discover and develop high-capacity sorbent materials that can operate at ambient temperatures and be efficiently and quickly charged on-board with minimum energy requirements and minimum penalties to the hydrogen fuel infrastructure. Overcome barriers to 2010 DOE system goals and identify pathways to meet 2015 goals.

- Develop materials which utilize mechanisms that bind H with an optimal energy for room temperature operation (15 - 20 kJ/mol H_2).
- Rapidly correlate capacity, structural, and energetic information to reduce time between discovery, assessment, and down-select.
- Integrate experiment and theory seamlessly in both “feed back” (explanation) and “feed-forward” (discovery) modes.
- Devise facile synthetic routes using low cost approaches.
- Create a nimble, flexible yet structured, teaming environment to accelerate discovery, evaluation, and selection of promising development directions.

DOE 2010 Technical Targets for Storage System

- Gravimetric 0.06 kg H_2/kg
- Volumetric 0.045 kg H_2/L

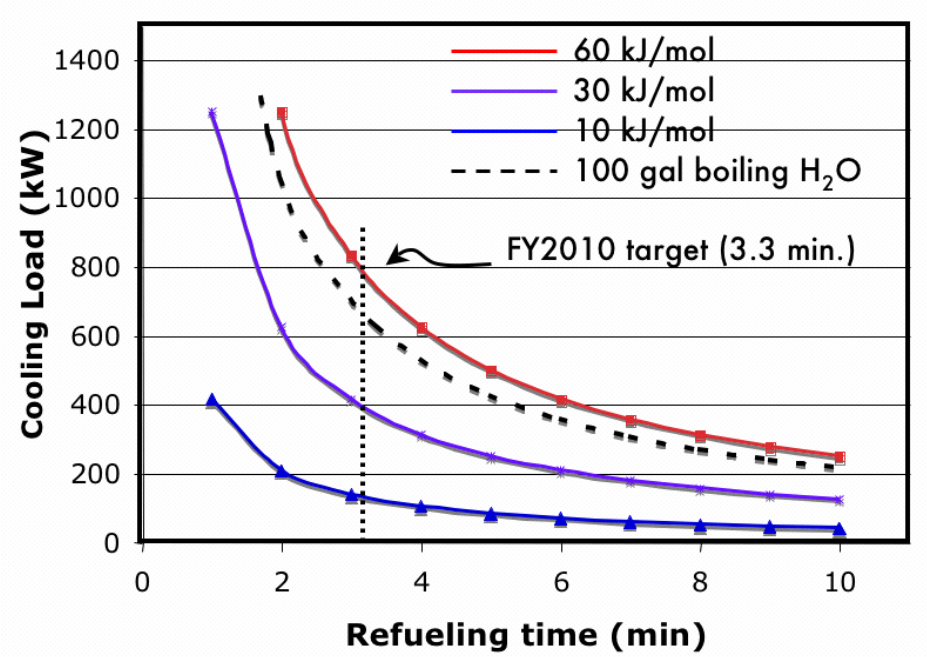
Center Resources



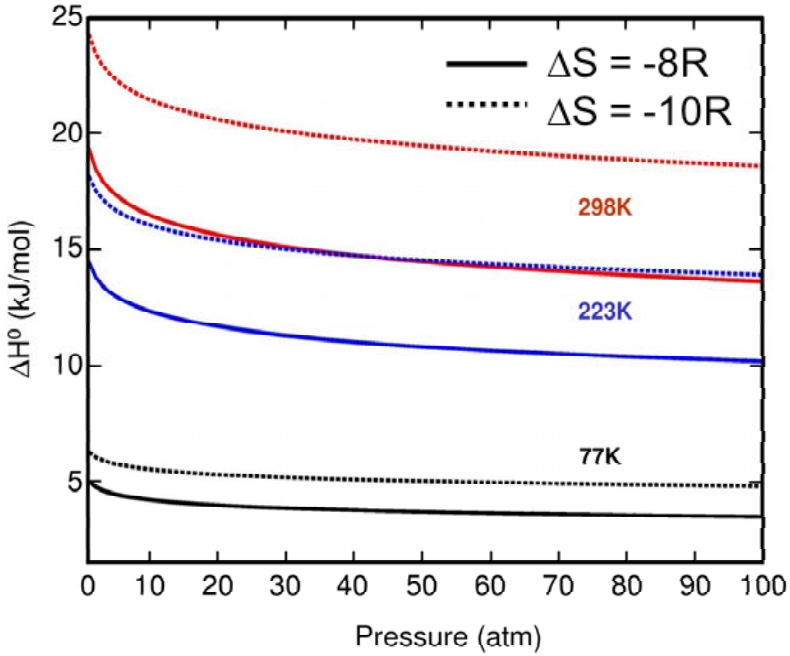
- Level of effort in Materials >> Measurements > Theory (~4:~1.5 :~1)
- No significant effort in producing 1 kg system in agreement with new DOE goals

Importance of the Enthalpy for RT Operation

Heat removal challenge



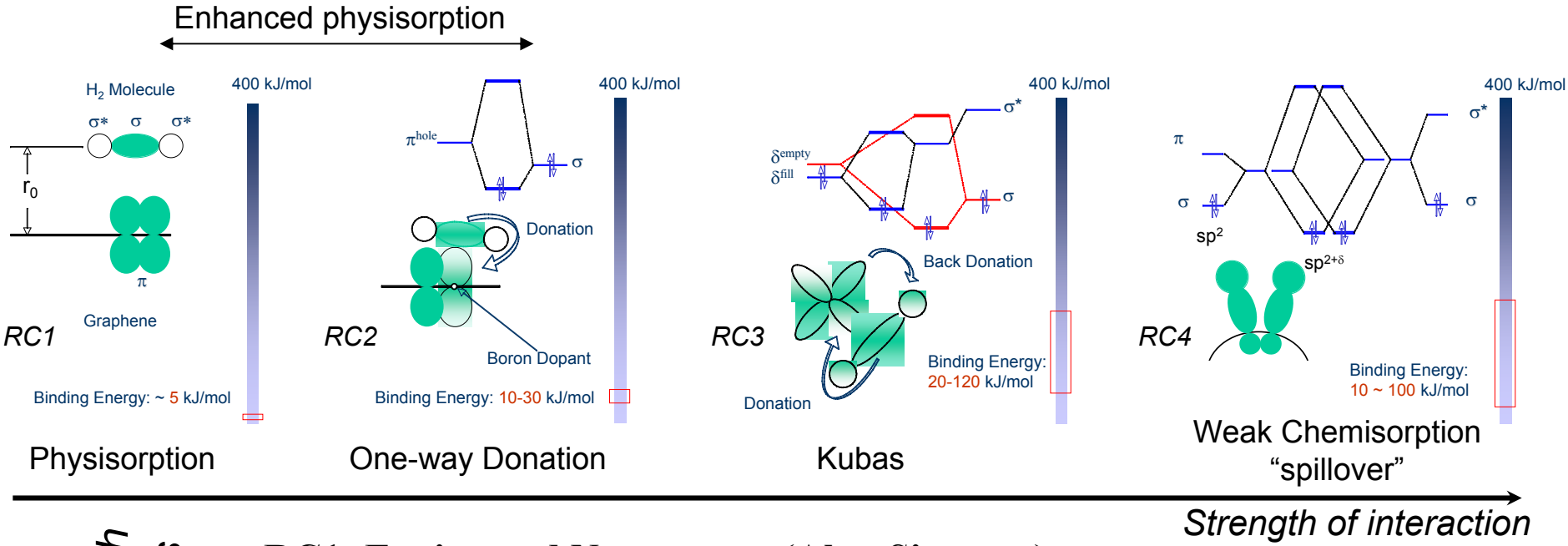
Optimal enthalpy to maximize delivered hydrogen



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

- Heat removal with loading 5 kg of H_2 adversely impacts system capacities (heat exchangers) and refueling rates.
- The enthalpy should be the absolute minimum required to store the hydrogen.
- Sorbent materials offer the highest round trip (charge/discharge) energy efficiencies.
- High efficiencies are necessary for any technology to be viable.

Mechanisms Define the Research Clusters



Research Clusters

- **RC1: Engineered Nanospaces (Ahn, Simpson)**
- **RC2: Doped Materials (Cooper, Blackburn/Heben)**
- **RC3: Strong Binding of Dihydrogen (Brown/Neumann, Dillon)**
- **RC4: Spillover (Yang, Parilla)**

- RCs are co-led by senior NREL staff and SC members
- "Roadmaps" stand-alone, but roll-up to address DOE's MYRDDP
- Group expertise, create focus around central challenges, permit "separation of variables" approach to this complex problem
- Advances in individual RCs are additive and can be combined
- Partners have Primary home in one Cluster, but collaborate with other clusters.

see partner homes in back-up slides

Example Roadmap: Doped Materials (RC2)

Roadmaps have been developed with input from Partners, DOE, and the Tech Team, and bring structure and quantitative short-term goals to the RC-level (*work in progress*).

Present R&D Activities and Portfolio

Near Term R&D

- Increase isolated B content beyond 10%. Quantify limits of N-doping.
- Investigate methods to build "off" these scaffolds (e.g. "naked" fluoride)
- Show clear evidence, benefit, and interplay between doping and H_2 binding
- Utilize advances in RC1 to produce and stabilize high SSA structures
- Feed materials into RC3 & 4

2010 Milestones

- Materials for testing that meet 2010 targets
- Go/No-Go for doped materials as stand-alone sorbents relative to 2010 goals
- Plans to meet 2015 targets with RC2 materials
- Role-up of RC2 concepts and materials for use in other and new approaches

Go:

- Provide materials (g's) for validation and engineering evaluations
- Identify viable development efforts to meet 2015 targets

No-Go:

- Propose resource reallocation in proposal for follow-on work.

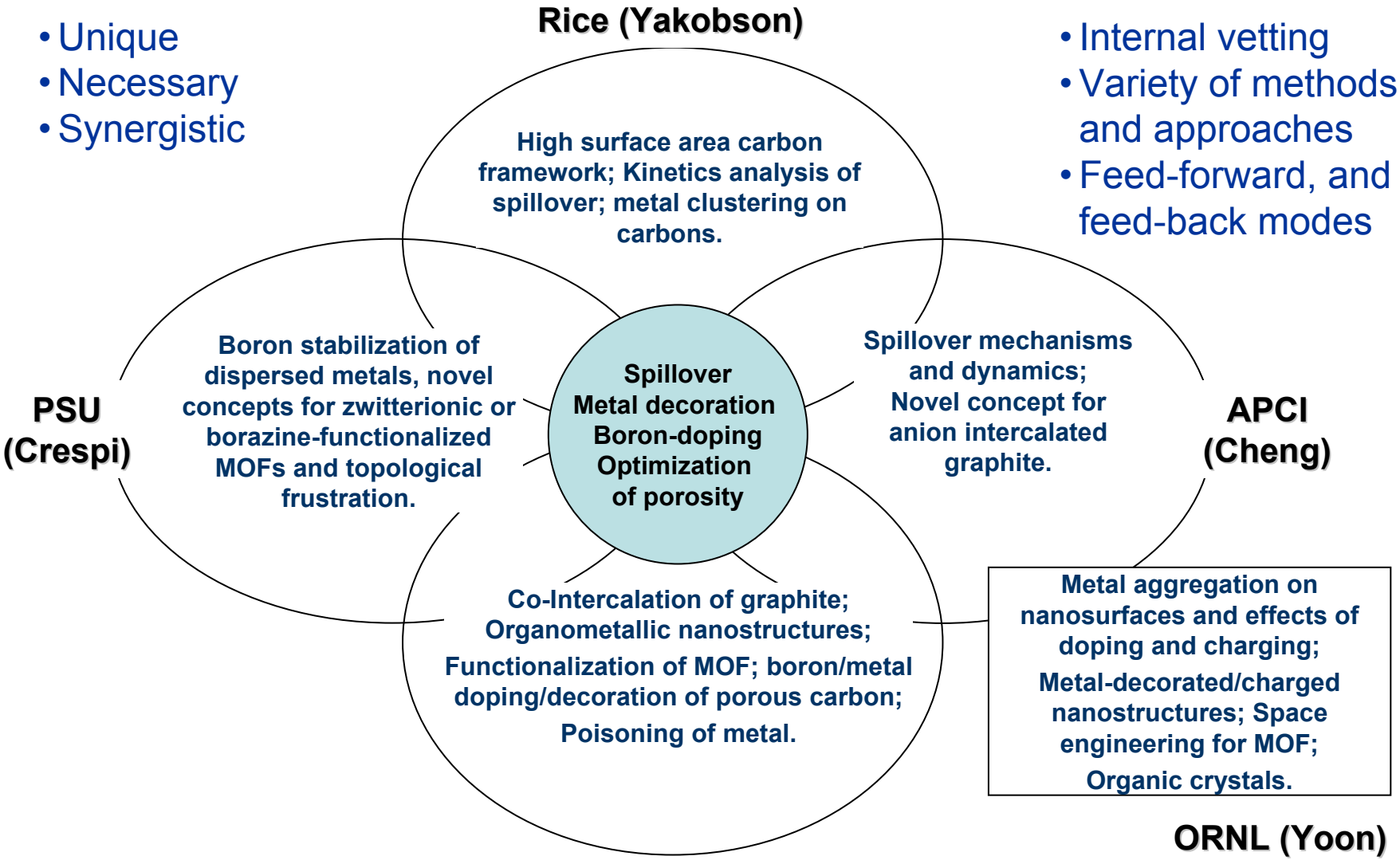
Output at CoE's five year point

- Ranked portfolio of doped materials that can or cannot meet 2015 targets with low, med, high probability.
- What parts of RC2 should be retained and what parts should be jettisoned. Does RC2 retain an identity, or will its concepts be folded into another existing or new Roadmap?
- Recommendations for follow-on work.
- Identify expertise and capabilities needed for next generation of doped materials efforts.
- Specify clear engineering routes for development of materials that can meet DOE 2015 targets, including possible opportunities for integration with Kubas, spillover, and nanospace development --> new Roadmaps.

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

Example Activity in RC2 (Doped Materials)

Motivation: Enhanced H_2 binding energy w/ boron

C-B-H_2 theory (NREL, PSU)

Materials Synthesis

B-doped materials:
pyrolysis of B-containing polymers (PSU)
laser and arc synthesis (NREL, PSU)

Measurement & Characterization

Small volumetric & TPD - NREL

Volumetric - PSU

NMR - UNC

Prompt Gamma
NIST

High Accuracy
Volumetric - APCI

Progress?

yes

no

Clusters focus and accelerate efforts to, e.g., synthesize materials with higher SSA and higher boron content, for improved hydrogen storage.

Examples of Down-selection, Redirection of Resources

Duke (Liu): RC1

- Work on small diameter nanotubes phased-out
- New project focuses on synthesizing high surface area materials through templating and sol-gel routes.

NREL (Dillon): RC3

- Chemical synthesis work on Fe:C_{60} is being wrapped up
- New directions focus on more tractable routes to stabilizing multiple dihydrogen ligands on solid supports.

Rice (Tour): RC1

- Expertise developed for functionalizing nanotubes being applied to building propped structures from much cheaper materials (graphite).

Spillover (Yang, *et al.*): RC4

- Many new resources, Center-wide, have been brought to bear
- Concentrating on reproducibility of processing, kinetics, increasing capacities, etc.

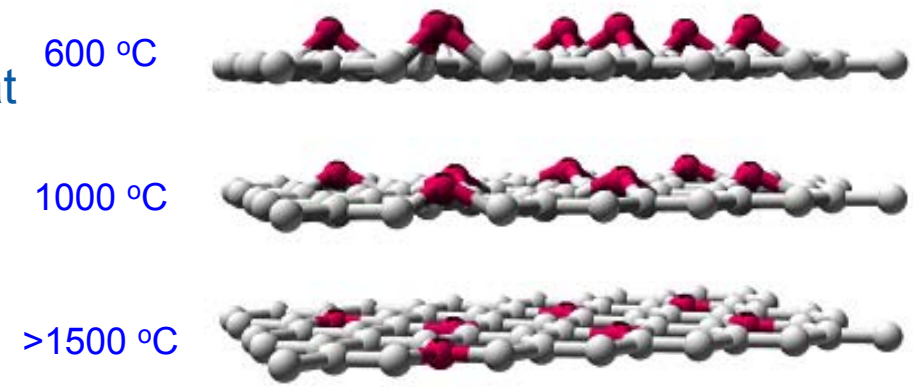
PENNSTATE

Increased Boron Content

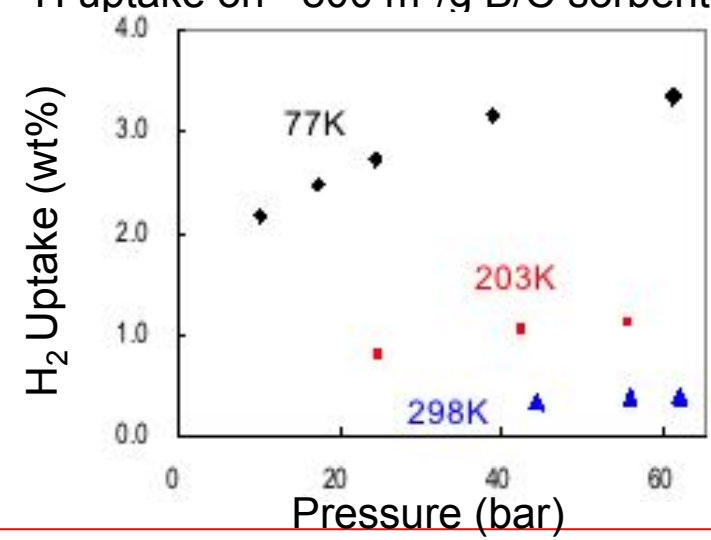
- B-doped materials store 2-3 times more H than activated carbon on a per SSA basis at both 77 K and RT.
- ~8 at% B from pyrolysis of polymers

  via NIST prompt gamma analysis
- B content decreases with pyrolysis temp.
- B/C materials enhance metal binding and nanoparticle uniformity.
- Next steps to improve hydrogen storage.
  - Increase B with higher B content precursors and reactive gases
  - Increase SSA
  - Form optimized/stabilized metal atoms for Kubas sorption and spillover catalysis

Structure controlled by pyrolysis temp.



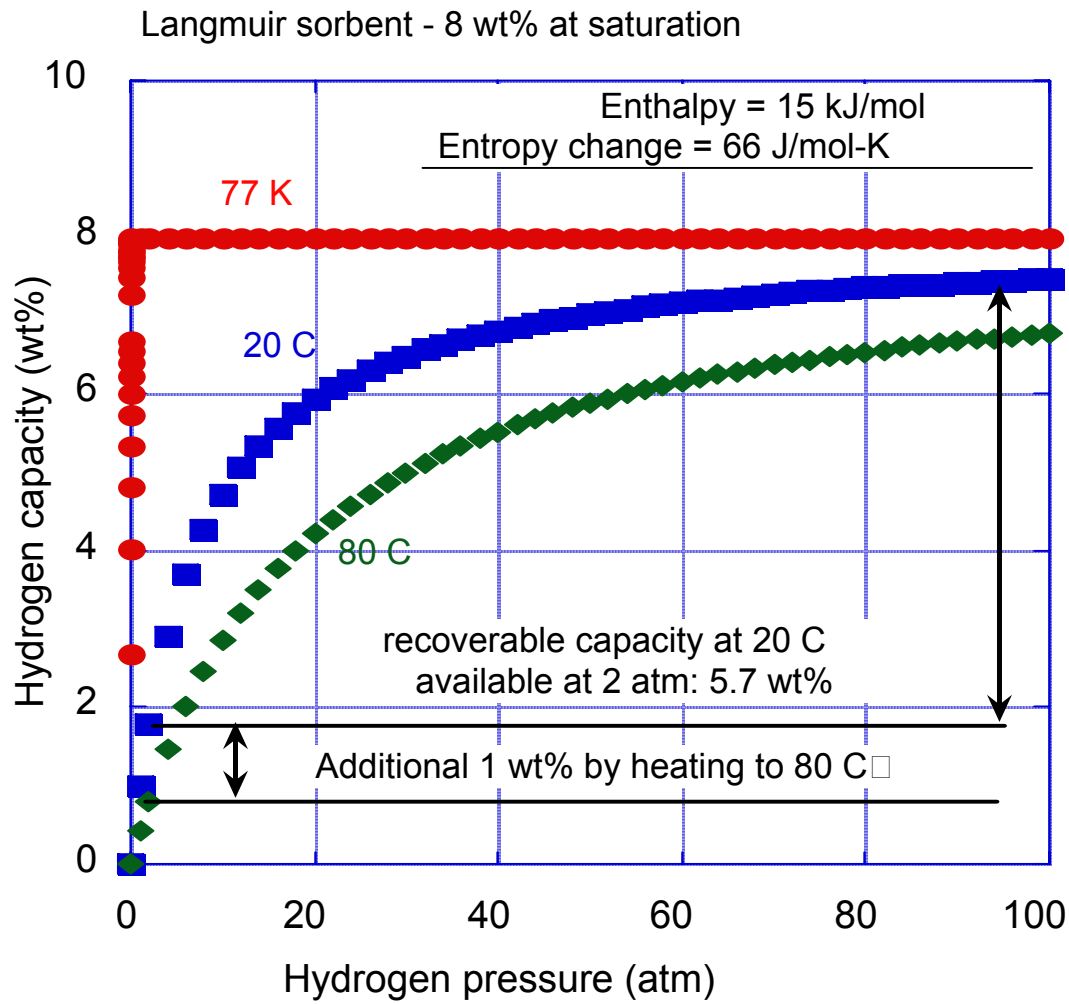
H uptake on ~800 m^2/g B/C sorbent



Boron doping enhances hydrogen binding and also stabilizes metal nanoparticles/atoms. B/C materials provided viable path to design materials that will meet DOE hydrogen storage goals.

What Will Deliverable Capacity Be at Ambient Temperatures?

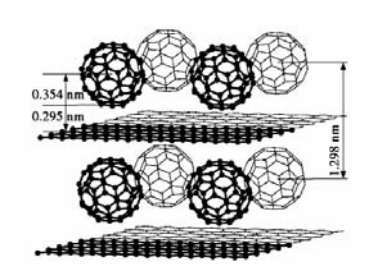
- As enthalpies are improved, low T (77 K) isotherms become more abrupt.
- Consider model sorbent with optimized enthalpy and entropy of sorption.
- Much larger deliverable capacity with P swing at RT than at 77 K.
- Shape of isotherm is strong function of enthalpy and entropy of sorption.
- Saturation capacities near 8 wt% - shown by Yaghi et al. and Mokaya et al. - are possible with high surface area materials.



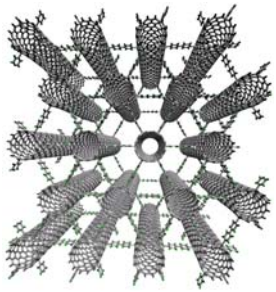
Synthesis of Graphene-based Sorbents

Idealized systems are amenable to conceptualization and modeling, and show desirable characteristics, but how can the jump be made to real systems?

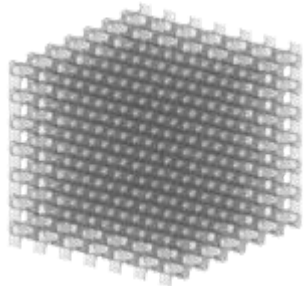
5.5 wt%
>45 kgH_2/m^3
250 K, 10 Mpa
Kuc et al., 2007



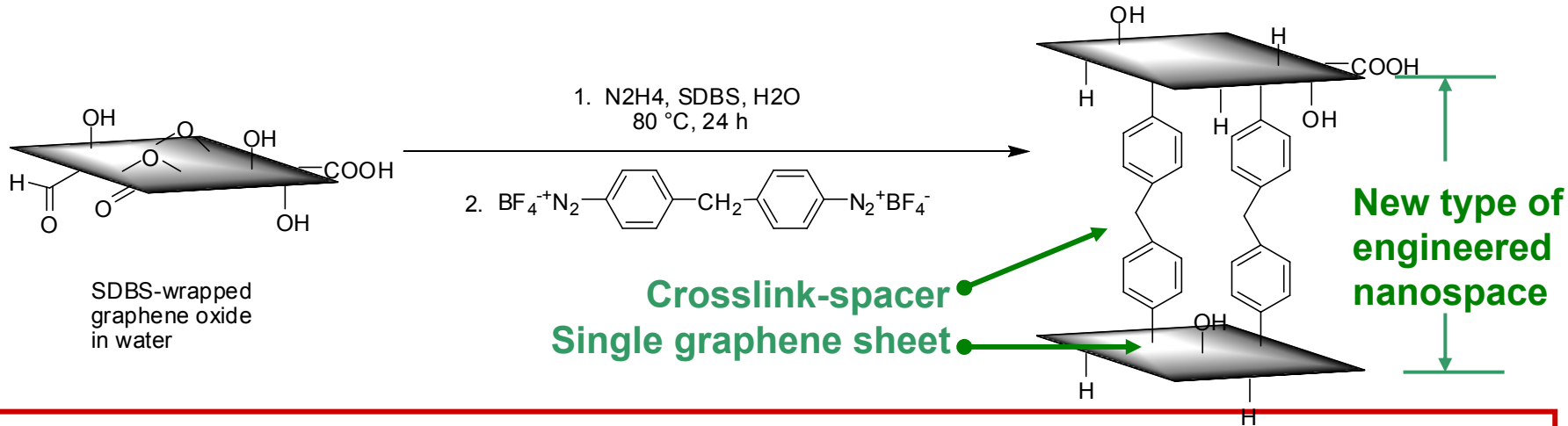
4 wt%
50 kgH_2/m^3
77K, 5 MPa
Yakobson et al.



5-6 wt%
50 - 60 kgH_2/m^3
77K, <5 MPa
Ding et al., 2007



- **Diazonium chemistry developed for functionalizing SWNT sidewalls now put to work functionalizing and crosslinking graphene sheets**
- **Example of resource redirection, as well as importance of work on model systems**



Broad knowledge of the chemistry of SWNTs is proving invaluable for rapidly developing single sheet graphene chemistry to make an engineered nanospace for H_2 at RT

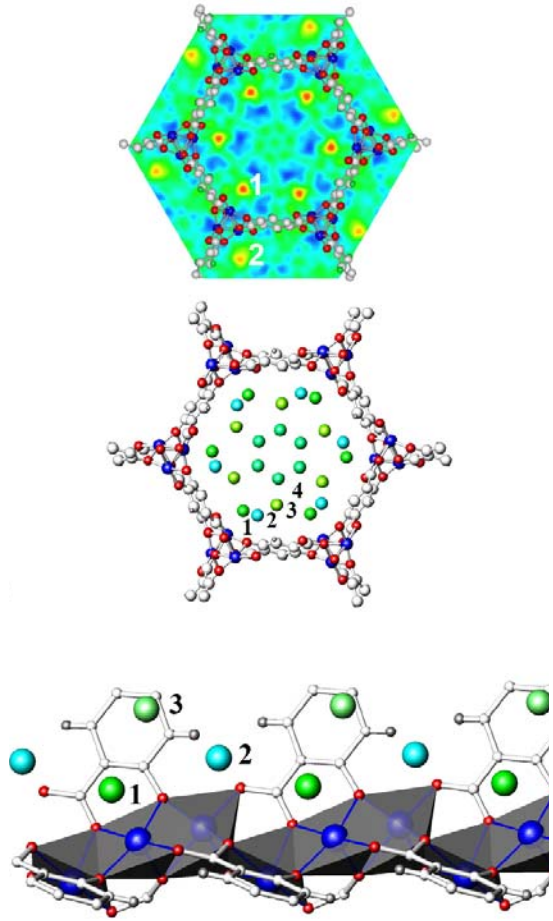
Increasing the Packing Density of Hydrogen

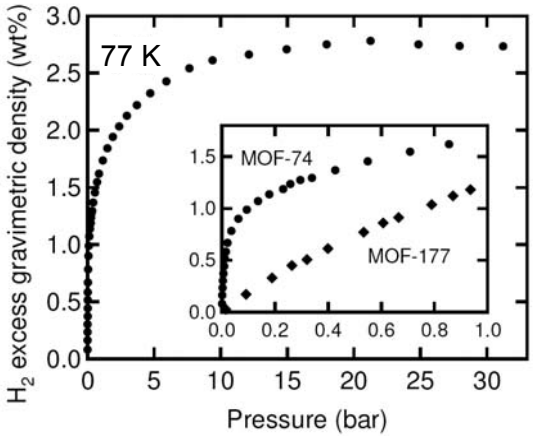
Zn-based MOF-74

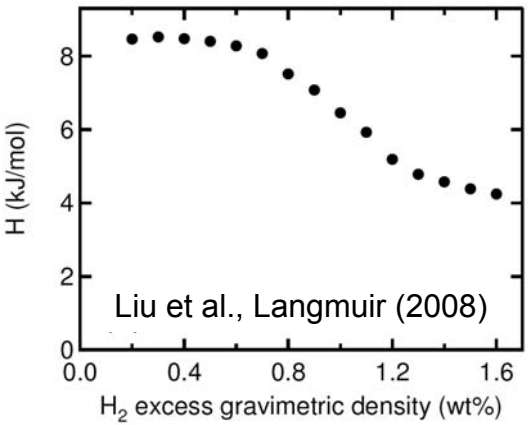
- High initial enthalpy due to interaction with coordinatively unsaturated metal centers

<u>Distances</u>

- Zn-H_2 : ~ 2.6 Å.
- H_2 @ site 1 to 2: ~ 2.9 Å
- H_2 @ site 1 to 3: ~ 2.85 Å
- D_2-D_2 in solid: ~ 3.6 Å
- Close-packed H_2 layer on graphite: 3.51 Å

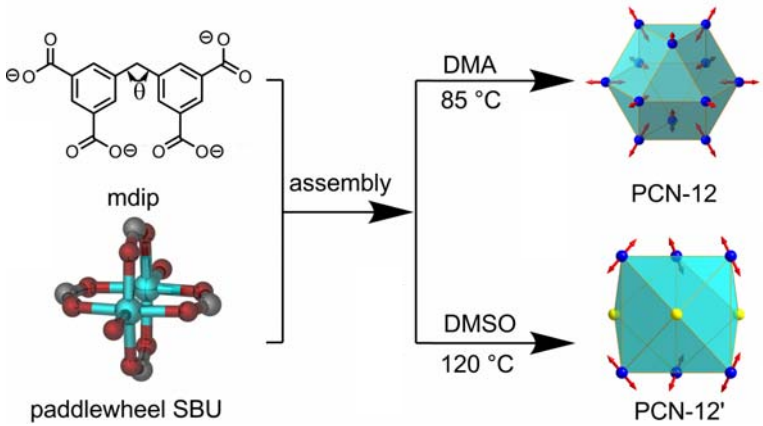




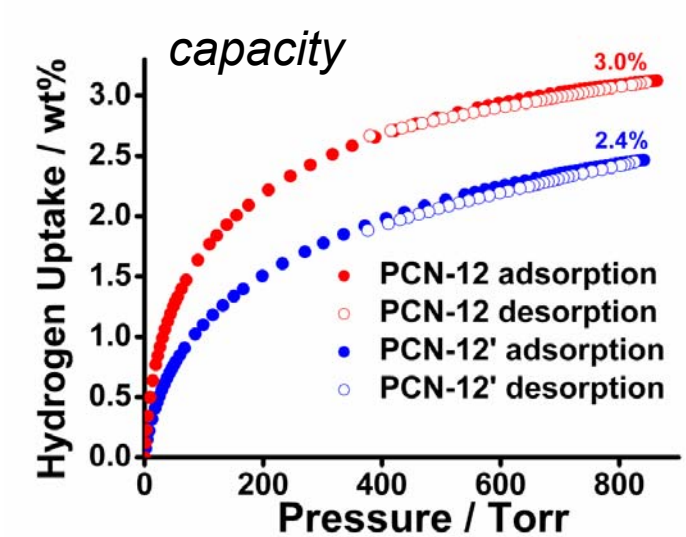


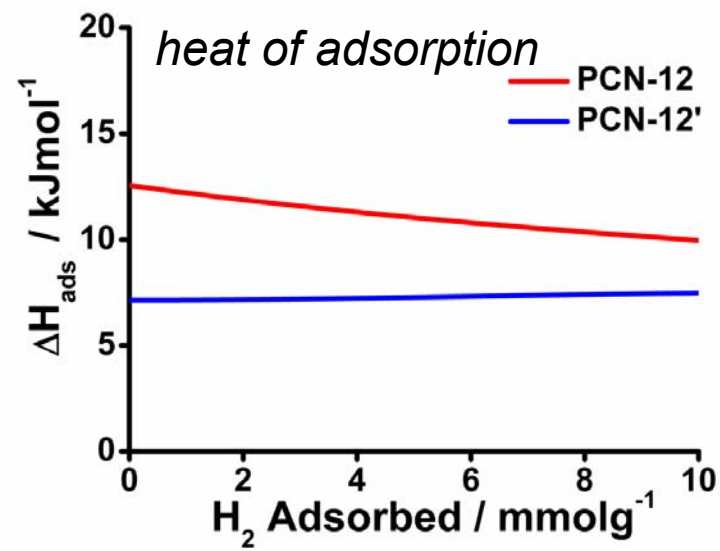
- Located 4 adsorption sites in MOF-74, no elongation of H-H bond: not 'Kubas'
- First observation of denser packing than hydrogen monolayer!
- Implications for enhanced H2 packing and improvements in volumetric performance.

Metal Alignment in MOFs Enhances Enthalpy



- **Polymorphs have identical composition and atom-to-atom connectivity, but different metal alignments.**
- **Enhanced heat persists to relatively high coverages. (2 H_2/Cu ~ 1.7 wt%)**





PCN-12 exhibits **3.0 wt%** at 77K and 1 bar, with a volumetric density of 24.6 mg/cm^3

ΔH of PCN-12 is ~**12.5 kJ/mol** at low coverage, and **~10 kJ/mol at 2 wt%**

Spillover is a Major Focus of the Center

U Mich: Synthesis/measurement/theory

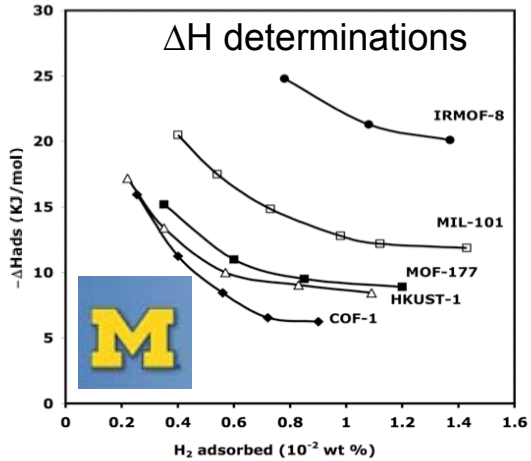
Mechanistic Investigations: e.g combined dosing of D_2 then H_2,
ΔH determination for several systems.
Desorption rate exceeds DOE target.

Materials Development

NREL: Pt:AC, Surface optimization, Kinetics, Large volume synthesis.
- Demonstrated 2 wt% reversible at 1 bar (on at RT, off at 250C).
- Identified some pitfalls to reproducibility of active material production

LLNL and Caltech incorporating catalyst into aerogels.
- Isotherm for 2400 m^2/g Pt-CA extrapolates to 1.2 wt% H_2 at 100 bar

ORNL (SWNH)/NIST spillover starts occurring between 150 and 298K



Measurements

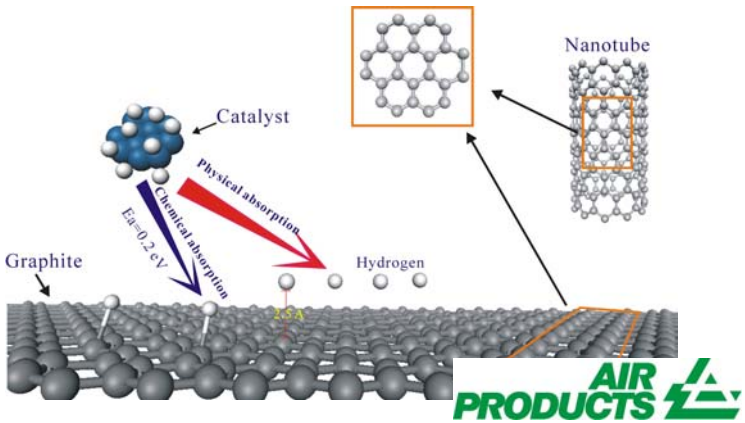
SWRI NIST UNC
CIT NREL APCI

UM results validated

Thermodynamics and Kinetics of Spillover

Rice: First principles models identified nucleation issues
APCI: Calibrated models with MoO_3 system, propose H physisorption as transport mechanism.
NREL: Previously developed models for hydrogenating endohedral fullerenes and metcars are applicable.

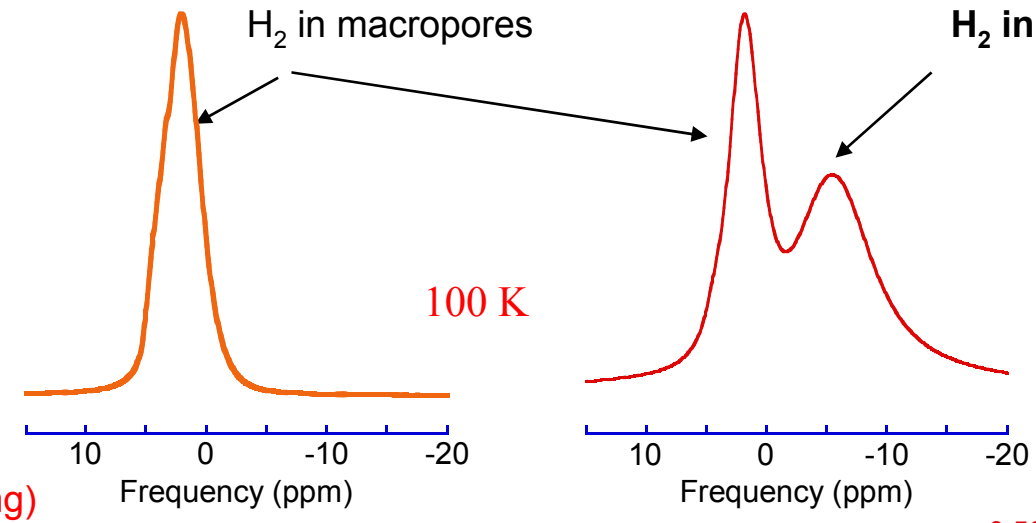
- Consensus that thermodynamics are allowed.
- Prehydrogenation of the receptors may be required.



Spillover enables substantial RT hydrogen storage. **Kinetics and capacity can be enhanced by understanding and improving catalyst, bridge, and receptor properties**

Conventional Measurement Protocol "Misses" H_2

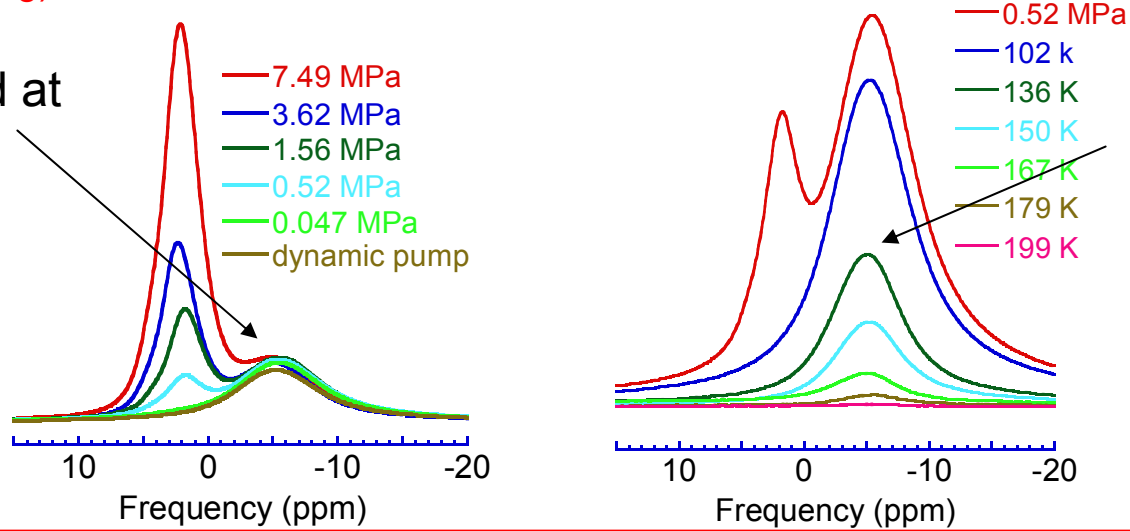
Typical protocol:
1 - Evacuate
2 - Cool sample
3 - Expose to H_2



Modified protocol:
1 - Evacuate
2 - Expose to H_2
3 - Cool under H_2

B-doped graphite (Chung)

Sites not emptied at 100 K (slow kinetics)



Heating speeds depopulation

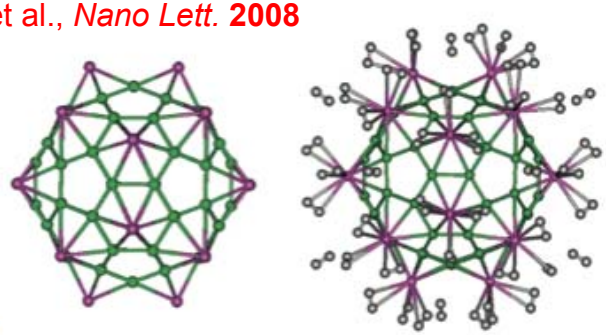
The very sites we hope to create and maximize (nanoporous, high binding energy) may be totally missed in typical measurements (!)

New and More Readily Synthesized Sorbents

Non-Carbon materials

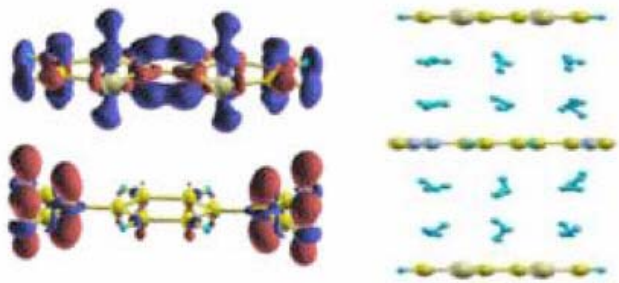
$Sc_{20}B_{60}$ (left) adsorbs 72 H_2 (8.6 wt%) (right). Each Sc binds three H_2, each pentagon binds one H_2. Metals are locked in place and cannot agglomerate.
Zhao, et al., *Nano Lett.* **2008**

● Sc
● B



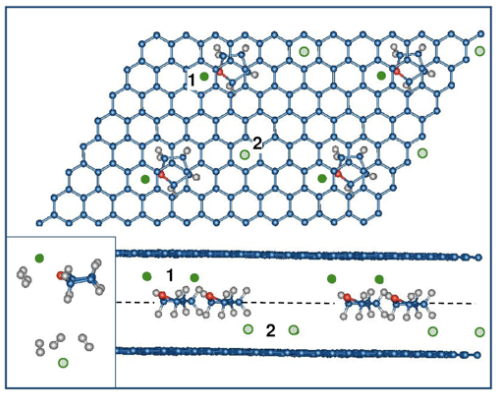
TTF-TCNQ

20 kJ/mol H_2, > 10 wt%



A synthesizable system with expandable space

Graphite co-intercalated with Li & THF

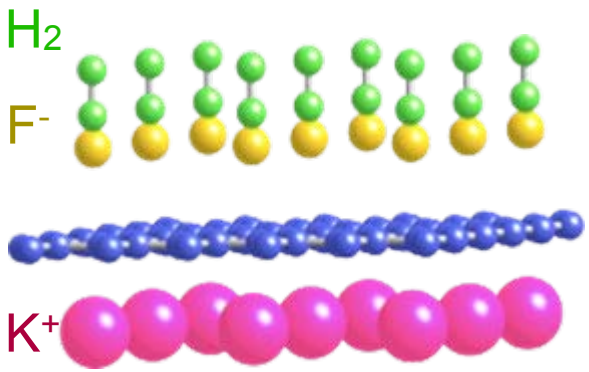


~3.4 wt% at RT

A synthesizable system that has the appropriate interplanar spacing for enhanced physisorption and isolated metal sites for dihydrogen bonding.

Topological frustration

28 kJ/mol H_2



A totally new concept

HSCoE FY08 and FY09 Areas of Emphasis

- **Clusters:** Constantly assess progress and reallocate resources as needed to initiate new, more promising activities. Stimulate effective teaming to increase rate of progress in investment areas. Leverage resources within and outside to make the CoE greater than the sum of its parts. Maintain awareness of advances made in different clusters, and insure seamless combination of these.
- **Close the gap between Theory and Experiment:** Iterative, intimate interactions in the CoE have already taught theoreticians what is possible experimentally, and *vice versa*. Continued work at this interface will increase the rate of discovery and synthesis of viable materials.
- **Co-Intercalation of Graphite:** Theory/experiment interactions to characterize the synthetic process, to parameterize the material components as a function of hydrogen storage properties, and address issues found. Next steps are to complete the degree of intercalation (e.g. all the way to stage 1), and remove trapped, unneeded solvent species to expose active sites.
- **Intercalation of BC_3:** Introduce intercalating species, such as F and K, into BC_3 to induce both physisorption and chemisorption; Enhance H_2 adsorption kinetics; Perform ab initio MD simulations and minimum energy path calculations on BC_3-intercalated compounds; Explore the optimal concentration of intercalating species in both BC_3 and N-doped F-intercalated graphite
- **Organometallic structures:** More tractable reactions schemes with identification of atomic structures, characterize the reactions, simulate their H-storage properties, and improve the properties. Non-equilibrium reactive syntheses in gaseous and condensed phase environments to “trap” structures in desired, active configurations.
- **Porous materials:** Study boron doping and metal decoration of porous carbons produced by, eg., Zeolite templates, propped graphenes, carbon and non-carbon aerogesl. Work interactively to characterize the structure properties, analyze the optimal pore effect, and investigate the highest potential for H storage through B-doping and metal decoration.
- **Spillover Materials:** Determine the contributions of bridges and receptor to kinetic limitations. Identify features leading to reproducible sample prep. Prepare samples on the multi(tens)-gram scale for system testing. Perform very high pressure measurements (> 350 bar) to determine saturation capacities.
- **MOF Materials:** Further enhance H2-MOF interactions by preparing materials with a higher density of coordinatively unsaturated metal centers, improve H2 uptake at temperatures higher than 77 K by ligand and MOF design, increase MOF thermal stability while maintain its porosity. Increase volumetric performance using denser H2 packing. Understand how spillover works with MOFs.
- **Non-carbon Materials:** Take lessons learned through extensive experience with carbon-based materials and extend to determine if other light elements can be used to implement mechanisms more straightforwardly, or if brand new, more desirable approaches may be found.

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