

Summary Report from
Theory Focus Session on Hydrogen Storage Materials
DOE Hydrogen Program

Assessment of Modeling Needs for Hydrogen Storage

This report provides a summary of feedback from co-organizers, speakers and participants of the Department of Energy's (DOE) **Theory Focus Session on Hydrogen Storage Materials**, held Thursday, May 18, 2006, Crystal City, VA, in conjunction with the DOE Hydrogen Program Annual Merit Review, May 16-19, 2006.

Session co-organizers: Chris Wolverton (Ford), Karl Johnson (University of Pittsburgh), Maciek Gutowski (Pacific Northwest National Laboratory)

Goal of focus session:

Identify critical areas, key barriers and gaps in current theory/modeling approaches for hydrogen storage materials and technologies

Role of modeling and simulation in design of H₂ Storage Materials:

Modeling, theory, and simulation can enhance our understanding of known systems, and enable the design of new materials systems and prediction of their performance. Benchmarking and validation is a key part of modeling and simulation.

Simulations can provide quantitative results, and thus can serve as an alternative to experiments that are too difficult or expensive to perform. Simulations can also extend limited available experimental data into new domains of parameter space. In many cases, prediction of accurate thermodynamic and kinetic data may be accomplished more inexpensively and efficiently by numerical simulations than by accurately measured data.

1. Prediction of Novel Reactions and Materials

Methods for Crystal Structure Prediction:

There are a variety of methods currently available in various stages of development to provide an ability to predict new structures. Each of these methods needs further exploration to test its limitations and strengths:

- "Brute Force" / ICSD searching "rounding up the usual suspects"
- Simpler models formed by integrating out the unessential physics (e.g., electrostatic ordering, force fields...)
- Monte Carlo methods
- Cluster Expansion/Structural Enumeration

Critical gaps are:

- Accurate and efficient methods for global optimization of crystal structures of complex materials for use with accurate methods of calculating crystal binding energies.
- High-quality experimental data on crystal structures for hydrogen storage materials with hydrogens accurately located are required for benchmarking and validation
- Ability to model complex kinetic processes associated with hydrogen release/uptake in hydrides.
- Ability to predict *decomposition* pathways. Even if we can predict the crystal structure of novel hydride materials, it is often non-trivial to predict preferred reaction pathways decomposition in the solid state. Automated methods that can be used for this purpose would be highly beneficial.

2. Thermodynamics of Storage Materials

There are a variety of methods for predicting the thermodynamics of hydrogen storage materials based on electronic structure theory. These range from highly accurate quantum Monte Carlo and molecular orbital (MO) theory based methods such as coupled cluster theory (CCSD(T)) to the more approximate methods such as MP2 and density functional theory (DFT) methods with gradient corrected functionals. High-level molecular orbital methods can be applied to reliably predict the thermodynamics of small (10s of atoms) gas phase species, but cannot at present be applied to condensed phase systems such as solids or solutions. Solid-state systems with strong bonding can be reliably treated with periodic DFT. Problems arise, however, when considering reactions involving both solid-state and molecular species, or when considering weakly bound solids, such as molecular crystals.

Critical gaps are:

- DFT calculations are presently useful for *screening* candidates of hydrogen storage materials; however, DFT accuracy is currently not sufficient to *design* new materials via computation alone. This requires that new functionals be developed that treat non-bonding interactions correctly and all interactions with higher accuracy with a minimum of parameters. Improvements in accuracy over DFT are crucially important for chemical hydrides and for physisorbed systems. More study of "beyond-DFT" methods for the physisorbed systems is crucial. The presented QMC results call into question the quantitative accuracy of many of the DFT predictions of physisorbed systems. Similar results are found for chemical hydride applications in terms of accuracy.
- Highly accurate MO based approaches are computationally too expensive (scaling as N^7 for N basis functions and needing large basis sets) to apply to large systems and cannot be used for solid state predictions. These methods need to be made computationally more efficient and also be developed for the solid state to provide benchmarks for more approximate methods.
- A broad range of systems need to be benchmarked to better understand where standard DFT methods (e.g., LDA/GGA) work acceptably, and where more

accurate methods such as quantum Monte Carlo (QMC) or MO approaches are required. This will require benchmark calculations as described above and additional experimental measurements with small and well-established error limits.

- Linear scaling QMC is a promising tool for studying (physi)sorption binding energies at zero temperature. This method can be used to compute single point energies of systems with hundreds of electrons, which is sufficient for many materials being proposed. This will enable the calculation of interactions, including forces, of weakly-bound systems. The computational efficiency of the method needs to be improved.
- New approaches need to be developed to deal with dynamical properties such as the vibrational motion and hindered motions such as internal rotation. For example, for caged sorption structures, we need to go beyond modeling storage capacity based only on the depth of the well (the binding energy) but also its width. The zero point energy (ZPE) and other vibrational energy components play a substantial role in determining the required binding energy. The temperature dependence of the ortho/para ratio can be important as these structures "feel" quite different potential energy surfaces. We need to analyze possibilities of using Path Integral Monte Carlo approaches for the prediction of the vibrational energies.
- Finite temperature effects are often quite important: DFT-MD simulations are possible, as are DFT phonon calculations of the ZPE. For incremental improvements to accuracy at finite temperature, QMC calculations can be used to "correct" the energies coming out of snapshots from DFT-MD simulations.
- New methods are needed for the prediction of properties in solution to enable improved phase space sampling methods for predicting entropies and vibrational contributions to the enthalpies. Similar approaches are needed for the solid state, especially methods for sampling different unit cells for optimization of structures.

3. Kinetics of Storage Materials

The release/regeneration issues for hydrogen storage systems are at the center of the design of systems for practical use, especially for the transportation sector. Thus, kinetics plays a key role in addition to the need for accurate thermodynamic predictions to obtain the limits at the end points. True H₂ storage materials *design* will require quantitative information about *transition states*, currently *only* readily accessible by computational methods.

Critical gaps are:

- We need more robust potentials and/or faster electronic structure methods. There is a great need for development of the middle ground between fast interatomic potentials and extremely slow but much higher accuracy electronic structure methods. New generations of the tight-binding method (self-consistent charge) and reactive force fields (such as ReaxFF) need to be advanced.
- There is danger in "business as usual" approach, in which we use our intuition to specify (often incorrectly) dynamical pathways and then calculate accurate barrier

heights for these pathways using electronic structure methods. We need improved potential energy surface (PES) sampling techniques which enable us to choose the important regions for sampling.

- Obstacles to the more wide-spread use of accelerated molecular dynamics methods are the difficulty in treating low-barriers and size-scaling issues (PES sampling) for accelerated molecular dynamics
- There is a need to incorporate quantum dynamical effects into accelerated molecular dynamics in order to deal with light elements such as hydrogen. Currently, there are some ideas on how to approach this, but none have been directly tested and are just now being attempted.
- There is a need to extend long time scale methods with the capability to directly use forces and energies from electronic structure methods such as DFT.
- There is a need to enhance the accessibility of long time scale methods by interfacing these methods with existing codes so they can be used by a greater range of modelers.
- There is a need for improved methods which can use the results from atomic scale calculations as input to larger scale models (e.g., complex multi-atom processes are important at the atomic scale, but there is often no good way of building this information into course grained models). Examples of this include kinetic Monte Carlo methods which are being developed for the prediction of complex heterogeneous catalytic systems.

4. Mesoscale Modeling

In spite of its importance, the area of mesoscale modeling in hydrogen storage is virtually unexplored at this point. This will play major fundamental science and practical roles in solid hydrogen storage program and ultimately, it will link the molecular level models (quantum and empirical) to experiments. It will also define the experimental material characterization needs.

- The kinetics and thermodynamics processes of hydrogenation and dehydrogenation of storage media are highly convoluted with each other via the microstructure. Mesoscale modeling will give a great deal of insight into the role of various processes and their microstructure dependence.
- Molecular level models handle unit thermodynamics or kinetic processes and mechanisms. They relate to experimental data only indirectly because of the microstructure sensitivity of the experimental data. Only through mesoscale models it becomes possible to correlate molecular levels with experimental observations.
- Storage media are highly dynamical media due to the phase change processes. Modeling the microstructure changes, with its physical, chemical and mechanical aspects, is a key part of mesoscale modeling.

- Mechanics plays an important role in the phase change processes. It also plays a significant role in kinetics and thermodynamics of the storage media. The mechanical response of storage media is highly microstructure sensitive. Mechanical response and the elasto-chemical interactions in the solid storage media are vital to the overall mesoscale modeling activity.

Appendix: Detailed discussion/feedback from various participants

A core tenet of any modern research program in materials development is the importance of the intimate coupling between accurate electronic structure and kinetic calculations and experimental measurements in which the calculations are used to interpret data and to guide the design of new structures. Over the past decade, major advances have been made in the development of experimental and theoretical tools for chemistry that make it realistically possible to design or optimize the physical and chemical properties of a material system for a specific application. These advances present the opportunity to design new chemical systems for the storage and release of hydrogen for the transportation sector.

Theory, modeling and simulation will play an important role in the design of hydrogen storage systems, especially for chemical and metal hydrides. The goal of any such work is to minimize the amount of expensive experimental work and to more rapidly discover new prototypes and efficient process optimization pathways. For example, first principles computational chemistry approaches on advanced computer architectures can be used to predict the electronic structure of molecules to obtain thermodynamic and kinetic information in support of the design of hydrogen storage materials and of catalysts to effect easy release and addition of H₂. This is especially important because of the cost of making good thermochemical and kinetic measurements and the loss of expertise in these areas. There are a number of important roles that modeling and simulation play in the design of H₂ storage systems. First, modeling, theory, and simulation can enhance our understanding of known systems, for example hydrocarbon-based ones or borane-amines as shown by work in the Chemical Hydrogen Storage Center of Excellence and that of Air Products. Second, it can provide qualitative/quantitative insights into experimental work and guide the choice of which experimental system to study or enable the design of new systems. This is most useful if the simulation has been benchmarked on well-established systems to validate the approach. This shows that there is an important link between the computational and experimental efforts. Third, simulations can provide quantitative results to replace experiments that are too difficult or expensive and can extend limited experimental data into new domains of parameter space. For example, accurate thermochemical and kinetic calculations for the design of new reactions for the regeneration of H₂ storage materials such as NaBH₄ are needed due to missing experimental data. In addition, simulation techniques allow scientists and engineers to explore temporal and/or spatial domains that are not accessible by present experimental methods. For example, it is now possible to explore different chemical reaction pathways not directly accessible by experiment to learn why they are not favorable or to find missing steps in a mechanism. This is critically important in the design of hydrogen

storage systems which are all about improving kinetics of the release and regeneration of the storage system. True H₂ chemical storage materials *design* will require quantitative information about *transition states* for critical reaction processes. Currently, information about transition states, especially geometric and spectral information, is *only* readily accessible by computational methods. The effective use of computation and theory will be needed to meet DOE's aggressive 2010 and 2015 goals for H₂ storage systems, especially for the transportation sector.

The idea of a focus session on theory, modeling and simulation for H₂ storage was very good as it exposed researchers to the types of tools that can be used to address such complicated issues as H₂ storage systems. The session had a substantial amount of breadth at the basic research end ranging from reliable computational methods for small to modest size systems up to much larger systems with a focus in the latter on materials behavior. In future years, the session may also want to include information about computational engineering aspects. For example, how does one evaluate conceptual implementations of chemical H₂ systems to provide an on-board H₂ delivery system including factors such as: thermal integration of the on-board system, on-board water management, hydride stability, fuel cycle efficiency, and life cycle cost? A discussion of how to link engineering and basic science computational efforts would be useful, for example via mesoscale modeling. The session may also want to be extended to include a tutorial about the computational methods and their reliability such as given at the Spring 2006 MRS meeting with respect to H₂ storage system design. This could be used to show how one can answer the following types of questions:

- How reliable are the computational methods that are readily available to the research community?
- What are the computational costs?
- How can they be used for H₂ storage design?
- What types of catalysts can activate and deactivate strong M-H bonds? Can we do this with transition metals that are cheap, i.e., from the first row?
- What are the fundamental rules governing the thermodynamics and kinetics of hydrogen storage/release processes and how can we use this information to optimize the processes?
- What role does the storage material microstructure play and what are the mesoscale modeling needs in hydrogen storage media?

- Need for more robust potentials and/or faster electronic structure methods

There is considerable complexity in many, if not most, of the systems we would like to study with our molecular dynamics (MD) and accelerated dynamics methods to make progress on the hydrogen storage problem. They often involve a mix of metallic, covalent and ionic bonding. Fitting good interatomic potentials to such systems is still more or less a black art, requiring a fair amount of work and custom tailoring for each new system. And there are many systems we would like to study. On the other hand, while accurate electronic structure methods (quantum chemistry, density functional theory, or quantum Monte Carlo) can be applied immediately to any of these systems, they are vastly more computationally expensive, limiting MD time scales to picoseconds

and making accelerated dynamics just barely feasible at the present time. Computers will continue to get faster, but this will offer little qualitative change over the next few years (especially since computer speeds are now starting to fall off of the Moore's law curve).

There is thus a great need for development in the middle ground between fast interatomic potentials and extremely slow electronic structure methods. This might be accomplished by developing new potential fitting methods that are robust and transferrable, perhaps involving forms of interatomic potential that are more complex, and hence more expensive, but which have the flexibility to correctly capture the correct chemistry of the bonding. These potentials will not be as accurate as full electronic structure calculations, but they will be many orders of magnitude faster. Alternatively, this might be accomplished by developing faster, more approximate electronic structure methods. We should not be afraid of these methods being somewhat more approximate. Key results can always be checked using more accurate methods. The far greater danger is to continue in the mode we currently rely on too often, in which we use our intuition to specify dynamical pathways and then calculate accurate barrier heights for these pathways using electronic structure methods. For systems in which we could afford to carry out a true dynamical treatment, we have invariably discovered that the intuitive description was incomplete, at best, and often completely wrong. It is not terribly useful to have accurate barriers for unimportant pathways.

Low-barrier and size-scaling issues for accelerated molecular dynamics (MD)

Accelerated molecular dynamics methods offer a powerful way to reach much longer time scales than direct MD when states are well defined and barriers are high relative to the temperature. There are at least two remaining obstacles that limit their utility for treating the full range of realistic systems and comparing to experiments (for hydrogen storage problems as well as more generally). One is the low-barrier problem. When a system makes most of its transitions over low barriers (as often happens as systems get more complex and realistic), the efficiency of the methods is much lower, limiting the total time that can be reached. In bad cases, the boost factor can be so low that not much is gained relative to conventional MD. Some progress has been made on this problem, but it is possible that much more general and powerful solutions can be found. If so, they could substantially improve the range of utility of these methods.

The other major issue is the size scaling. The methods typically require computational work that scales as the system size to a power greater than unity. Finding ways to achieve linear or near-linear scaling is important, so that systems larger than a few thousand atoms can be treated.

Incorporating quantum effects into accelerated molecular dynamics

Because hydrogen storage systems involve hydrogen, a light atom, quantum effects in the dynamics will be important in some situations –at lower temperatures, for example. It will thus be useful to develop ways to include quantum effects into accelerated molecular

dynamics methods. We believe we know some ways to approach this, but none have been directly tested or even attempted. Approximate treatments will suffice in most situations, where quantum effects are weak. It should then be easy to monitor whether the quantum effects are strong as a simulation proceeds, at which point more accurate (and more expensive) methods can be used instead.

Mesocale modeling needs

A critical part of advancing our understanding of the performance of hydrogen storage media hinges upon the ability to model and predict the complex mechanical-physical-chemical interactions in the storage media. In addition to thermodynamic considerations, the ultimate performance of hydride storage media will be determined by the kinetics of hydrogen uptake and release from these materials and the impact of such processes on the material chemical and mechanical stability. In this regard, microstructural (morphological) aspects of the hydride systems play a decisive role. To put this into perspective, it is important to underline the connection between the kinetics of hydrogenation and dehydrogenation and the microstructural changes in these materials. Hydrogenation takes place by adsorption and accommodation of hydrogen into outer and pore surfaces, followed by dissolution and diffusion into the bulk, which also involves grain boundary diffusion. There are both thermodynamic and kinetic barriers associated with this step of bringing hydrogen into the material, which are all microstructure sensitive. As the concentration of hydrogen in the bulk becomes higher, phase transitions start to take place. These transitions could be single step transitions, e.g., formation of simple hydride, or multiple step transitions such as in complex and some solid chemical hydrides (for example: $\text{NH}_4\text{Al}(\text{or B})\text{H}_4 \rightarrow \text{NH}_3 \text{Al}(\text{or B})\text{H}_3 \rightarrow \text{NH}_2 \text{Al}(\text{or B})\text{H}_2$). Metal hydride systems undergo free volume change that can reach 30% (e.g., in alanates) in certain cases upon phase changes, and in most cases, this free volume change is in the range 10-20%. In the solid state, such free volume changes have great impact on the microstructural thermodynamics and kinetics of almost all elementary processes of hydrogenation. Experiments showed that the materials undergo severe micro-fracture and plastic deformation due to the high stresses induced by such free volume changes. Both phase transition and deformation and fracture processes lead to microstructural (or mesoscopic morphological) changes in the storage medium, which further influence both thermodynamics and kinetics of hydrogen uptake. During the dehydrogenation stage, reverse or new types of phase changes take place and the hydrogen diffuses outward. Similar thermo-mechano-chemical processes take place which contribute to further evolution of the microstructure, and result in additional changes in the thermodynamics and kinetics of hydrogen in the medium because of the effect of lattice strain on the elementary energetics of hydrogen reactions and diffusion processes.

Acknowledgements

Co-organizers:

Chris Wolverton, Ford (affiliation after Jan. 08- Northwestern University)

Karl Johnson, University of Pittsburgh

Maciek Gutowski, Pacific Northwest National Laboratory (new affiliation: Heriot-Watt University, UK)

Contributors:

David Dixon, University of Alabama

Anter El-Azab, Florida State University

Graeme Henkelman, University of Texas at Austin

Kazutoshi Miwa, Toyota CRDL

Susanne Opalka, United Technologies Research Center

Vidvuds Ozoliņš, University of California at Los Angeles

Art Voter, Los Alamos National Laboratory

Andrew Williamson, Lawrence Livermore National Laboratory

For further information, contact:

Dale Koelling, U.S. Department of Energy (Basic Energy Sciences, Office of Science)/

Sunita Satyapal, U.S. Department of Energy (Office of Hydrogen, Fuel Cells and Infrastructure Technologies, Office of Energy Efficiency and Renewable Energy)

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