Reports from the Breakout Sessions

MATERIALS-BASED HYDROGEN STORAGE SUMMIT:
Defining pathways for onboard automotive applications

hosted by

National Renewable Energy Laboratory
Golden, CO

January 27 & 28, 2015

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Metal Hydride Session Report-out

METAL HYDRIDES BREAKOUT SESSION REPORT
– Objectives and Approach –

OBJECTIVES

- To candidly assess the current status of metal hydride materials as hydrogen storage media for vehicular and stationary power applications.
- To identify the *critical challenges and obstacles* that must be overcome for successful deployment of metal hydrides in practical hydrogen storage systems.
- To explore approaches and research directions that might address those challenges.
- To define research collaborations that may be appropriate to expedite the successful development of suitable candidate materials.

APPROACH

- Provide background information about problem; Identify/prioritize barriers
- Outline R&D approaches to address barriers
- Discuss details of proposed R&D pathways and recommendations for future work (sort into near-term and longer term success possibilities)
- Vote (straw poll) on barriers and R&D paths – select top 3-5 topics

METAL HYDRIDES

– Some R&D Challenges/Questions Discussed in Session –

- ***Kinetics and reversibility***: What principal processes limit the hydrogen sorption kinetics in complex metal hydrides? Is there one predominant mechanism or class of mechanisms? (e.g. phase separation/segregation; limited diffusion of hydrogen and/or matrix atoms between phases; formation of unwanted intermediates or products that inhibit the primary sorption reactions, etc.) Can additives and nanostructure materials play an important role? (If so, how do you overcome the volume/gravimetric penalties?) How do you prevent/minimize agglomeration of nanoparticles during hydrogenation/dehydrogenation cycling? What can we do to mitigate the problem(s)? Are multi-disciplinary research teams needed?
- ***Thermodynamics:*** Reaction enthalpy "sweet spot": ~25-30 kJ/mole–H_2 – only waste heat from fuel cell is needed to liberate H_2. Higher enthalpies require H_2 combustion and fuel cell waste heat; lower enthalpies – not enough H_2 retained. Only limited set of materials satisfy "sweet spot" enthalpy.
- ***Theory/simulation and MH material development**:* What is the most critical "metal hydride problem" that theorists should address? (e.g., hydrogen capacity, reaction kinetics, diffusion, detailed reaction pathways…). What collaborations are needed to rapidly develop and test new ideas?
- ***High capacity "light" metal hydrides are needed to meet DOE targets:*** Are complex borohydrides the best option? What are their limitations; are there "showstoppers? Are stability and air sensitivity important issues? Are there unwanted reaction products can limit fuel cell operation. Are there other suitable candidates besides borohydrides?
- ***Impurity issues:*** Unwanted reaction products can limit fuel cell operation. How do you ensure that these products don't form?
- ***Thermal management problems during charging/discharge***
- ***How do we address the "white spaces" in the spider chart(s)?***

MH ISSUES AND STRATEGIES (including votes)

Thermodynamics

- 6 • Better understanding of reversibility - what limits reversibility in MH systems (see "Basic Studies section)
- 2 • Unconventional thinking re/ reversibility in AlH_3; (is alane the "ultimate" MH)?
- • Consider relaxing requirements on FC (200°C) instead of 1-100 bar, <80C hydride

Kinetics and Pathways

- 1 • Identify reaction intermediates
- 6 • Understand effects of nano-confinement on kinetic and thermo properties? How do you improve nanoconfinement effects
- 1 • Understand composition and stability changes in nano-structured materials
- 1 • Explore "active" scaffolds (scaffolds that participate directly in reaction)
- 1 • Explore entirely new approaches to improving kinetics

Reaction Systems

- 2 • Develop improved understanding of mechanisms and pathways
- 2 • Accelerated testing protocol to improve understanding of cycling issues
- 3 • "Out-of-box thinking re/ new states of matter/composition in low-Z systems
- • Consider "hybrid" reaction systems (binary or multi-reaction systems where one drives another)
- 2 • Understand risk/reward of materials discovery vs. mechanistic studies

Basic Studies

- 6 • Combined theory/exp't to develop better understanding of structure/properties (focus on multi-scale)
- 2 • "Rapid" new material discovery using combi methods
- 9 • What limits reversibility in systems that "should" be reversible?
- 6 • Understand interfaces/interfacial in exchange reactions across phases
- • Greater focus on combined theory/expt'l/Engr teams
- 4 • Explore un-conventional approaches to mt'l discovery; focus on nonequilibrium syst.

Other

- • Test materials under realistic operating conditions
- • Understand how to manage thermal load during charge/discharge
- 3 • Increase emphasis on other industrial applications (focus on forklifts)
- • Increase focus on safety issues

FOUR TOPICS RECEIVING GREATEST NUMBER OF VOTES IN MH STRAW POLL –

Develop improved understanding of limited reversibility observed in many MH systems; create strategies to overcome limitations: Focus on understanding why reversibility in inhibited in systems that "should" be fully reversible? Use results as a foundation for developing strategies to improve reversibility.

15 votes

Fully explore use of nano-confinement and nano-structured materials to improve kinetics and thermodynamic properties: Initial results on the effects of nanoconfinement on kinetics and thermodynamics are promising. However, many critical questions remain. More comprehensive studies are needed to understand and exploit these effects.

6 votes

Understand role of interfaces and interfacial reactions across phases: Interfacial reactions may strongly influence transport. Characterization and understanding interface reactions may be key to create strategies for improved storage and reversibility

6 votes

Use combined theory/experimental approaches to develop improved understanding of structure/properties (focus on multi-scale)

6 votes

MH BREAKOUT – Summary

- Deeper understanding of reaction mechanisms, limits to reversibility, and structure/composition needed to overcome major challenges facing MH systems.
- Identified poor reversibility in systems that "should be reversible" as most critical problem. Based on progress so far, a keener focus on fundamental processes is needed.
- Group fully understands that these needs don't fall under traditional purview of EERE. Group strongly urges EERE to explore collaborative funding opportunities with organizations that support more fundamental research.

Final Thoughts From the Group

Can we develop a MH material that is competitive with compressed H_2 in five years?	**Yes: 12** **No: 4**
Can we make MH materials discovery and understanding more directed (focused) and meaningful in 5 years?	**Yes: 20** **No: 0**
Is this a dead horse?	**Yes: 0** **No: 20**

Our session brings to mind the immortal words of Donald Rumsfeld

(U.S. Sec’y of Defense, 2001-2006)

(*From a DoD news briefing, 2002*)

“….. because as we know, there are known knowns; there are things we know we know. We also know there are known unknowns; that is to say we know there are some things we do not know. But there are also unknown unknowns -- the ones we don't know we don't know. And if one looks throughout the history of our country and other free countries, it is the latter category that tend to be the difficult ones.”

… and so it is with metal hydrides, too.

Chemical Hydrogen Session Report-out

CHS Breakout Synopsis

- Attempted to focus on directions that would address shortcomings of current materials
  - Fuel cost, mainly related to regen
  - WTPP efficiency, mainly related to regen
  - Regeneration complexity
  - Regeneration kinetics

- Maintain the advantages of many CHS materials
  - Gravimetric and significant volumetric capacity advantages
  - Adequate non-equilibrium limited kinetics of dehydrogenation observed from exothermic materials
  - Low pressure

Areas Where Potential Improvements May Be Found (1)

- 27 Once-through fuels (aka ‘unidirectional’ H_2 release); enables direct fuel cells(2)
- 2 Integration of renewable energy into fuels synthesis, regen pathways
- 9 Inexpensive regeneration feedstocks
- 6 Modify existing materials for improvements
  - Regen effic., matl. Properties failings, impurities
- 7 Solids handling engineering and technologies (e.g. cartridges) to enable previously ‘discarded’ materials types
- 3 M-BN compounds that may offer improved regenerability, properties

Areas Where Potential Improvements May Be Found (2)

- Fuel blends to improve regenerability
  - Endo/exo blends to improve on board energy effic.
  - Blends to improve phys or rheological props (deal with phase changes)
  - Blends to balance protic/hydridic character to minimize impurities, improve regenerability
- Magic received one vote.

Strategies

- Once-through fuels (must generate innocuous gas phase products??) – no onboard spent fuel, no regen, rather fuel resynthesis
  - Energy analysis to provide bounding energy intensity of fuel synthesis – how much more energy cost/intensity vs. compressed H_2
  - Low T dehydrogenation of YHx, e.g. NH3, carbohydrates, CHxOy, etc will require low T catalysis of dehydrogenation as well as for fuel synthesis

Strategies (2)

- Fuel Blends
  - Optimize physical props to improve kinetics selectivity of dehydrog to impact regen control
  - Improve phase control
  - Minimize impurities
- Exo-Endothermic blends
  - Optimize thermodynamics
  - Approaches to kinetics control of dehydrog of blended phases to match rates closely

Strategies (3)

- Solids handling engineering and technologies for onboarding solids to enable promising, but phase-challenged materials
  - Engineering of cartridge systems for ‘onboardability’, safety, flexibility,
  - Develop onboard/offboarding solids handling approaches for system fill

Adsorbent Session Report-out

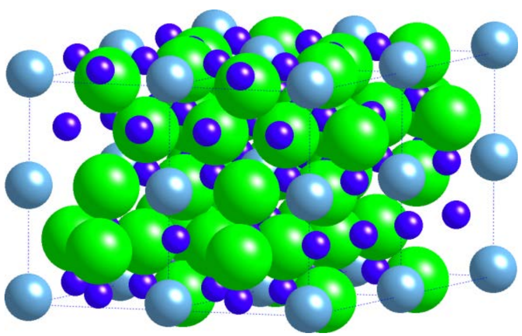
Adsorbent Breakout Report Out

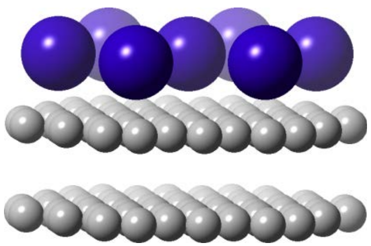
Some background on adsorbents:

a) Atomic hydrogen < 1Å, molecular ~3.5Å

- Physical limit on volumetric density (71 g/L LH_2)

$LaNi_5H_6$





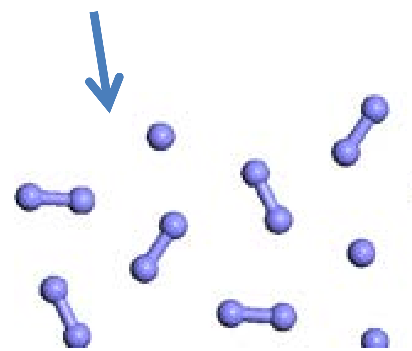
H_2 on graphite

Landolt-Bornstein ($P6_3/mmc$)
solid H_2 at 4.2 K, a=3.76, c=6.14

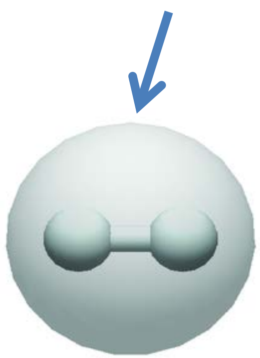
Koresh and Soffer
liq H_2 (3.62 Å, 3.44 x 3.85)

Nielsen, McTague and Ellensen
adsorbed H_2, 3.51Å

So not this



But this



Some background on adsorbents (cont'd):

b) Molecular interactions weak (van der Waals)

- Low temperatures needed (77 to 160 K).
- High number of sites needed for effective adsorption.
- High energy sites occupied initially, desorbed last.

c) Still a poor understanding of measurement/analysis

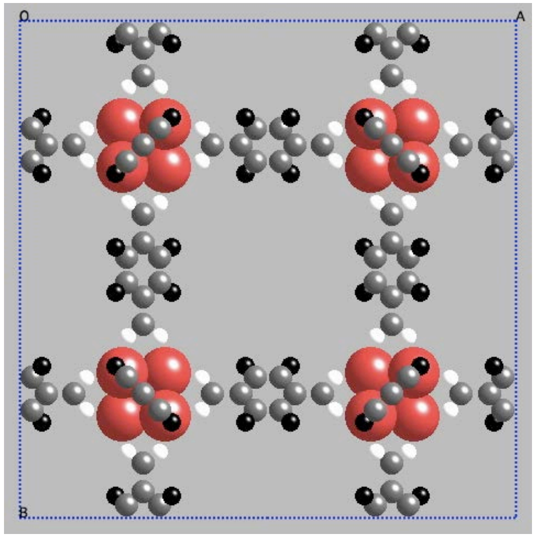
d) No H_2 bond breaking needed.

e) No kinetic limitations.

f) Modest pressures needed compared to 700 bar.

Top Issues

- Volumetric and gravimetric density trade-off
  - Higher surface areas inconsistent with high volumetric
- Pore structure and pore structure collapse
- Thermal conductivity
- Packing density maximization
- Optimal distribution of ΔH values
- Ambient temperature hydrogen
- Usable capacity vs. total capacity



Top Barriers

- Gravimetric and volumetric capacity
- Operating temperatures
- Stability/Robustness of materials
- Increasing capacity for usable hydrogen
- Hydrogen binding and enthalpy sites under ambient temperature
- Solvents used for MOF-5 synthesis– too expensive

Recommended R&D Activities (Top 3)

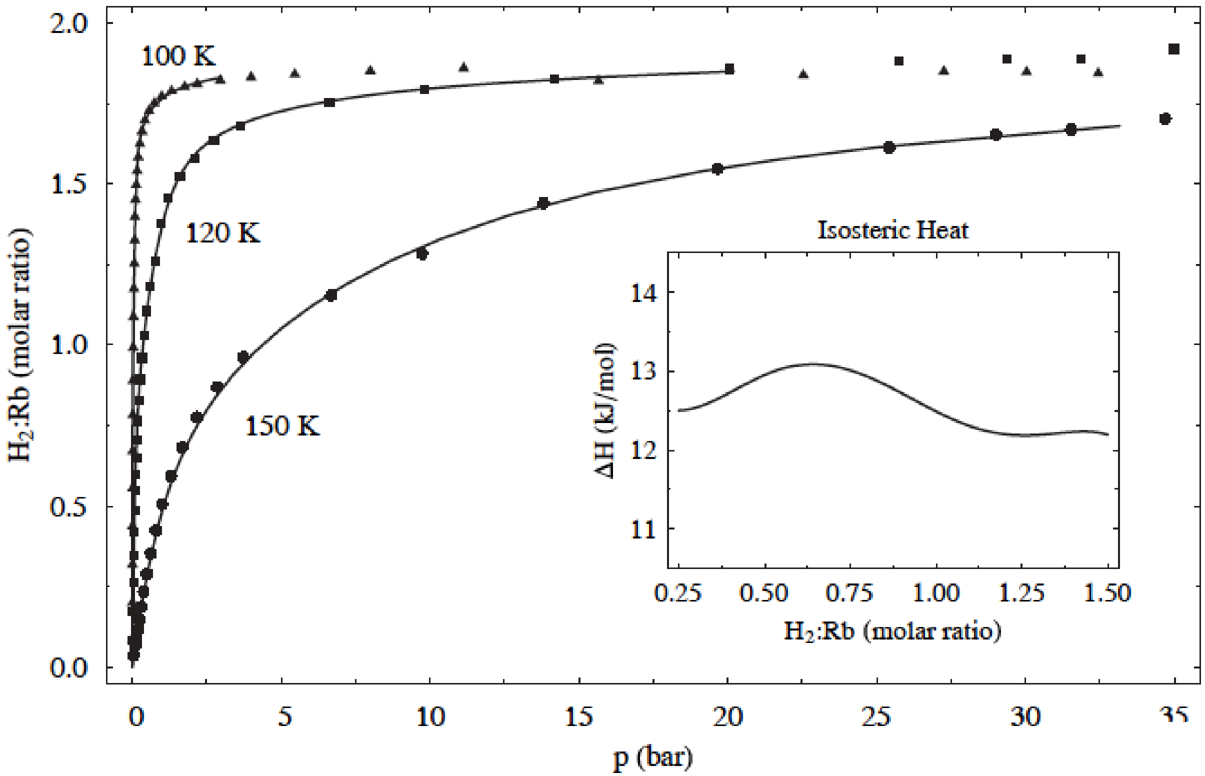
1. Use computation to optimize geometry of micro/meso pores and pore distribution to guide synthesis
2. Room temperature emphasis as a means to motivate larger ΔH
3. Practical ways/materials to prevent pore collapse and approach to crystal density that improves conductivity

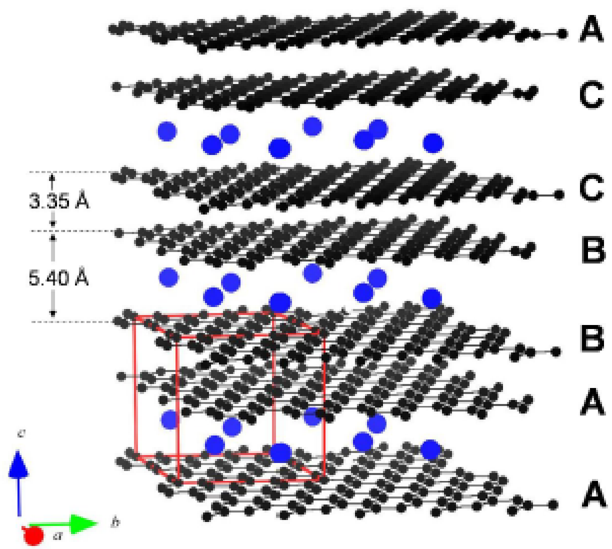
Voting Results

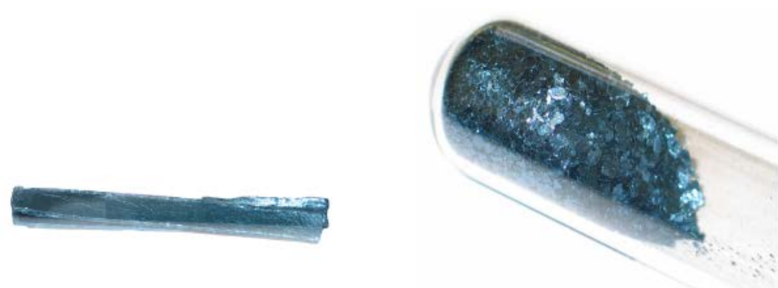
Rank	Recommended Topic	Score
1	Use computation to optimize geometry of micro/meso pores & pore distribution to guide synthesis	16
2	Room temperature emphasis as a means to larger ΔH	15
3	Practical ways/materials to prevent pore collapse and approach to crystal density that improves conductivity	11
4	Engineering analysis to optimize operating temperatures	10
5	Multiple di-hydrogens/metal/unsaturated metal centers	9
6	Approaches to maximize volumetric and gravimetric density targets simultaneously	6
7	Soft materials/porous organics	5
8	Quadrupole Interactions	0
9	Flexible frameworks/ aerogels/ templated	0

Other Relevant Ideas? (Optional)

- Discovery of new materials sets or interactions vs. optimizing what we already know
- Is there a low hanging fruit in set of materials we already know that we can take advantage of to help fill in the gaps?
- Connect atomistic to continuum to predict system performance

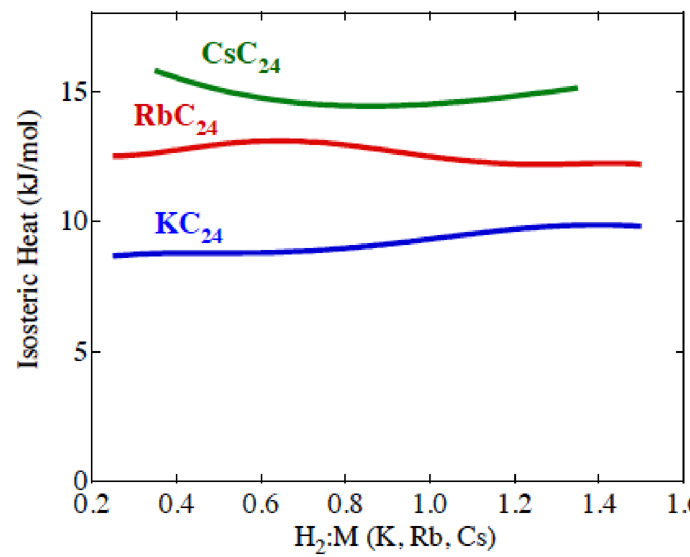






(a) Grafoil (b) Flake graphite

Figure 2.5: Samples of KC_{24} synthesized from Grafoil and natural flake graphite.



From: J. Purewal, “Hydrogen Adsorption by Alkali Metal Graphite Intercalation,” Ph.D. Caltech 2010.