INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 38 (2013) 4533–4576

Available online at www.sciencedirect.com

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5 Years of hydrogen storage research in the U.S. DOE Metal Hydride Center of Excellence (MHCoE)

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Keywords:
Hydrogen storage materials
Complex metal hydrides
Borohydrides
Amides
Alane
Destabilized hydrides

ABSTRACT

This report summarizes the 5-year R&D activities within the U.S. Department of Energy Metal Hydride Center of Excellence (MHCoE). The purpose of the MHCoE was to conduct highly collaborative and multi-disciplinary applied R&D to develop new reversible hydrogen storage materials for light-duty vehicles. The MHCoE combined three broad areas: (a) mechanisms and modeling, which provided a theoretically driven basis for pursuing new materials, (b) materials development, in which new materials were synthesized and characterized and (c) system design and materials engineering, which provided the foundational information to enable new materials to be realized as practical automotive hydrogen storage systems. The MHCoE was organized into four materials-oriented "projects," along with one engineering project. Results from all of the projects are given, as well as an account of the downselection process that identified materials to be pursued further after initial investigation. The downselected materials are compared against material goals derived from the revised 2010 DOE hydrogen storage system targets for light-duty vehicles. Suggestions and recommendations for further R&D directions are given, based on the MHCoE findings.

1. Introduction

Keller et al. have made a compelling case [1] that a hydrogen-based energy infrastructure must be built if our global concerns of fossil fuel depletion and global climate change are to be addressed in a meaningful way. Hydrogen can be produced from zero-carbon methods (wind, solar, nuclear power, fossil sources using complete carbon capture and storage), and the energy conversion devices that use hydrogen (hydrogen internal combustion engines, fuel cells) are efficient and don't release carbon dioxide at the point of use [2]. Storing hydrogen is a key aspect of a hydrogen energy infrastructure. The book entitled "Hydrogen Storage Technology, Materials and Applications" edited by Klebanoff reviews all methods of hydrogen storage for a variety of applications [3].

The importance of hydrogen storage for hydrogen-powered light-duty vehicles was realized by the U.S. Department of Energy in 2005 when it established three U.S. DOE Centers of Excellence for solid-state hydrogen storage: the Metal Hydride Center of Excellence (MHCoE), the Chemical Hydride Center of Excellence (CHCoE) and the Hydrogen Sorption Center of Excellence (HSCoE). These three Centers were funded from 2005 to 2010. In 2009, a Hydrogen Storage Engineering Center of Excellence (HSECoE) was also created to develop advanced engineering approaches to utilizing materials for hydrogen storage. Highlights from the three materials Centers MHCoE, CHCoE and HSCoE have been recently

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http://dx.doi.org/10.1016/j.ijhydene.2013.01.051

reviewed [4]. A more in-depth review of the MHCoE R&D effort is given here.

The purpose of the MHCoE was to conduct highly collaborative and multi-disciplinary applied R&D to develop new reversible hydrogen storage materials for light-duty vehicles. The MHCoE combined three broad areas: theoretical study of new materials and hydrogen storage reaction mechanisms, synthesis and characterization of new materials, and system design and engineering in support of the construction or practical automotive hydrogen storage systems. Driving all of this work were the original hydrogen storage system specifications contained in the DOE targets for 2010 and 2015 that existed at the time and which have since been revised. Although the MHCoE did conduct some hydrogen storage system design and engineering, as described above, this latter responsibility shifted to the HSECoE which was established in 2009.

The MHCoE tackled well-defined technical barriers associated with reversible solid-state hydrogen storage systems in which hydrogen is desorbed and re-absorbed on-board the vehicle. This specification of "on-board" reversibility was an important consideration for the vast majority of the materials search, and distinguished the MHCoE from the CHCoE that was focused on "off-board" hydrogen storage materials. The goals for the MHCoE R&D program were made quantitative by the original "system storage targets" outlined by the original FreedomCAR and Fuel Partnerhship Program for 2010 and 2015. Table 1 shows a subset of the original and revised DOE targets. The targets were revised in 2009. It is evident that the revised 2010 targets are relaxed somewhat in comparison to the original 2010 targets with regard to system gravimetric capacity, system volumetric capacity, and refill time. Later in this paper, comparison will be made of MHCoE materials properties to the revised 2010 requirements.

The following organizations and institutions were partners in the MHCoE, providing technical leadership and making important technical contributions to the MHCoE R&D program:

Brookhaven National Laboratory (BNL), California Institute of Technology (Caltech), Carnegie Mellon University (CMU), General Electric (GE), Georgia Institute of Technology (GT), HRL Laboratories, LLC, Intematix, Jet Propulsion Laboratory (JPL), National Institute of Standards and Technology (NIST), Oak Ridge National Laboratory (ORNL), Ohio State University (OSU), Sandia National Laboratories (SNL), Savannah River National Laboratory (SRNL), Stanford University, United Technologies Research Center (UTRC), University of Hawaii at Manoa (UH), University of Illinois at Urbana-Champaign (UIUC), University of Nevada, Reno (UNR), University of New Brunswick (UNB), University of Pittsburgh (PITT), University of Utah.

Sandia National Laboratories served as the project lead for the MHCoE. L.E. Klebanoff served as the Director of the MHCoE, with J.O. Keller serving as Deputy Director. Klebanoff also led the Sandia technical program. The technical work was divided into five "project groups," A–E:

Project A (Destabilized Hydrides), whose objective was to develop strategies for reducing hydrogen storage thermal requirements and improve kinetics by destabilizing metal hydride systems. Project A also aimed to enhance kinetics through nanoengineering.

Project B (Complex Anionic Materials), whose goal was to predict and synthesize highly promising new complex anionic metal hydride materials, with a particular focus on borohydrides.

Project C (Amide/Imide Storage Materials), organized to assess the viability of amides and imides (materials containing $-NH_2$ and $-NH$ moieties, respectively) for on-board hydrogen storage.

Project D (AlH_3 and $LiAlH_4$), whose objective was to understand the dehydrogenation and regeneration properties of alane (AlH_3) and $LiAlH_4$ for hydrogen storage. AlH_3 is a nearly ideal hydrogen releasing material, but to regenerate AlH_3 directly from the end product Al with gaseous H_2 requires unreasonably high pressures, which the MHCoE sought to circumvent. Project D also examined regeneration routes for $LiAlH_4$. These two materials were considered in the context of "off-board-reversible" hydrogen storage and were the only two materials systems in this off-board context that the MHCoE considered.

Project E (Engineering Analysis and Design), whose objective was to understand the materials engineering properties of metal hydrides and strategies for tank design. The responsibilities of Project E ended with the commissioning of the HSECoE at SRNL in 2009. Nonetheless, a review of selected Project E highlights is given here.

In addition to these formal projects, the MHCoE established a Theory Group (TG). The MHCoE TG made use of first-principles methods to predict new materials and their thermodynamic properties. In addition, the TG provided new directions for experimentalists, insight into hydrogen adsorption and desorption reaction mechanisms, and helped interpret experimental results. A very close collaboration existed between the MHCoE theorists and experimentalists.

The MHCoE was engaged in applied research with the goal of finding a practical material that satisfied the original DOE

Table 1 – A subset of original and revised DOE targets for on-board hydrogen storage systems for light-duty vehicles. The most current DOE targets are contained in the "revised 2010", 2017 and ultimate categories.

Storage system parameter	Original 2010 target	Revised 2010 target	2017 target	Ultimate target
Gravimetric capacity kgH_2/kg system	6%	4.5%	5.5%	7.5%
Volumetric capacity g H_2/L system	45	28	40	70
Operational cycle life	1000	1000	1500	1500
Fill time (min, for 5 kg)	3	4.2	3.3	2.5
Minimum full flow rate (gH_2/s/kW)	0.02	0.02	0.02	0.02
Min. delivery pressure @ 85 C PEMFC, (atm)	8	5	4	3
Fuel purity	99.99%	99.97%	99.97%	99.97%