IV.A.1a Five-Year Review of Metal Hydride Center of Excellence

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Start Date: March 2005
End Date: October 2010

Introduction

The DOE Metal Hydride Center of Excellence (MHCoE) comprises 10 universities (Caltech, Georgia Institute of Technology, Stanford, University of Hawaii, University of Illinois-Urbana Champaign, University of Nevada-Reno, University of New Brunswick, University of Pittsburgh, The 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) and two industrial partners (HRL Laboratories, and United Technologies Research Center). SNL is the lead laboratory, providing technical leadership for the Center and a structure to guide the overall technical program and to advise the DOE.

The purpose of the MHCoE is to develop hydrogen storage materials with engineering properties that allow the use of these materials in a way that satisfies the DOE/FreedomCAR Program system requirements for automotive hydrogen storage. The Center is a multidisciplinary and collaborative effort with technical interactions divided into two broad areas: 1) mechanisms and modeling (which provide a theoretically driven basis for pursuing new materials) and 2) materials development (in which new materials are synthesized and characterized). 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. The four areas are summarized below.

Project A (Destabilized Hydrides) is led by Prof. Bruce Clemens, Stanford University. The objective of this project is to controllably modify the thermodynamics of hydrogen sorption reactions in light metal hydrides using hydride destabilization strategies. The technical approach involves altering the thermodynamics of the metal hydride by forming a stable alloy in the dehydrogenated stage. This effectively destabilizes the hydride, thereby reducing the energy

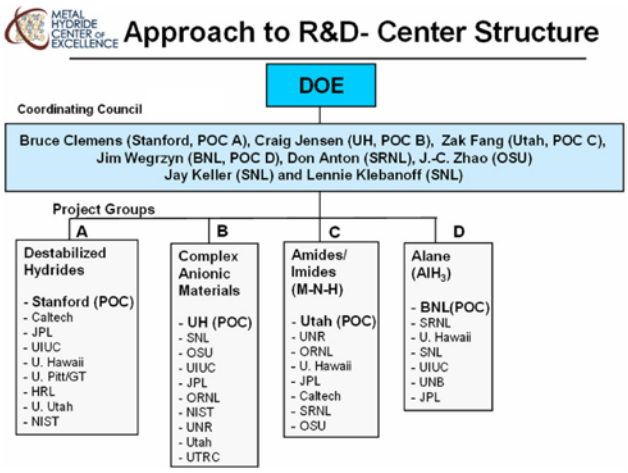

FIGURE 1. Organization of the MHCoE, with Project Areas Given

needed to liberate hydrogen from the material, and reducing the desorption temperature. Project A also aims to enhance kinetics by evaluating nanoengineering approaches to minimize the required hydrogen diffusion distance by decreasing particle size and by incorporating the metal hydride reactants in nano-engineered scaffolds.

Project B (Complex Anionic Materials) is led by Prof. Craig Jensen (UH). The objective 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 the past year 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 (inorganic materials containing–NH_2 and–NH moieties, respectively) for onboard hydrogen storage. The technical approach is to reduce thermal requirements of these materials by alloying, to understand and elucidate the chemical pathways by which these materials release and absorb hydrogen, and to determine the initial engineering issues (thermal cycling) of these materials.

Project D (Alane, AlH_3) is headed by Dr. Jim Wegrzyn of BNL. The objective of Project D is to understand the sorption and regeneration properties of 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 the past year has been on regenerating AlH_3 from Al, using solution-based and electrochemical methods. Project D also examines the properties and reversibility of $LiAlH_4$.

In addition to these formal "Projects", a Theory Group (TG), coordinated by Dr. Mark Allendorf (SNL), supports all of the experimental efforts in the Center. The TG makes use of first-principles methods to predict new materials and their thermodynamic properties, and suggests new directions for experimental investigations and interpretation of results. The TG consists of researchers at five institutions: SNL, U. 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 synergy with the experimental efforts.

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 for practical, on-board storage system applications. These barriers are reproduced below from the onboard Hydrogen Storage section of the Multi-Year Research, Development and Demonstration Plan (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 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 MYRDDP are addressed, our main emphasis has been 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 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 Fiscal Year (FY) 2010

During the past year, the MHCoE has published 65 papers (29 of these collaborations between MHCoE partners) in the leading journals of chemistry, physics, materials science and crystallography. In addition, MHCoE scientists delivered 76 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.

Selected highlights from the MHCoE technical work over the period March 2009 to June 2010 are presented in the following. We point out that the five-year scheduled lifetime of the MHCoE ends in 2010. Please consult the annual reports from individual MHCoE partners for specific details about technical activities in 2010, and the MHCoE final report which covers the five-year history of the Center.

MHCoE Technical Highlights (March 2009 to June 2010)

1. Five distinct pathways were identified for forming AlH_3 adducts from H_2 + Al, thereby increasing prospects for AlH_3 regeneration. (BNL)
2. An electro-catalytic additive was discovered that increased the rate of electrochemical production of alane. (SRNL)
3. A highly efficient, low-temperature and low-pressure method to regenerate $LiAlH_4$ from (LiH + Al[Ti]) using dimethyl ether was developed. (UH and UNB)
4. The cycling capacity of $LiNH_2$ was increased to 10 wt% by introducing 20% nitrogen into the hydrogen gas phase. (UNR)
5. The first example of "kinetic coupling" in the $LiBH_4/Mg_2NiH_4$ destabilized system was discovered. The ΔH (15K J/moleH_2) and ΔS (62 J/moleH_2K) are the lowest reported so far for a reversible system. (HRL)
6. The structure of the important intermediate $MgB_{12}H_{12}$ in $Mg(BH_4)_2$ storage reactions was established by neutron vibrational spectroscopy studies. (NIST)
7. The rate of hydrogen release from $Mg(BH_4)_2$ was dramatically increased by adding $TiF_3/ScCl_3$. (SNL)
8. The rate of hydrogen absorption kinetics for the $2LiNH_2 + MgH_2$ system was increased by introducing KH, confirming prior work by P. Chen. (SNL)
9. The hydrogen desorption kinetics of $Ca(BH_4)_2$, and to a lesser extent $Mg(BH_4)_2$, were enhanced by incorporating the metal hydrides into a C-aerogel. (UTRC, UH)
10. Mild conditions ($<200^oC$, <100 atm) have been found for the reversible partial (2.4 wt%) dehydrogenation of $Mg(BH_4)_2$, which circumvents the unwanted formation of $Mg(B_{12}H_{12})$. Analogous effects are seen for $LiSc(BH_4)_4$, $NaSc(BH_4)_4$ and $KSc(BH_4)_4$. (UH)

Special Recognitions & Awards

1. The MHCoE received a DOE Hydrogen Program 2010 "Special Recognition Award," In Recognition of Outstanding Contributions to the Department of Energy." This award was made June 8, 2010.

2. DOE Hydrogen Program Research Award was given to Ragaiy Zidan for his Electrochemical Studies of Alane Regeneration. The award was made June 8, 2010.

Acknowledgements

It is our pleasure to acknowledge funding for the MHCoE from the DOE Fuel Cell Technology Program.