IV.A.4 DOE Metal Hydride Center of Excellence

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Start date: March 2005
Projected End Date: October 2009

Introduction

The DOE Metal Hydride Center of Excellence (MHCoE) consists of eight Universities (Caltech, Carnegie Mellon, Stanford, University of Hawaii, University of Illinois-Urbana Champaign, University of Nevada-Reno, University of Pittsburgh, and the University of Utah), six National Laboratories (Brookhaven National Laboratory [BNL], Jet Propulsion Laboratory [JPL], National Institute of Standards and Technology [NIST], Oak Ridge National Laboratory [ORNL], Sandia National Laboratory [SNL], and Savannah River National Laboratory [SRNL]) as well as three industrial partners (GE Global Research, Hughes Research Laboratory [HRL], and Intematix). SNL is the lead laboratory, providing technical leadership for the center and a center structure to guide the overall technical program and advise the DOE.

The purpose of the MHCoE is to develop hydrogen storage materials and engineering solutions that allow the use of these materials, in a way that satisfies the FreedomCAR Program system requirements for automotive hydrogen storage. In an overall sense, our center is a multidisciplinary and collaborative effort in three general areas, as indicated in Figure 1. At the highest level, the collaborations are divided into three broad areas: mechanisms and modeling (which provide a theoretically driven basis for pursuing new materials), materials development (in which new materials are synthesized and characterized) and system design and engineering (which allow these new materials to be realized as practical automotive hydrogen storage systems). Driving all of this work are the hydrogen storage system specifications outlined by the FreedomCAR Program for 2010 and 2015.

The MHCoE is organized as indicated in Figure 2.

Currently the technical work is divided into five project areas. The purpose of the project areas is to organize the MHCoE technical work along appropriate and flexible technical lines.

Project A (Destabilized Hydrides), led by Greg Olson of HRL. The objective of this project is to develop strategies for reducing hydrogen storage thermal requirements and improve kinetics by destabilizing metal hydrides systems. The technical approach is to alter the thermodynamics of the storage system by destabilizing the metal hydride through alloying, thereby reducing the energy needed to liberate hydrogen from the material, and reducing the desorption temperature. The project aims to enhance kinetics by evaluating nanoengineering approaches towards minimizing the required hydrogen

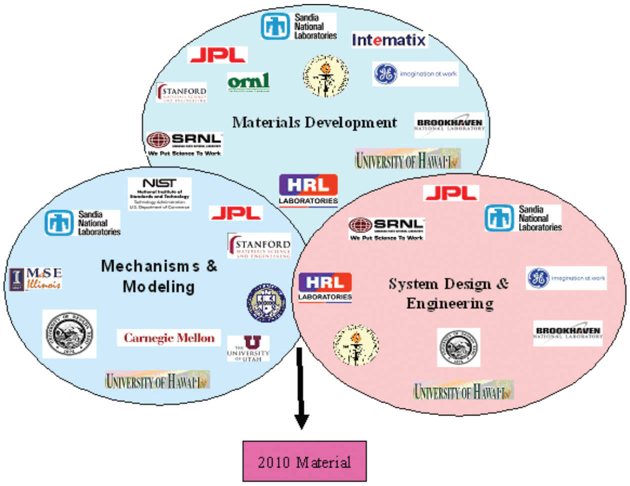

FIGURE 1. MHCoE Collaborations along Broad Technical Areas

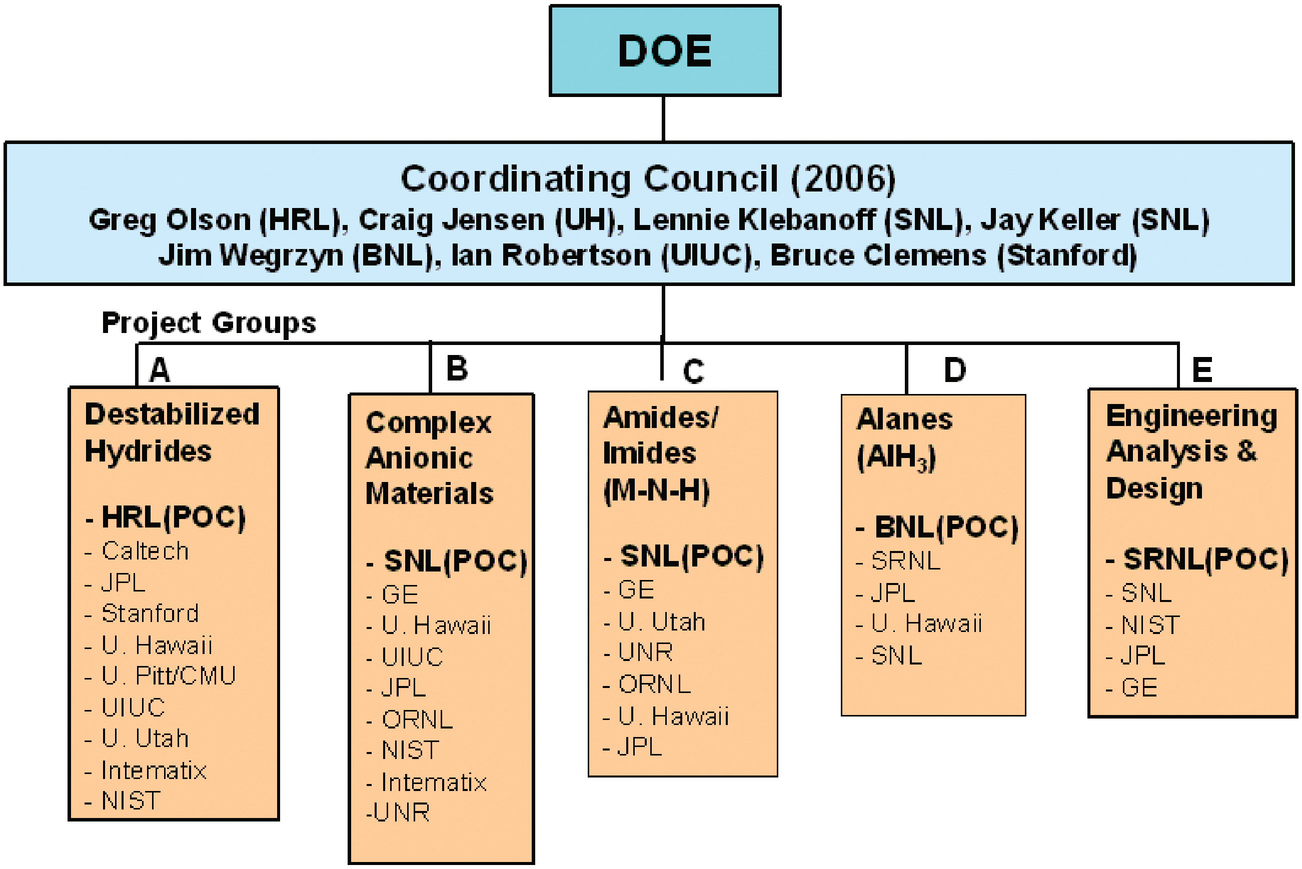

FIGURE 2. Organization of the MHCoE, with Project Areas Given

diffusion distance by decreasing particle size and creating nano-engineered scaffolds.

Project B (Complex Anionic Materials), led by Ewa Ronnebro of SNL. The objective here is to predict and synthesize highly promising new complex hydride materials. The technical approach involves using theory and chemical intuition to select promising target complex hydrides. Candidate materials are then synthesized by high hydrogen pressure sintering, followed by extensive structural and hydrogen sorption characterization.

Project C (Amides/Imides Storage Materials), headed for most of the year by Weifang Luo of SNL but more recently by Zak Fang of Utah. The objective of Project C is to assess the viability of amides and imides (organic materials containing $-NH_2$ and $-NH$ moieties) for onboard hydrogen storage. The technical approach is to reduce thermal requirements of these materials by alloying, understand and elucidate the chemical pathways by which these materials release and absorb hydrogen, and determine the initial engineering issues (thermal cycling expansion) of these materials.

Project D (Alanes), headed by Jim Wegryzyn of BNL. The objective of Project D is to understand the sorption and regeneration properties of Alanes (AlH_3) for hydrogen storage. The technical approach has been to synthesize the various structural forms of AlH_3, and characterize the structure and hydrogen sorption properties of these forms.

Project E (Engineering Analysis and Design), led by Don Anton of SRNL. The objective of Project E is to provide engineering analysis and design supporting DOE system performance goals. The technical approach has been to develop engineering system-level storage models, use theory and modeling to provide target materials properties, perform thermal modeling of candidate hydride materials, and conduct expansion, heat transfer and stress measurements of promising materials.

The activity of the MHCoE is driven by the FreedomCAR Program system targets, with the activity coordinated by use of a milestone tracking chart which has been implemented center-wide. The chart allows progress to be checked against milestones on a quarterly basis, aids planning and tracks technical risk. Our MHCoE milestones roll up to the Multi-Year Research, Development and Demonstration Plan (MYRDDP) milestones.

MHCoE Objectives

Our highest level objectives are as follows:

- To develop new reversible hydrogen storage materials to meet or exceed DOE/FreedomCAR 2010 and 2015 system goals.
- To deliver a 1 kg hydrogen storage system prototype to DOE by 2010.

Technical Barriers

The MHCoE tackles well-defined technical barriers associated with reversible solid-state hydrogen storage systems in which hydrogen is desorbed and re-absorbed on board the vehicle. These barriers are reproduced below from the onboard hydrogen storage section of the MYRDDP:

A. Cost. Low-cost materials and components for hydrogen storage systems are needed, as well as low-cost, high-volume manufacturing methods.

B. Weight and Volume. Materials and components are needed that allow compact, lightweight, hydrogen storage systems while enabling greater than 300-mile range in all light duty vehicle platforms. Reducing weight and volume of thermal management components is required.

C. Efficiency. The energy required to get hydrogen in and out of the material is an issue for reversible solid-state materials. Thermal management for charging and releasing hydrogen from the storage system needs to be optimized to increase overall efficiency.

D. Durability. Materials and components are needed that allow hydrogen storage systems and lifetime of 1,500 cycles and tolerance to fuel contaminants.

E. Refueling Time. There is a need to develop hydrogen storage systems for the refueling times of less than three minutes for 5 kg of hydrogen, over the lifetime of the system. Thermal management during refueling is a critical issue that must be addressed.

G. System Life Cycle Assessments. Assessments of the full lifecycle, costs, efficiency, and environmental impact for hydrogen storage systems are lacking.

Technical Targets Addressed by MHCoE

While all of the targets detailed in the DOE MYRDDP will be addressed, our main emphasis initially focuses on the material requirements, specifically the DOE specifications for specific energy density (2.0 kWh/kg [2010], 3.0 kWh/kg [2015]) and volumetric energy density (1.5 kWh/L [2010], 2.7 kWh/L [2015]).

Selected MHCoE Highlights for FY 2006

- Partial reversibility demonstrated for $LiBH_4$ destabilized with MgF_2, MgS, and MgSe; gravimetric capacity: 5.5-7.6 wt%, T (1 bar-calculated) 70-170°C. Results show that destabilization by alloy or compound formation is a promising approach for overcoming thermodynamics limitations in light-metal systems. However, the experimental temperatures are much greater than calculated T(1 bar) values – implying that the systems are kinetically limited. (HRL, Project A)
- Significantly improved sorption kinetics demonstrated for $LiBH_4$ incorporated into nanoporous carbon scaffold structures. Dehydrogenation temperature lowered by ~100°C and cycling capacity (reversibility) improved compared to $LiBH_4$ in non-porous carbon host. Results indicate this is a promising approach for addressing the kinetics challenges in reversible light metal hydride systems. (HRL, Project A)
- Catalysts were successfully synthesized in combinatorial fashion onto Mg_2Si, proving the feasibility of the combinatorial method. No effective catalysts were identified during initial screening for Mg_2Si hydrogenation, suggesting a high barrier for the reaction. (Intematix, Project A)
- Solid state nuclear magnetic resonance (NMR) has demonstrated its usefulness for characterizing new hydrogen-storage materials investigated by the MHCoE. Distinct Al sites have been identified from the ^{27}Al magic angle spinning nuclear magnetic resonance (MAS-NMR) spectra and discovered unexpected new phases (e.g., $Li_xSi_yH_z$) and incomplete reversibility of phase conversion (e.g., $LiBH_4$-MgH_2). (JPL, Project A)
- We have provided a proof-in-principle that we are able to compute vapor pressures (van't Hoff plots) for hydride reactions, including destabilized hydrides. This should prove useful for estimating the potential usefulness of a given reaction scheme, beyond the simple reaction enthalpy approach. (U. Pittsburgh and Carnegie Mellon, Project A)
- First-principles-based electronic-structure and thermodynamic calculations of the destabilized reaction $LiBH_4 + MgH_2$ were completed. van't Hoff plots were predicted and revealed that assessed latent heat is not the true enthalpy of reaction due to the affect of assessing discrete data and slopes on van't Hoff plot. The work also showed the importance of rotational modes in these molecular solids. (U. of Illinois at Urbana-Champaign, Project A)
- Anelastic spectroscopy has proven to be a powerful tool for the detection of the hydrogen containing point defects whose generation is greatly promoted in the Ti-doped $NaAlH_4$. The observation of an isotopic shift in the low temperature spectrum

$NaAlD_4$ provides direct evidence that the defects in the hydride are a hydrogen containing species. (U. Hawaii, Project B)

- In FY 2006 a very robust metal hydride discovery approach was made with a demonstrated combinatorial/high-temperature shift (HTS) methodology and a unique in situ x-ray diffraction (XRD) apparatus. Together with up-front theoretical analysis and rigorous pressure-composition-temperature (PCT) tests and mechanistic understanding, the general approach will accelerate metal hydride discovery. (GE, Project B)
- A bialkali alanate, K_2LiAlH_6, was synthesized and characterized in the space group *R*-3*m* (no. 166) being isostructural with the high-temperature form of K_2LiAlF_6. *Ab-initio* total energy calculations verified the Rietveld refined structure. Investigations of hydrogen storage properties revealed that desorption starts at 200°C, but absorption starts at 320°C resulting in 2.5 wt% reversible hydrogen capacity. (SNL Project B)
- A Monte Carlo-based method was developed which allows crystal structures to be generated by minimizing the electrostatic energy of a combination of alkali or alkaline earth metals with negatively charged anions. The procedure is rapid, and yields results equivalent to, or better than, database structure searching. (SNL, Project B)
- Thermodynamic modeling efforts we have revealed several promising consequences of reducing the dimensions of metal hydride systems into the nano-scale regime. When the increasingly dominant surface energy effects are taken into account, the thermodynamics and hydrogen storage properties of materials are significantly altered (Stanford, Projects B and C).
- A new reaction of lithium amide with lithium hexahydroaluminate was discovered that yields 7 wt% reversible hydrogen storage capacity at <300°C, which hence has a very high potential as a storage material. Comprehensive kinetics characterizations using PCT instrumentation are currently under way. (Utah, Project C)
- Extrinsic pressure cycling using industrial grade hydrogen was conducted on amide/imide system (baseline material) and a comparison between the 1^{st} and $1{,}101^{st}$ cycle shows a 2.3 wt% hydrogen loss. The characterization tests show that the hydrogen loss can be attributed to formation Li_2O and other undesirable phase due to cycling. (U. Nevada-Reno, Project C).
- Detailed chemical mechanism for hydrogen uptake and release determined for the ($2LiNH_2 + MgH_2$) storage system (5.5 wt%). Ammonia concentration in released hydrogen gas measured to be 280 ppm at the desorption temperature of 200°C. (SNL, Project C)
- Decomposition thermodynamics of α, β and γ-AlH_3 were measured and used to predict the H_2 pressure required to re-hydride the spent Al ($P > 10^5$ bar). Based on these results a no-go decision was given on direct gas re-hydriding of spent Al. Three polymorphs of AlH_3 (α, β, γ) were prepared that meet the DOE fuel flow target of 1.0 g H_2/s (50 kW fuel cell) at a temperature of 112 °C. (BNL, Project D)
- Experimental facilities were constructed and validated to measure, transport properties and expansion forces for complex hydrides. We also developed a systems analysis tool for engineering simulations of heat and mass transport in solid state materials. This model is linked to Simulink to allow dynamic simulations in the future. (SRNL and SNL, Project E)

Acknowledgements

It is our pleasure to acknowledge funding for the MHCoE from the DOE Hydrogen, Fuel Cells and Infrastructure Technology Program (HFCITP).