IV.A.5 DOE Metal Hydride Center of Excellence

Lennie Klebanoff (Director, Primary Contact),
Jay Keller (Sandia Hydrogen Program Manager)
Sandia National Laboratories (SNL)
Mail stop 9161, P.O. Box 969
Livermore, CA 94551
Phone: (925) 294-3471; Fax: 925-294-3231
E-mail: lekleba@sandia.gov

Partners:

- Brookhaven National Laboratory (BNL)
- California Institute of Technology
- Carnegie Mellon University
- General Electric-Global Research
- HRL Laboratories, LLC
- Intematix Corp.
- Jet Propulsion Laboratory (JPL)
- National Institute of Standards and Technology (NIST)
- Oak Ridge National Laboratory (ORNL)
- Savannah River National Laboratory (SRNL)
- Stanford University
- University of Hawaii at Manoa
- University of Illinois at Urbana-Champaign (UIUC)
- University of Nevada, Reno
- University of Pittsburgh
- University of Utah

DOE Technology Development Manager:
Ned Stetson
Phone: (202) 586-9995; Fax: (202) 586-9811
E-mail: Ned.Stetson@ee.doe.gov

DOE Project Officer: Paul Bakke
Phone: (303) 275-4916; Fax: (303) 275-4753
E-mail: Paul.Bakke@go.doe.gov

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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, Jet Propulsion Laboratory, National Institute of Standards and Technology, Oak Ridge National Laboratory, Sandia National Laboratories, and Savannah River National Laboratory) as well as three industrial partners (GE Global Research, HRL Laboratories, 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.

Currently the technical work is divided into five project areas (see Figure 2). The purpose of the project areas is to organize the MHCoE technical work along appropriate and flexible technical lines.

Project A (Destabilized Hydrides) is led by Ian Robertson of UIUC. 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

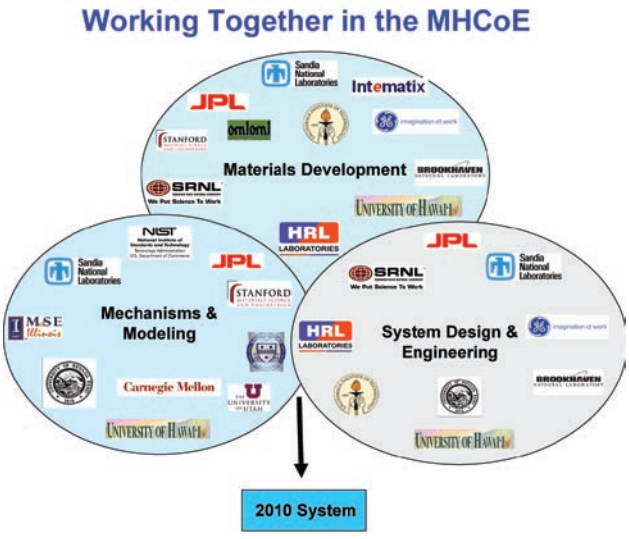

FIGURE 1. MHCoE Collaborations in Broad Technical Areas

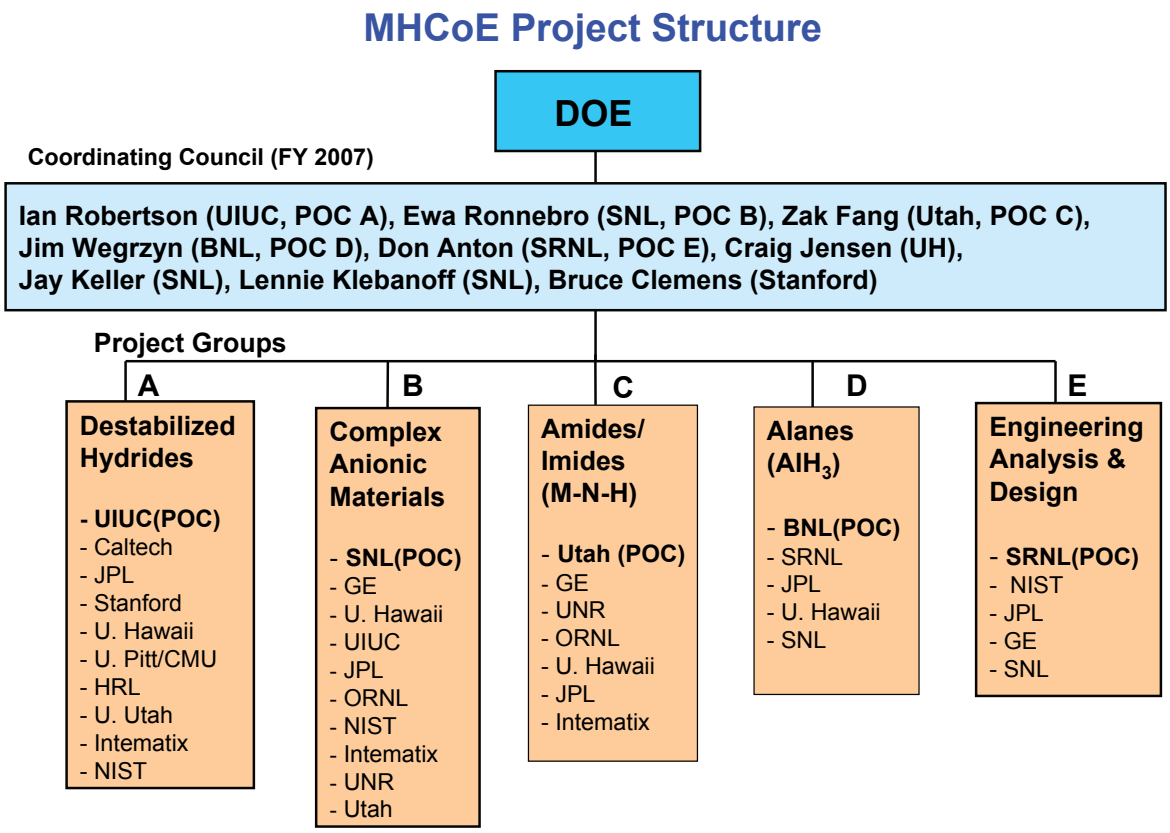

FIGURE 2. Organization of the MHCoE with Project Areas Indicated

aims to enhance kinetics by evaluating nanoengineering approaches towards minimizing the required hydrogen diffusion distance by decreasing particle size and creating nano-engineered scaffolds.

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

Project C (Amides/Imides Storage Materials) is led by Zak Fang of the University 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) is headed by Jim Wegrzyn 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. More recently, studies have demonstrated that complexation of AlH_3 can lead to a more reversible hydrogen storage system.

Project E (Engineering Analysis and Design) is 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 onboard 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 in 2010, 3.0 kWh/kg in 2015) and volumetric energy density (1.5 kWh/L in 2010, 2.7kWh/L in 2015).

Selected MHCoE Technical Highlights for FY 2007

During FY 2007, the MHCoE published 62 papers (20 of these collaborations between MHCoE partners) in the leading journals of chemistry, physics, materials science and crystallography. In addition, MHCoE scientists delivered 87 talks at national and international meetings, and filed 10 patent applications. MHCoE scientists are professional leaders in the general field of hydrogen interactions with materials. MHCoE scientists Craig Jensen (Hawaii), Terry Udovic (NIST), and Bob Bowman (JPL) were the co-chairs and organizers for MH2006, which is the major international venue for all metal hydride research. There were nearly 360 participants from across the world, including many from MHCoE, with over 150 papers being published in the Journal of Alloys and Compounds as the MH2006 Proceedings.

Below we present selected highlights from the MHCoE technical work in FY 2007. Please consult the partner's individual annual reports (following) for more details.

- Studies have shown that nanoconfinement of $LiBH_4$ in carbon aerogel increases the dehydrogenation rate by 50 times. Mg has also been incorporated in carbon aerogel and has shown fast hydrogen exchange rates (HRL, Project A).
- Material combinations among all known stoichiometric metal hydride compounds have been screened by combining a large collection of first principles calculations with a thermodynamic optimization method. This process has identified a number of material combinations predicted to have attractive properties (University of Pittsburgh/ Carnegie Mellon University, Project A).
- New isomorphic Li_4Si_2H and Li_4Ge_2H phases were discovered and characterized by neutron scattering methods and first-principles calculations. All H atoms in the orthorhombic structures are located in identical, Li_6-defined, corner-shared octahedra separated by sheets of zigzagging Si or Ge chains (NIST, Project A).
- A modified Deal-Grove model was developed and shown to account for the rate of hydride growth in epitaxial Mg films. The epitaxial relationships at the MgH_2 /Mg interface, as well as the degree of structural order, were measured by X-ray diffraction (XRD) (Stanford, Project A).
- Used ab-initio theory to successfully predict a high-T $LiBH_4$ phase (relevant phase for H uptake) that correctly incorporates non-harmonic vibrations and effects arising from BH_4 rotations. We also found simple mode-counting can be used to determine accurate transition enthalpies (UIUC/SNL, Project A).

- Demonstrated utility of combinatorial/high throughput approaches to catalyst discovery by identifying and confirming Mn as an improved catalyst for MgH_2 + Si dehydrogenation (Intematix/ HRL, Project A).
- Successfully prepared $Ca(BH_4)_2$ from its decomposition products (CaB_6 + $2CaH_2$ +10 H_2) by sintering at 700 bar and 400°C, without forming by-products. Reversibility demonstrated using catalysts (SNL, Project B).
- Demonstrated synthetic capability and *in situ* diagnostics for micro hot-plate technology. Demonstrated synthesis of $NaAlH_4$ and MgH_2, and quantified sensitivity of *in situ* H_2 detection, differential scanning calorimetry diagnostics (SNL, Project B).
- Discovered new anionic Mn and Zr borohyride complexes. These materials were found to release hydrogen at temperatures at or below 150°C (U. Hawaii, Project B).
- Monte Carlo Theory technique improved to calculate accurate ground state structures. Technique was validated and has led to the discovery of several new borohydride materials (SNL, Project B).
- $Mg(BH_4)_2$ and the new compounds $Mg(BH_4)_2(NH_3)_2$ and $Mg(BH_4)(AlH_4)$ were synthesized, and characterized by *in situ* XRD. These materials were found to release >10 wt% hydrogen at moderate temperatures (GE, Project B).
- Conducted the first studies of alanate/amide mixtures. The synthetic and nuclear magnetic resonance studies indicate that the reactions between lithium alantes ($LiAlH_4$, and Li_3AlH_6) and amides ($LiNH_2$ and $Mg(NH_2)_2$) lead to new reversible hydrogen storage materials (University of Utah/JPL, Project C).
- MHCoE theory predicts that LiMgN can potentially be used as a solid hydrogen storage material. Experiments confirm that LiMgN can be reversibly hydrogenated and stores up to 8 wt% H_2 at temperatures below 250°C (University of Pittsburgh/ Carnegie Mellon University/University of Utah, Project C).
- Successfully synthesized the aluminum hydride adduct of triethylenediamine (AlH_3-TEDA) from activated aluminum powder at a hydrogen pressure of <35 bar and temperatures below 100°C. The reaction is reversible, suggesting that the reversible hydriding of aluminum metal should no longer be considered an insurmountable obstacle for using aluminum hydride as a hydrogen storage material (BNL, Project D).
- Succeeded in electrochemically recharging Al to AlH_3 on the surface of an aluminum electrode in a non-aqueous electrochemical cell. Experiments are underway to further identify the mechanism and intermediate reaction steps in order to minimize the voltage and current required for alane formation (SRNL, Project D).
- Demonstrated that the hydrogen release rate of 100-200 nanometer sized α-AlH_3 particles meet DOE's fuel full delivery target of 0.2 g-H_2/kw-sec at temperatures from 110 to 115°C. Although AlH_3 is thermodynamically unstable at ambient temperature and pressure conditions, it can be made kinetically stable by controlling its size and surface coatings (BNL, Project D).
- Completed a model study of a high-pressure, metal hydride hybrid tank. The analysis revealed the effects of storage tank construction material, operating pressure, media gravimetric density and void fraction on system gravimetric and volumetric storage densities (SRNL, Project E).

Acknowledgements

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