

Summary Report from DOE Theory Focus Session on Hydrogen Storage Materials

San Francisco, 24 March 2008

In conjunction with the Spring 2008 Materials Research Society Meeting

Assessment of Modeling Needs for Hydrogen Storage

This report provides a summary of feedback from co-organizers, speakers and participants in the Department of Energy's (DOE) "Theory Focus Session on Hydrogen Storage Materials," held Monday, March 24, 2008 (8:30 am to 5:30 pm), Room Golden Gate C3, San Francisco Marriott Hotel, San Francisco, California.

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Goals of Focus Session

- Provide an overview of the state-of-the-art and most recent technical progress in theory and modeling of hydrogen storage from experts in the field
- Identify critical areas, key barriers and gaps in current theory/modeling approaches for hydrogen storage materials and technologies
- Follow up on issues and problems identified in the 2006 Theory Focus Session¹, and identify progress or opportunities in these areas.
- Promote potential theory/modeling research collaborations, identify and reduce duplication, and create and strengthen partnerships

This workshop assessed recent progress in the field of theory, modeling and simulation of hydrogen storage materials. Due to significant advances in the application and development of theoretical and computational techniques, theory has emerged as a reliable tool that can be used to understand the current state-of-the-art hydrogen storage materials and predict exciting new materials with improved thermodynamics and high storage densities. However, key barriers and gaps still exist, and hence further refinement and application of theoretical modeling techniques will be needed to achieve the system performance targets set forth by the DOE technology development programs such as EERE.

¹ Information regarding the first theory focus session held in 2006 in conjunction with the DOE Hydrogen Program Merit Review and Peer Evaluation Meeting can be found in these websites:

http://www1.eere.energy.gov/hydrogenandfuelcells/wkshp_proceedings.html#storage and
http://www1.eere.energy.gov/hydrogenandfuelcells/wkshp_theory_focus.html

Cutting Edge Electronic Structure Methodologies (beyond Density Functional Theory)

The ability to obtain highly accurate hydrogen binding energies is crucial not only for studying known materials, but also for screening and suggesting new candidate hydrogen storage systems. Density-functional theory (DFT) is currently the most popular first-principles method for treating hydrogen-material interactions. The workshop addressed benchmarking state-of-the-art approaches for obtaining accurate energy landscapes, identified problems with the current DFT approaches based on the local-density approximation (LDA) or generalized gradient approximation (GGA), and outlined possible pathways to overcome these problems. Even though the existing DFT techniques seem to work reasonably well for complex metal hydrides, significant improvements in accuracy are required for physisorbed systems and chemical hydrides. Hence, particularly for these types of materials, there is a compelling need to go beyond the current formulations of DFT. This requires that new functionals be developed that treat non-bonding interactions accurately and capture the correct energetics in small molecules and chemical hydrides.

Recent technical progress:

Current DFT implementations have several known deficiencies: local or semi-local forms of electronic exchange and correlation functionals, errors in dispersive (e.g. van der Waals) interactions, incorrect self-interactions, electronic states that are too localized, and kinetic barriers that are too low. There are several high-accuracy, “beyond-DFT” methods, which properly treat the long-range nonlocal exchange and correlation energies that are omitted in LDA and GGA. However, these methods are not yet mature, and the calculations are computationally expensive. Widespread adoption of wave-function-based methods (e.g. coupled cluster methods) faces severe obstacles due to poor scaling with system size. More approximate wave function based methods that exploit locality and exhibit better scaling with system size are not yet ready for general use.

Fixed node diffusion Quantum Monte Carlo (QMC) has emerged as a computationally robust, highly-accurate, and fully correlated approach. QMC exhibits favorable scaling with system size ($\sim n^3$), gives a variational upper bound on the total energy, and several good, well-documented packages (e.g., Casino and QWALK) are available for general use. On the downside, QMC is computationally expensive, and highly accurate calculations for very large systems are challenging due to high levels of statistical noise. Kinetics calculations with QMC are prohibitively expensive and so is the evaluation of forces and vibrational frequencies. These shortcomings limit the applicability of QMC to cases where DFT geometries are reasonable.

Recently, new hybrid DFT methods have been developed that incorporate long-range nonlocal exchange and correlation energy functionals omitted in LDA and GGA. This is currently viewed as one of the most promising and computationally efficient routes to fixing serious deficiencies of LDA/GGA. As an example, the workshop highlighted activity in the area of double-hybrid DFT functionals that are fitted to large, judiciously constructed training sets of atomization and intermolecular interaction energies. These functionals can simultaneously describe the thermochemistry of interatomic bonds and reproduce dispersive van der Waals interactions within a satisfactory degree of accuracy.

Critical gaps:

- There is a need for systematically optimized and tested exchange-correlation functionals that give accurate binding energetics, kinetic barriers, and vibrational thermodynamics for a wide class of hydrogen storage materials. There is also a need for exchange-correlation energy functionals that have intermediate computational cost and accuracy relative to, on one hand, the current DFT functionals (LDA, GGA, B3LYP, etc.) and, on the other hand, highly correlated QMC and wave-function-based methods. These needs are particularly strong for sorbents and chemical hydrides. Further development of physics-based hybrid functionals and orbital-based non-local correlation methods are promising research directions that could prove highly beneficial for treating weak dispersive interactions in sorbents.
- There is a need to develop comprehensive training sets for hybrid functionals to be used in hydrogen storage materials, including data from extended systems. These training sets should add meaningful physics into the functional so that the effects of changing parameters can be understood and controlled.
- There is a need to develop guidelines for choosing between the different quantum chemistry methods and exchange-correlation functionals, and to communicate the physical and chemical reasons for making these choices. For instance, self-interaction is the most serious error in the current LDA/GGA, which must be corrected first. All DFT functionals have parameters, either determined from "known conditions" (which the physics community refers to as "derived"), or by fitting to a training set (which is the chemistry community approach). A systematic testing and comparison of these methodologies is needed.
- There are two main approaches to improving DFT: one focuses on self-interaction and puts priority on the inclusion of sophisticated exact exchange, while the other focuses on the omission of non-local correlation energy. There is a need to develop empirical training set approaches that exploit QMC and CCSD(T) [coupled cluster theory] results and combine both the self-interaction and non-local correlation corrections for bridging the technology gap between DFT and QMC or CCSD(T).
- Though traditional DFT methods seem to work reasonably well for complex and traditional metal hydrides, it still remains to be proven whether the "beyond DFT" methods would provide significantly enhanced accuracy for these solid-state, chemisorbed systems. Also, many of the "beyond-DFT" methods are not currently capable of treating solid-state, periodic-boundary-condition systems.

Kinetics

Recently, through joint efforts of experimental studies and theoretical calculations, several new promising hydrogen storage reactions have been suggested that have the potential to meet the DOE EERE performance targets for on-board storage systems. While the focus of these studies has mostly been on the gravimetric storage capacity and thermodynamics, kinetics will play a key role in the development of next-generation hydrogen storage materials for transportation applications. Fast hydrogen release and regeneration or uptake are crucial, especially in the transportation sector, and have turned out to be extremely difficult to achieve. Improving the kinetics will require quantitative microscopic information about *transition states* and kinetic

barriers to hydrogen release and uptake, so that appropriate catalysts can be chosen to target kinetic bottlenecks. The workshop discussed catalyst design for accelerated hydrogen uptake and release, multi-length scale physics methods, and accelerated molecular dynamics.

Recent technical progress:

Two crucial challenges were identified during the previous 2006 DOE Theory Focus workshop: (1) develop the ability to model complex kinetic processes, and (2) predict reaction pathways of hydrogen release and uptake in complex multicomponent systems.

Since then, significant progress has been achieved on both issues. Unbiased thermodynamic methods for predicting decomposition pathways (e.g., the grand-canonical linear programming approach) have been developed recently. These methods have been used to clarify the expected equilibrium pathways of hydrogen release and uptake in several multicomponent systems, as well as aided in the design of new reactions. Significant progress has been achieved in understanding the kinetic barriers in complex hydrides (in particular, sodium alanate) using judiciously chosen rate processes and configurations (e.g. dissociation of H_2 on Al with and without Ti, bulk diffusion of charged and neutral ionic species, bond energetics). Together with experimental measurements, these techniques have clarified many important aspects of kinetics. For instance, recent theoretical studies have provided quantitative values of activation energies for bulk diffusion of charged and neutral defects in $NaAlH_4$ and have shown that barriers to defect transport are very low, connecting with experimental measurements of mass transport in this prototypical complex hydride. However, new techniques are needed for *unbiased exploration of potential energy surfaces and inclusion of non-intuitive, previously unsuspected rates and processes*.

Direct molecular dynamics (MD) simulations of hydrogen release/uptake processes are currently limited by the time-scale problem. Using first-principles DFT, the limit on simulation length is tens of picoseconds. Classical MD simulations can access hundreds of nanoseconds. In contrast, realistic time scales of hydrogen release reactions are seconds to hours, and are beyond the reach of direct MD techniques. Kinetic Monte Carlo (KMC) methods can go to very long timescales, but require a-priori knowledge (or a “guess”) of all that can possibly occur in the system and therefore can miss important, unexpected events. Thus, the confidence threshold of KMC is hard to determine. Accelerated MD methods (e.g. hyperdynamics, temperature accelerated MD, stochastic MD) were identified as promising techniques for overcoming the time scale problem. For instance, stochastically accelerated MD was highlighted as an accelerated MD method that can speed up simulations by replacing the time wasted in oscillations about local minima and focusing on minima-to-minima dynamics. Boost factors of more than a thousand have been seen, extending the accessible time scale into hundreds of microseconds, sufficient to directly observe isolated hydrogen release events.

Critical gaps:

- The general consensus among the participants was that kinetics is emerging as the most important challenge for theory. There is a need to develop theory and computation to achieve a complete microscopic understanding of the rate-limiting processes for hydrogen storage. The

ultimate goal for the theory is to predict new catalysts that work in other systems. The community needs to generalize the work on the mechanism for Ti doping in NaAlH₄ to systems with higher gravimetric densities and more favorable thermodynamics than sodium alanate, e.g. borohydrides and amides.

- Modeling of the rate of hydrogen release will require a comprehensive study of phenomena on various time and length scales, starting from the energetics and kinetics of bond-breaking and diffusion on the atomic scale, which can be addressed by DFT, to intermediate time- and length-scale simulations of interfacial kinetics and long-time microstructural evolution of the morphology, which has to be addressed on the continuum scale. Modeling the microstructure changes, with its physical, chemical and mechanical aspects, is a key part of mesoscale modeling. In spite of its importance, the area of mesoscale modeling in hydrogen storage remains virtually unexplored.
- Materials problems in hydrogen storage should be studied not only from the catalytic chemistry point of view (as is currently done), but also from the microstructural evolution point of view (e.g., nucleation and growth, coarsening, diffusion). Continuum models of microstructural evolution in these systems would connect MD simulations and microscopic calculations of the kinetic barriers to the large-scale mass transport between the reactants and products. The community needs methods that can study these questions quantitatively and experiments that can differentiate between the different mechanisms to validate theories.
- There is a critical need for accurate, well-controlled experiments that could be used to test, validate, and benchmark theories and calculations. For instance, intermediate species in hydrogenation reactions should be identified, concentration of bulk defects and various activation energies associated with atomic-scale kinetic events should be measured. These experiments must be done on controlled samples that are easier to characterize than ball-milled materials; simple model systems and well-grown crystalline samples are crucial. Such experiments will settle important questions about the location of catalytically active Ti (e.g. bulk, surfaces, interfaces) and the relative roles of equilibrium thermodynamics versus non-equilibrium phenomena in determining the location and concentration of Ti in NaAlH₄.
- Most of the theoretical work addresses select aspects of the sequence of kinetic events involved in hydrogen storage. In the next step, theory needs to address how the proposed mechanisms work for both hydrogenation and dehydrogenation processes and what are the kinetic barriers associated with the complete sequence of events necessary for both types of processes. The effects of imperfect surfaces and interfaces on the kinetics of hydrogen dissociation and diffusion also need to be understood.
- There is a need for sufficiently accurate and efficient empirical potentials that could be used in accelerated MD. Several participants underlined the challenges facing this task due to the complicated nature of bonding in many modern hydrogen storage materials, varying from polar covalent to metallic and long-range dispersive, often all in the same material.
- There is a need for more robust potentials and/or faster electronic structure methods in the middle ground between computationally efficient empirical force fields and demanding yet highly accurate electronic structure methods. Further progress in this area is crucial for increasing the physical accuracy of MD simulations.

- There is a need to extend long time scale methods with the capability to directly use forces and energies from electronic structure methods. Development of DFT-capable accelerated MD methods is a very challenging problem that will need extensive petascale computing resources.
- There is a need to enhance the accessibility of long time scale methods by interfacing these methods with existing codes so a greater range of modelers can use them.
- Molecular dynamics simulations with quantum dynamics of hydrogen remain an unsolved problem. However, the effects of zero point energy (ZPE) on the calculation of kinetic barriers within TST can be treated straightforwardly. Quantum tunneling effects on hydrogen diffusion are expected to be small in most materials at room temperature, but could have a significant effect in low-temperature storage systems.
- Application of better electronic structure techniques may be needed to correct the LDA/GGA “band gap” problem and accurately understand the energetics and kinetics of charged defects in complex metal hydrides.

Thermodynamics

Hydrogen storage materials present challenges to both theory and experiment: synthesizing a material and measuring its crystal structure and properties is difficult; hydrogen positions are difficult to resolve experimentally; hydrogen fits in many sites and ZPE effects are important. The workshop addressed state-of-the-art DFT isotherm calculations and development of DFT-based predictive approaches. It demonstrated that theory has emerged as a reliable tool that can be used to understand the existing hydrogen storage materials and predict exciting new materials with improved thermodynamics.

Recent technical progress:

Significant progress has been achieved in two key areas: (1) determining the crystal structures of new materials and (2) determining the (often non-intuitive) reaction pathways in complex multicomponent hydrogen storage systems.

Crystal structures: Recent years have seen a surge of activity in developing new successful approaches for predicting crystal structures and calculating binding energies. Currently, there are three broad classes of methods:

- Methods that are based entirely on previously observed crystal structures and cannot suggest new structure types (e.g., “brute force” ICSD [Inorganic Crystal Structure Database] searching, data mining)
- Methods that use prior knowledge/intuition of certain structural properties to suggest entirely new crystal structures (e.g., cluster expansion and structure enumeration both assume an underlying lattice type and select relevant degrees of freedom, such as N-H dimer orientations)
- Methods that can suggest new crystal structures and do not need any *a-priori* guesses about structure type [e.g., genetic algorithms, prototype electrostatic ground state (PEGS) search].

Experimental data on structures is being accumulated at a rapid pace, serving as benchmarks and as feedback loops for the development of theoretical methods. Theoretical methods (e.g. ICSD searching, cluster expansion, PEGS) have predicted ground state structures of several new complex hydrides; and in many cases, these predictions have been confirmed by experimental results. There was an extensive discussion of the degree of accuracy that is required of these methods. In particular, accurate prediction of the local structure (e.g. interatomic distances, bond lengths, coordination) can provide sufficient thermodynamic accuracy; while long-range arrangement of ions in the structure has relatively weak secondary effects on the calculated reaction enthalpies, but can have very large effects on the measured diffraction patterns.

Reaction pathways: Even if we can predict the crystal structure of novel hydride materials, it is often non-trivial to predict preferred reaction pathways of hydrogen release from solid-state materials. Automated methods that can be used for this purpose would be highly beneficial. This problem has been essentially solved by the introduction of the grand canonical linear programming technique, which has been recently applied to a multitude of multinary systems and has yielded several new, previously unsuspected hydrogen storage reactions.

Critical gaps:

- 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 treating anharmonic, vibrationally stabilized high-temperature phases of complex hydrides.
- New, efficient computational DFT techniques are needed to study interfaces and surfaces. Knowledge of the interfacial energies would enable quantitative investigations of the nucleation barriers and kinetics of morphological evolution, providing information for continuum-level mesoscale studies. However, due to low symmetry, reconstruction, and lack of knowledge about the microscopic structure, interfacial and surface energetics are difficult to address using the existing general-purpose DFT codes.
- There is a need for new materials and tuning of the properties of existing ones via alloying. Theory needs to make predictions of what is possible in this regard since continuous tuning of complex hydrides is generally not feasible. Both accurate DFT-based and empirical potential-based methods would be very useful for this purpose.
- There is a need to find new ways to incorporate diffraction data into crystal structure prediction and search methods. This would enable better predictions of ground state structures and would facilitate predictions of metastable and/or high-temperature phases by constraining the global energy optimization to structures that are consistent with the measured diffraction patterns.

New 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. The workshop highlighted progress in designing hydride alloys, adsorbents and nanomaterials with potential to

meet the DOE EERE gravimetric and volumetric targets, as well as focused on select innovative concepts.

Recent progress:

Theory is leading the way in proposing new concepts for physisorption-based hydrogen storage. Guidelines for the prediction of thermodynamically correct hydrogen storage reactions have been proposed and applied to design new destabilized reactions based on complex metal hydrides. A fullerene-based nanomaterial with the chemical formula $\text{Ca}_{32}\text{C}_{60}(\text{H}_2)_{92}$ has been predicted to reversibly physisorb 8.4 percent hydrogen by weight. Theoretical studies of the spillover effect on graphene have clarified the hydrogen binding mechanisms and identified the nucleation kinetics of the hydrogen layer as the rate-limiting step for hydrogen uptake.

Critical gaps:

- There was a lively discussion of hydrogen storage in Ca-doped C_{60} . Many workshop participants found it highly improbable that upon cycling one could avoid formation of a very strongly bound CaH_2 phase. Though some modeling of Ca binding to C_{60} and Ca-clustering on C_{60} has been done, these issues have not been addressed in the presence of hydrogen. The modeling is largely relying on the assertion (with little experimental evidence) that Ca bound to a C_{60} molecule will be in a deep kinetic well, and the system will be "kinetically frozen" in this configuration.
- There is a gap between the researchers working on nanostructured sorbents and those working on hydrides. Thermodynamics is the common terminology of choice in the complex hydride community, but is rarely addressed in the sorbent community. The reason for this is that very few, if any of the sorbent nanostructures are thermodynamically stable. The debate over Ca doping of C_{60} clearly reflects such different views. There is an urgent need to establish criteria for down-selecting the predicted sorbent materials based on their kinetic stability.
- Thermodynamic "guidelines" were presented to help guide reactions. Though these were mostly used in complex hydride systems, these rules can be used to help "exclude" unrealistic possibilities in the metal-doped C_{60} type systems as well.
- There is a need to understand and further accelerate the kinetics of hydrogen storage on graphene using the spillover effect. The nucleation mechanism for spillover is predicted to have a very large activation barrier, thus implying that homogeneous nucleation would be difficult/slow in this system. Heterogeneous nucleation is a promising strategy.

Conclusions

The objectives of the 2008 Theory Focus Session for Hydrogen Storage Materials included providing an overview of the state-of-the-art in methods and recent technical progress and identifying critical gaps in current theory/modeling approaches. The main topics included cutting edge electronic structure methodologies, kinetics, thermodynamics and new materials predictions. The session participants identified a number of gaps in methods to enable broader design of improved hydrogen storage materials. These include the following:

- **Electronic Structure Methods:** There is a need for systematically optimized and tested exchange-correlation functionals that give accurate binding energetics, kinetic barriers, and vibrational thermodynamics for a wide class of hydrogen storage materials.
- **Kinetics:** This is emerging as the most important challenge for theory. There is a need to develop theory and computation to achieve a complete microscopic understanding of the rate-limiting processes. The ultimate goal for the theory is to predict new catalysts that work in other systems. Materials problems in hydrogen storage should be studied not only from the catalytic chemistry point of view, but also from the microstructural evolution point of view.
- **Thermodynamics:** 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 treating anharmonic, vibrationally stabilized high-temperature phases of complex hydrides. In addition, new, efficient computational DFT techniques are needed to study interfaces and surfaces.
- **New Materials:** Thermodynamic "guidelines" were presented to help guide reactions. Though these were mostly used in complex hydride systems, these rules may be used to help "exclude" unrealistic possibilities in the metal-doped nanostructured materials.

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