Advanced Hydrogen Storage: A System's Perspective and Some Thoughts on Fundamentals

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Summary

In the development of attractive hydrogen storage options, fundamental materials properties and their impact on system design are both critical.

- Compact, light, and efficient hydrogen storage technology is a key enabling technology for fuel cell vehicles and the use of renewable energy in vehicles
- Due to system-level limitations current hydrogen storage systems meet some of the requirements but none meet all of the requirements
  - Current storage materials do not offer clear advantages over compressed or liquid hydrogen storage
  - Improving storage capacity will require improvement in material performance such that a better system design is enabled
- To improve material characteristics the physics and chemistry of the material / hydrogen system must be considered at the fundamental level
- Computational modeling of hydrogen storage materials and system performance can help to fully characterize and understand the limitations of existing storage technologies and identify novel concepts of hydrogen storage

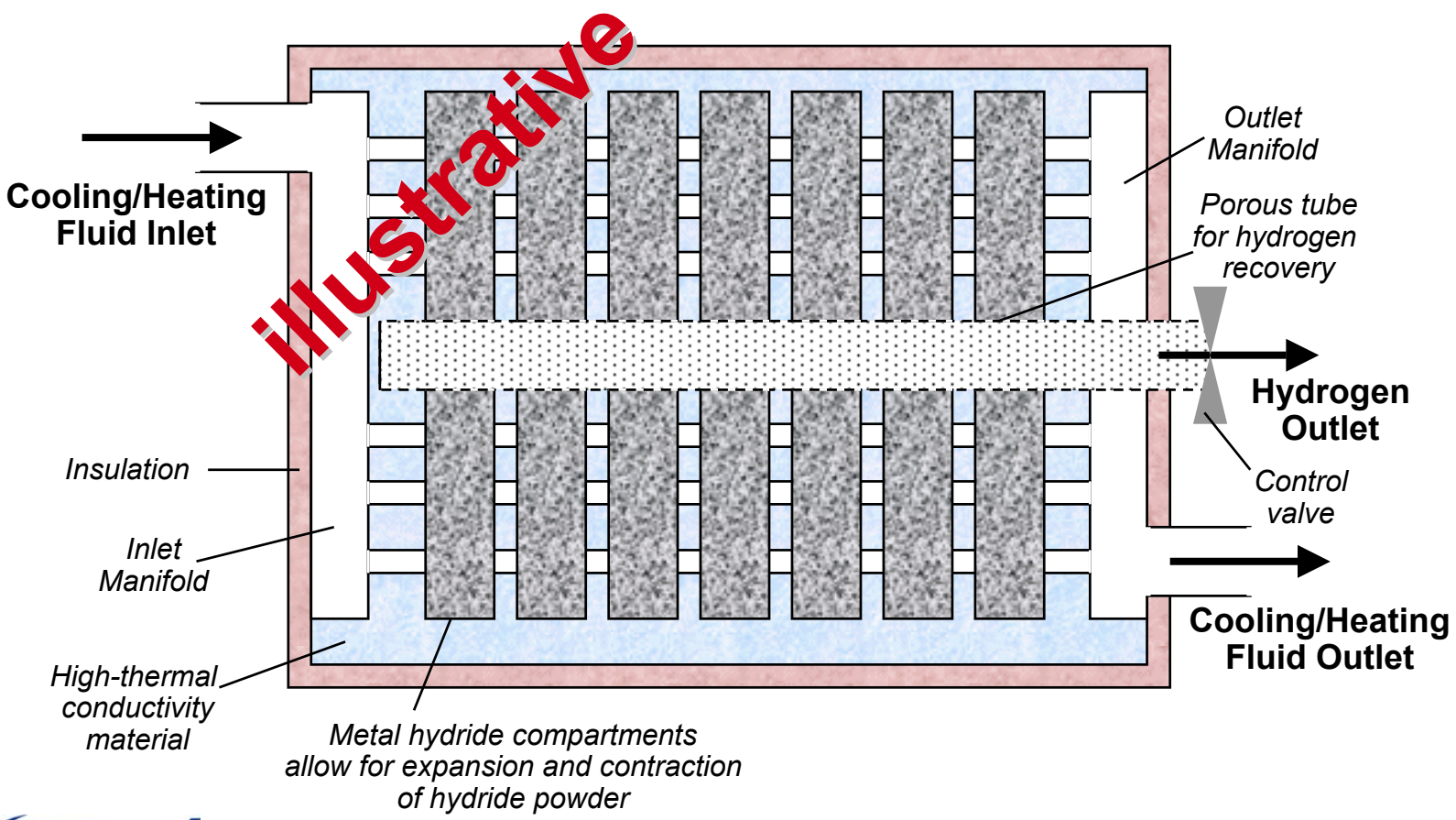
Background

Compact, light, efficient hydrogen-storage technology is a key enabler for fuel cell vehicles and the use of renewable energy in vehicles.

- The use of stored hydrogen is likely key to the success of FCVs, provided the hydrogen storage method is:
  - Compact, and light-weight
  - Is consistent with low-cost, energy-efficient hydrogen production
  - Allows easy refueling and safe operation
- A vision of hydrogen as a vehicle energy carrier offers the possibility of an eventual transition to use of a wide range of renewable resources for vehicles
- Better hydrogen storage could lead to cost-reduction of hydrogen fuel as it could allow the use of remote resources and long-distance transport
- However, until now hydrogen storage has been more a barrier than an enabler to all these technologies because of problems with:
  - Weight &volume
  - Energy use & cost
  - Fueling infrastructure
- Current storage materials do not offer clear proven advantages over compressed or liquid hydrogen storage

Advanced H_2 storage requires a relatively complex thermal and flow management system, which makes an impact to the system weight, volume and cost.

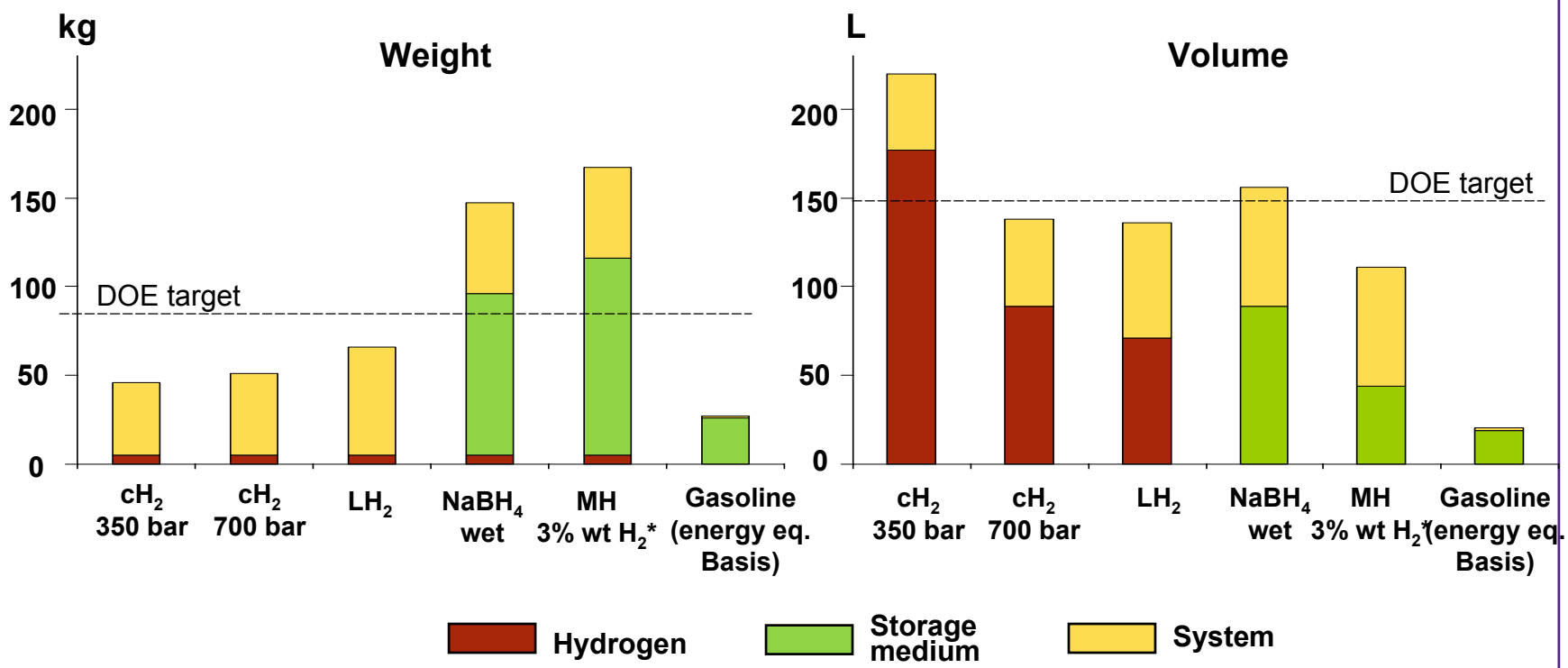
Metal Hydride Example



Current Storage System Characteristics Volume and Weight

Due to system-level limitations some current hydrogen storage systems meet some of the requirements but none meet all of the requirements.

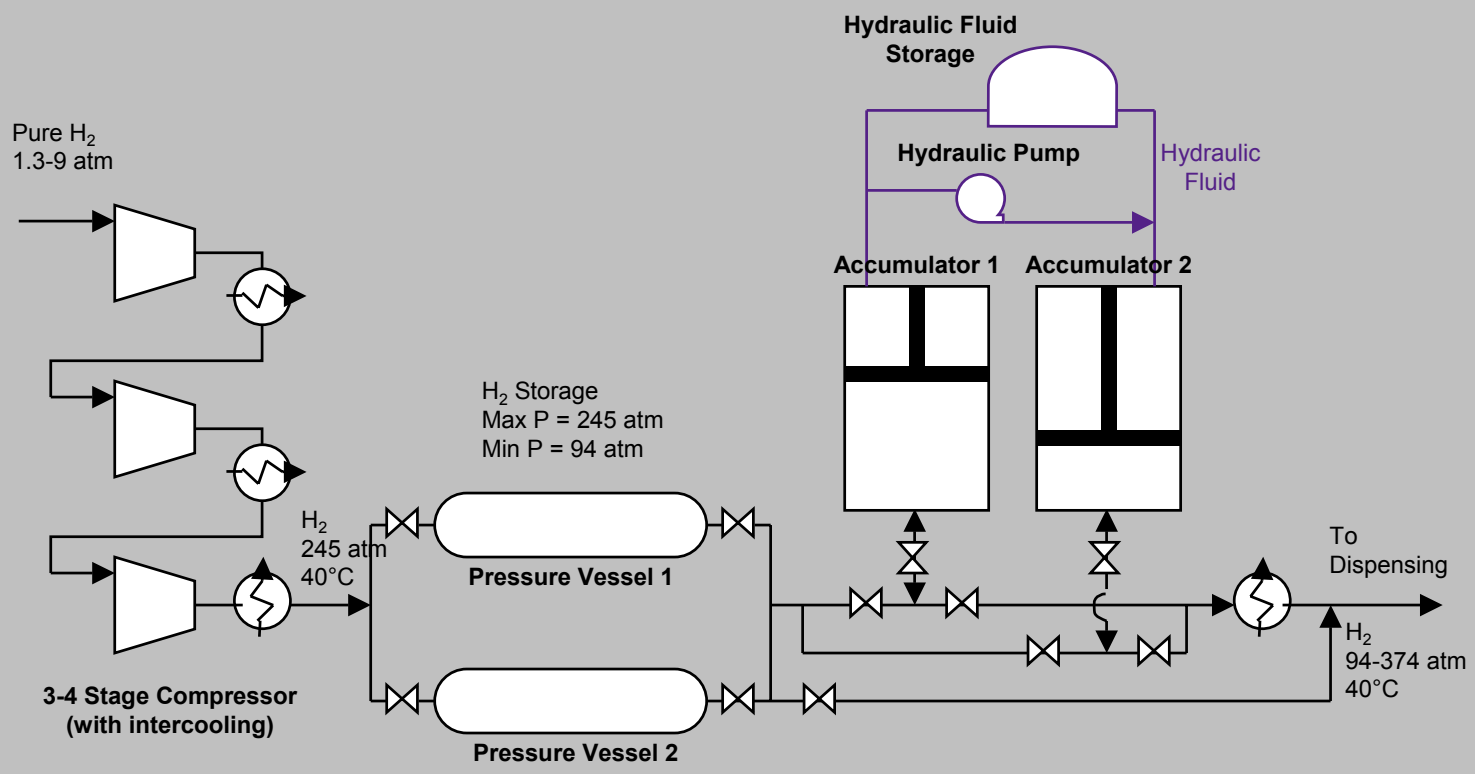
Typical Weight and Volume of Hydrogen Storage Systems (5 kg H_2)



MH example: $(V_{0.9}Ti_{0.1})_{0.95}Fe_{0.5}$

The high pressure cH_2 compression and storage scheme incorporates primary compressors, intermediate pressure storage, and accumulators.

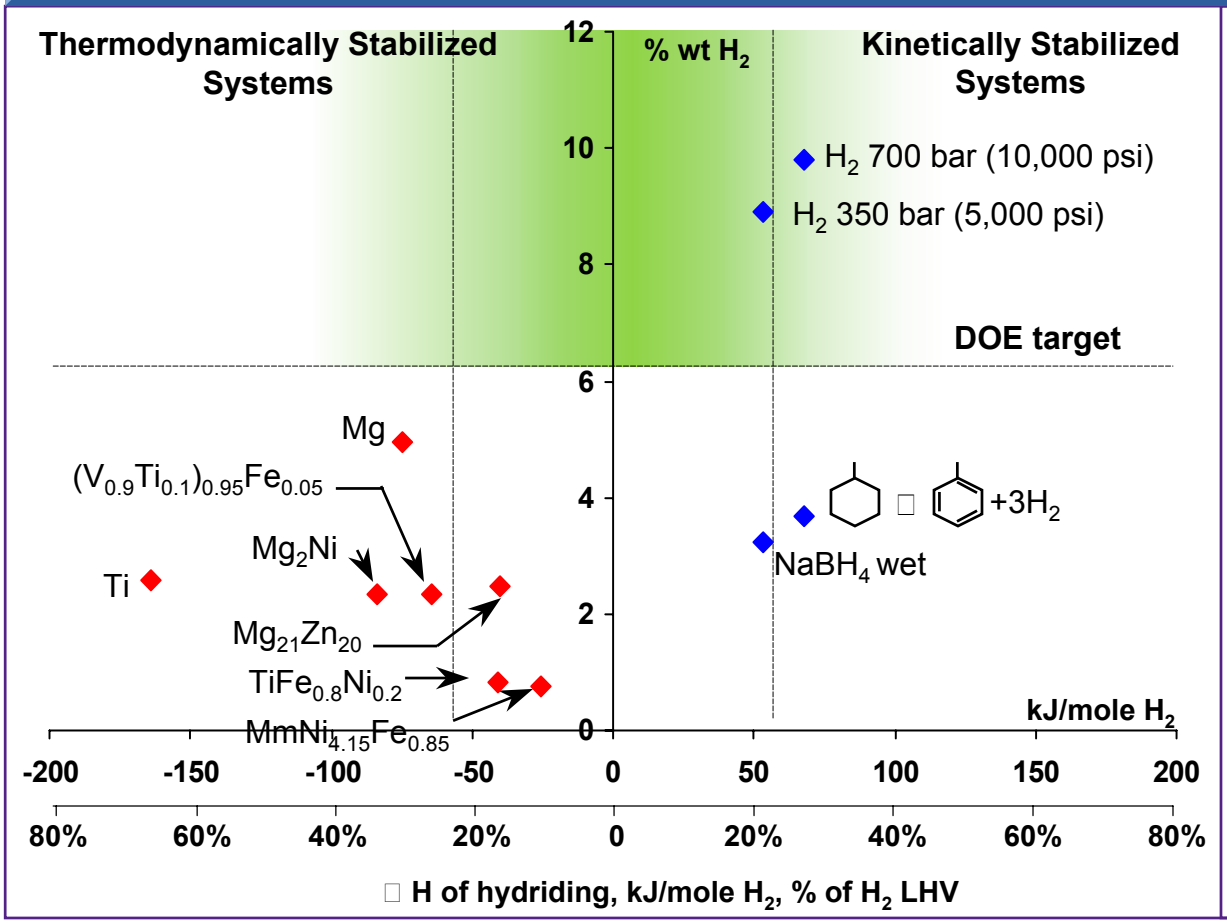
Compression and Storage. Example of H_2 fueling station PFD



Note: Not all components are shown

High storage density systems also appear to require higher energy to either store or liberate the hydrogen for current materials.

Tradeoff between Enthalpy of Formation and Storage Capacities



Thermodynamically stabilized system:

- higher capacity with deeper storage well

Kinetically stabilized system:

- higher capacity with higher stored chemical potential

Path to Improvement

Improving storage capacity will require improvement in material performance that will also enable a better system design.

- Better advanced storage materials are needed that will have:
  - Lower weight
  - Smaller volume
  - Lower cost
  - Better stability
- Additional material requirements must be met to allow improvement in system-level characteristics:
  - Low energy use for hydrogen liberation
  - Easy and energy efficient “recharging” or recycling
  - Low-temperature and pressure operation
- Achieving the necessary improvements will require:
  - A solid understanding of the fundamentals of hydrogen storage
  - Invention
  - Solid experimentation

Modeling Background

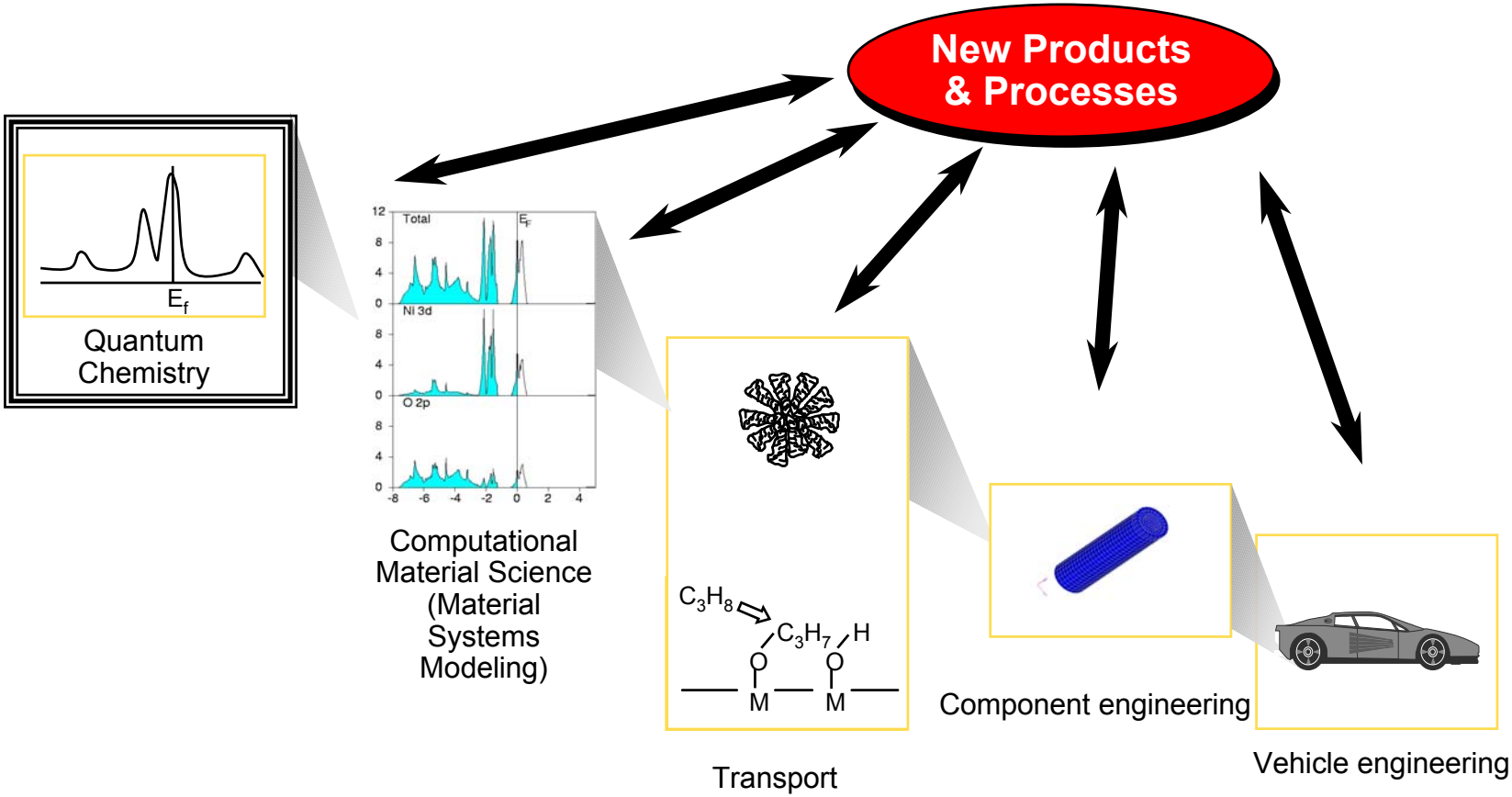
The ability of the chemistry and solid state communities to computationally model molecules, atomic and molecular clusters, and macroscopic materials has improved dramatically over approximately the last ten years.

- Kohn and coworkers have demonstrated that the theoretical and accompanying algorithmic efficiencies offered by expressing material system energies as functionals of the electron density rather than wave-functions make ab initio modeling of such systems practically feasible.
- The rapid improvement of the performance capabilities of desktop computers along the trajectory called Moore's Law has enabled various software companies to offer products based on the new trend in the physical theory.

It is now possible to study rapidly phenomena such as adsorption and diffusion, and the role of alloying and doping of host materials in energy storage systems, with minimum restrictions on capabilities and time.

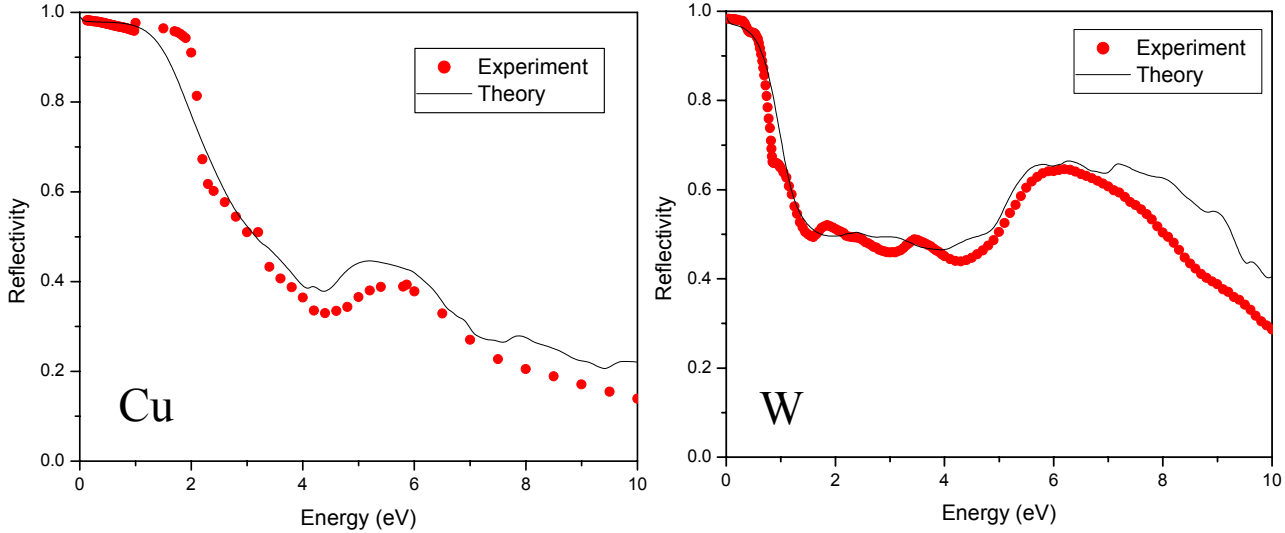
Modeling Overview

The fundamental characteristic of storage material options can be estimated using a combination of first principles models.



Modeling Optical reflectivity prediction

In a program to improve the efficacy of incandescent light bulb filaments for DOE, we developed a high-level model to predict the emissivity of materials based on first-principles computational modeling.



We verified the predictive power of our model by comparing the calculated optical properties to the available experimental data on elemental metals and refractory metal compounds*; here Cu and W are shown as examples.

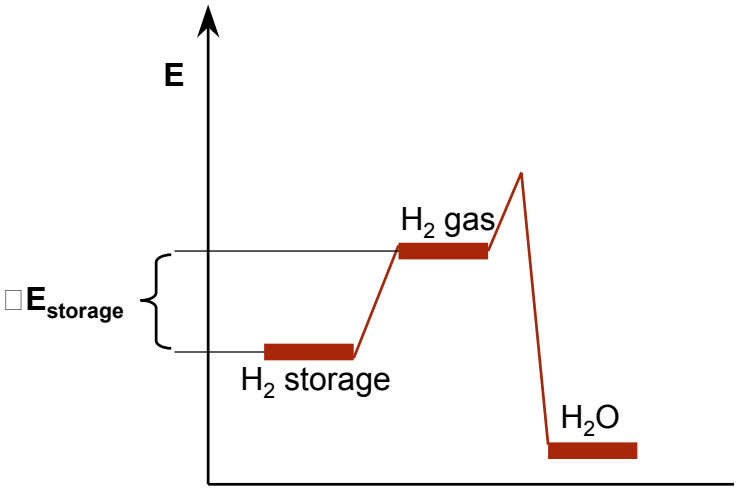
* E.D.Palik, Handbook of Optical Constants of Solids, Academic Press, 1985

Classes of Hydrogen Storage Materials

The two approaches to hydrogen storage can be distinguished by the work input requirements at different stages of the storage process.

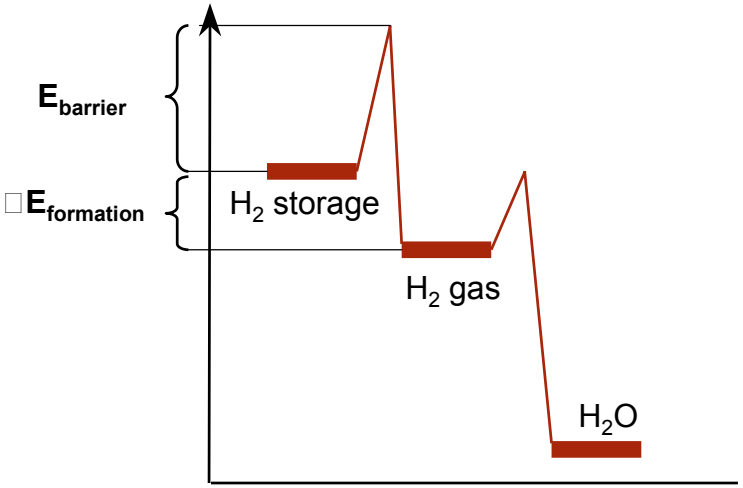
- As the storage density of a systems is increased it tends to increase the amount of energy required to form or dissociate the storage material, leading to potential losses
- Possibly, this phenomenon is related to the fundamental physical chemistry of hydrogen storage materials

Thermodynamically Stable System



Examples: MH, carbon, liquified hydrogen

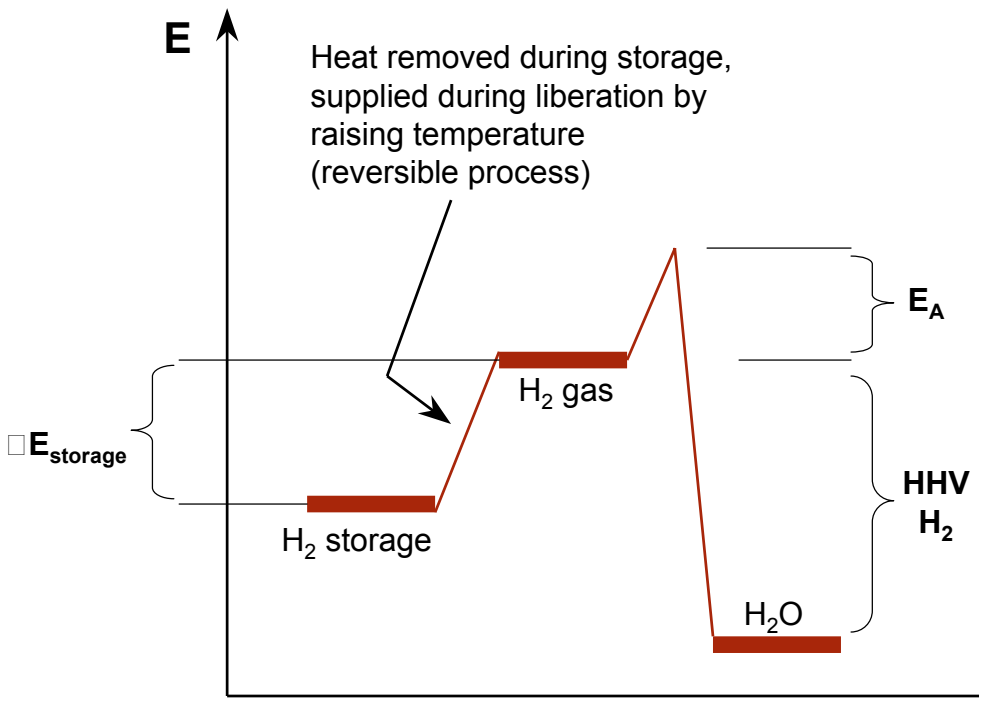
Kinetically Stable System



Examples: compressed hydrogen, chemical hydrides

Thermodynamically stabilized hydrogen storage systems require work input to release hydrogen in the free gas form.

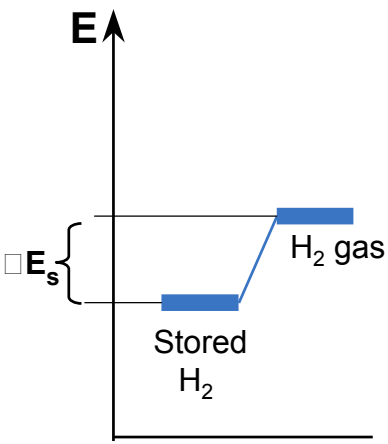
Energy Diagram of Thermodynamically Stabilized Hydrogen Storage System



- Examples include metal hydrides, carbon and liquified hydrogen
- Heat needs to be supplied to the system to liberate hydrogen
- For metal hydrides $E_{storage}$ is a strong function of compositon and structure

Quantum mechanical methods afford chemically accurate estimations of the energetics of hydrogen storage.

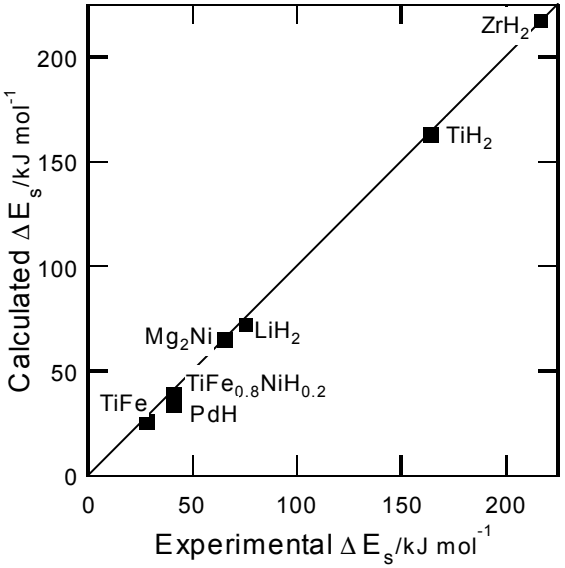
Example: Estimation of □Es, the energy of formation of metal hydrides



Input
Crystal structure
constituent atoms

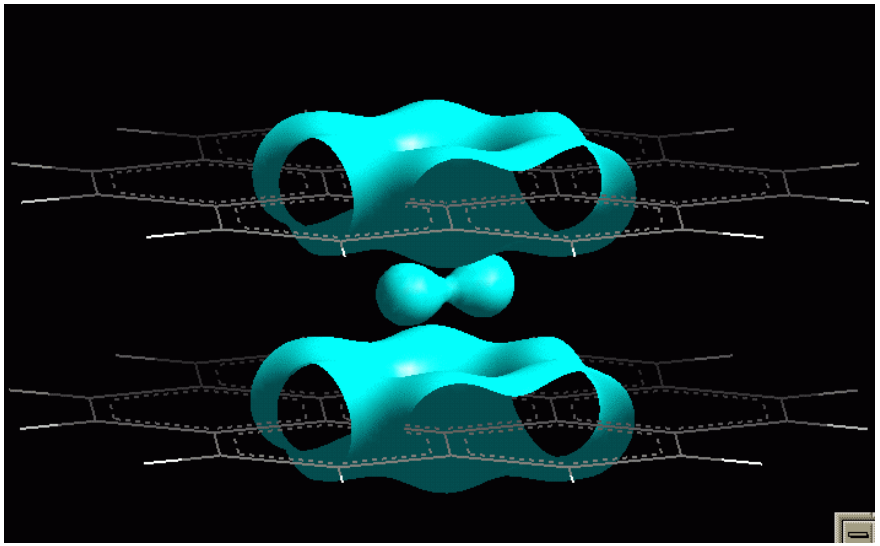
Method
Quantum mechanical computation
(WIEN, a Density Functional code)

Output
Enthalpy of formation
Energy barriers
Diffusion constants



As a preliminary step to studying hydrogen storage in carbon, we modeled a hydrogen molecule between two graphitic planes and found that, although there is some electron charge transfer from the graphite to the H_2 molecule, there is no localization potential pinning the hydrogen molecule.

- We saw that any charge transfer in or out of the graphitic planes results in a decrease of the in-plane lattice vector's magnitude.
- From our previous work on doped graphite, we expect the (interplane) c-spacing to diminish with electron charge transfer from graphite to the hydrogen molecule.
- This preliminary step suggests that it may be more fruitful to look at interactions of hydrogen with irregular clusters of doped-carbon.



Conclusions

Both system-level and fundamental material improvements will be required to achieve superior performance of advanced energy storage methods.

- System level issues can easily dominate characteristics and performance of hydrogen storage materials
- Materials improvements will be needed to allow mitigation of the system-level issues
- A comprehensive analytical approach that includes and understanding of the fundamentals could help focus efforts