IV.A.1a DOE Metal Hydride Center of Excellence

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- Jet Propulsion Laboratory (JPL)
- National Institute of Standards and Technology (NIST)
- Oak Ridge National Laboratory (ORNL)
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- Sandia National Laboratories (SNL)
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- University of Hawaii at Manoa (UH)
- University of Illinois at Urbana-Champaign (UIUC)
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Introduction

The DOE Metal Hydride Center of Excellence (MHCoE) consists of 10 universities (Caltech, Georgia Institute of Technology, Stanford, University of Hawaii, University of Illinois at Urbana-Champaign, University of Nevada, Reno, University of New Brunswick, University of Pittsburgh, Ohio State University 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 two industrial partners (HRL Laboratories, United Technologies Research Center). 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 properties 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 with the collaborations 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 organization of the MHCoE during the past year is show in Figure 1.

During the past year, the technical work was divided into four 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) was led by Prof. Bruce Clemens, Stanford University. 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. Project A also aims to enhance kinetics by evaluating nanoengineering approaches to minimizing the required hydrogen diffusion distance by decreasing particle size and creating nano-engineered scaffolds.

Project B (Complex Anionic Materials) is led by Prof. Craig Jensen (University of Hawaii). 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. A particular focus in Fiscal Year 2009 has been on borohydride materials.

Project C (Amides/Imides Storage Materials) is led by Prof. 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, respectively) for onboard hydrogen storage. The technical approach is to reduce thermal

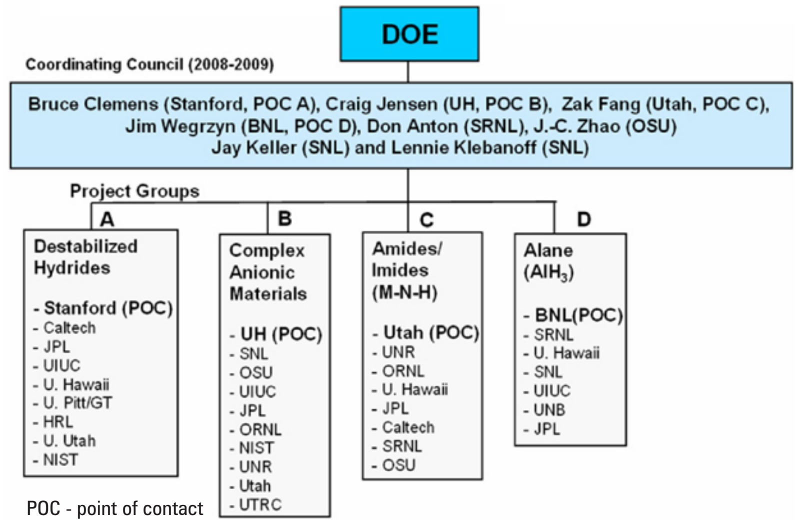

FIGURE 1. Organization of the MHCoE, with Project Areas

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) of these materials.

Project D (Alane, AlH_3) is headed by Dr. Jim Wegrzyn of Brookhaven National Laboratory. The objective of Project D is to understand the sorption and regeneration properties of alane (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. The emphasis in FY 2009 has been on regenerating AlH_3 from Al, using solution-based, electrochemical, and supercritical fluid methods.

In addition to these formal "Projects", we have three working subgroups in the MHCoE. The MHCoE Theory Group (TG) is coordinated by Dr. Mark Allendorf (SNL), and makes use of first-principles methods to predict new materials and their thermodynamic properties, and suggests new directions for experimentalists and interpretation of their results. The TG consists of researchers at five institutions: SNL, Pitt/GT, UIUC, NIST and UTRC. To make maximum use of the different areas of expertise, joint TG efforts are guided by SNL not only in terms of technical direction, but also to ensure that TG efforts are complementary and have an effective synergism with experimentalists.

A second working group in the MHCoE is the "Additive Screening Group". This group, coordinated by Dr. Eric Majzoub (University of Missouri-St. Louis, on leave from SNL) examines the effects of catalysts and other additives on the kinetic and thermodynamic properties of metal hydrides. The group makes use of MHCoE kinetics stations, Sieverts apparatus, and pressure-concentration-temperature instruments to screen many catalysts and additives for their effects on hydrogen desorption temperature, kinetics of adsorption/desorption, and material reversibility. This group involves almost all experimentalists in the MHCoE.

The third working group is the "Amine-Boro Complex" working group, led by Prof. J.-C. Zhao of Ohio State University. Recently, Prof. Zhao has shown that ammonia can complex with $Mg(BH_4)_2$ to produce an amine-boro complex that releases hydrogen at substantially lower temperature than $Mg(BH_4)_2$ alone. This finding has spawned a larger effort in such materials within the MHCoE, activity which is coordinated by the Amine-Boro Complex working group.

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MHCoE Objectives

Our highest level objective is to:

- Develop new reversible hydrogen storage materials to meet or exceed DOE/FreedomCAR 2010 and 2015 system goals.

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 Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

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 a lifetime of 1,500 cycles with 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 Multi-Year Research, Development and Demonstration Plan will be addressed, our main emphasis initially focuses on the DOE specifications for system specific energy density (2.0 kWh/kg [2010], 3.0 kWh/kg [2015]) and system volumetric energy density (1.5 kWh/L [2010], 2.7kWh/L [2015]). These targets, in an overall way, drive our "down-select" process for materials. The procedure used to select materials for further study has been documented in the following report submitted to DOE:

> "Materials Go/No-Go Decisions Made Within the DOE Metal Hydride Center of Excellence (MHCoE)," L.E. Klebanoff, October 5, 2007, Summary report posted on DOE Hydrogen Storage Website: http://www1.eere.energy.gov/hydrogenandfuelcells/hydrogen_publications.html#h2_storage

Selected MHCoE Technical Highlights for FY 2009

During the past year, the MHCoE has published 61 papers (26 of these collaborations between MHCoE partners) in the leading journals of chemistry, physics, materials science and crystallography. In addition, MHCoE scientists delivered 71 talks at national and international meetings, and filed five patent applications. MHCoE scientists are professional leaders in the general field of hydrogen interactions with materials.

Below we present selected highlights from the MHCoE technical work over the period 3/2008-6/2009. Please consult the partner's individual annual report (following) for more details.

MHCoE Technical Highlights

1. Developed capability to include important gas-phase species in phase equilibrium calculations for H_2 release from $LiNH_2$, $LiBH_4$/C (SNL, Pitt, GT).
2. Synthesized pure LiMgN, found ΔH desorption to be ~20–30 kJ/mole H_2, in overall agreement with MHCoE theory (Utah).
3. Found that slurry AlH_3 H_2 release rates are greater than for AlH_3 alone (BNL).
4. Achieved full destabilized system ($LiBH_4/MgH_2$) in C-aerogel (HRL).
5. Achieved breakthrough in electrochemical regeneration of AlH_3, producing gram quantities of high purity AlH_3 with high H_2 content (SRNL).
6. Found that discharged $LiAlH_4$ (LiH, Al[Ti]) can be conveniently regenerated at room temperature in 100 bar of Me_2O/H_2 (UNB, UH).
7. Demonstrated high loading of $NaTi(BH_4)_4$ in SiO_2 aerogel, with the aerogel improving hydride stability (UTRC, Albemarle).
8. Found a procedure that allows $Mg(BH_4)_2$ to reverse at 700 bar H_2, 350°C (UH, SNL).
9. Advanced our understanding of $MxB_{12}H_{12}$ (M = Li, Na, Ca, Mg) compounds, which are important intermediates during H_2 release from borohydrides (NIST, OSU, SNL, Caltech/JPL).
10. Discovered a liquid phase organometallic route to incorporating MgH_2 into a C-aerogel, and observed a concomitant 60x improvement in H_2 desorption rate (UH, HRL).
11. Successfully synthesized AlB_4H_{11}, found it to release ~8 wt% hydrogen at 250°C, and observed partial reversibility under mild conditions (200°C, 5 hours at 90 bar H_2) (OSU, ORNL, Caltech, JPL).
12. Developed a quartz-crystal microbalance chamber that is able to characterize P_{eq} in very thin films exposed to hydrogen. Facility will allow a determination if size reduction influences thermodynamics in thin films and islands (Stanford).
13. Combined state-of-the-art scanning transmission electron microscopy and reaction theory to reveal $Ca(BH_4)_2$ reaction mechanism (UIUC).
14. Successfully determined the effect of various gaseous impurities (O_2, CO, H_2O, CH_4, NH_3) in ultra-high purity hydrogen on the cycling behavior of $LiNH_2$. The study simulates the filling of hydrogen in a

future hydrogen gas station where these gases are expected to have ppm levels of impurities (UNR).

Awards and Honors

1. Jay Keller, the MHCoE Deputy Director and Sandia Hydrogen Program Manager, received the 2009 "DOE Hydrogen Program Special Recognition Award" for years of outstanding contributions to the DOE Hydrogen Program.

2. Jason Graetz, Brookhaven National Laboratory, received a 2009 DOE Presidential Early Career Award for Scientists and Engineers (PECASE). The PECASE award is the highest honor bestowed by the United States government on outstanding scientists and engineers beginning their independent careers.

3. Ian Robertson, University of Illinois at Urbana Champaign, was elected a "Fellow of the Society" by the Board of Trustees of ASM International. Dr. Robertson was cited "for pioneering studies using time-resolved transmission electron microscopy to study metal deformation processes in agressive environments, as well as production and annihilation of defects."

4. Don Anton, Savannah River National Lab, was also elected a "Fellow of the Society" by the Board of Trustees of ASM International. Dr. Anton was cited for "significant and sustained contributions to materials science and technology in the areas of fatigue, superalloys, intermetallics and hydrogen storage materials and systems."