Effect of Gaseous Impurities on Long-Term Thermal Cycling and Aging Properties of Complex Hydrides for Hydrogen Storage

Dhanesh Chandra

University of Nevada, Reno

A Partner in DOE Metal Hydride Center of Excellence (MHCoE)

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This presentation does not contain any proprietary or confidential information

Overview

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Timeline

Project start date – FY05

Project end date – FY09

Percent complete – New Start

Budget

Total project funding (5yrs.) - $ 1.5 M (Requested)

DOE share (5yrs.) - $ 1.2 M

Contractor share (5yrs.) - $ 301 K

Funding received in FY04: None (New Project)

Funding expected for FY05: $ 75 K

Partners

- SNL, CA
- Univ. of Illinois
- NIST, PNNL,
- JPL, SRNL, LANL

Barriers Addressed

- **Long-term reliability of Li-based complex hydrides when charged with hydrogen with gaseous impurities**
- **Surface and bulk hydrogen sorption mechanisms in catalyzed Li-based complex hydrides**

Objectives

The overall objective of the UNR Project is to determine the effects of gaseous impurities (ppm levels of O_2, CO, H_2O etc.) in the H_2 charge on the hydriding/dehydriding kinetics during long-term thermal cycling and aging.

The relevance to the DOE MHCoE program is that in practical use, trace impurities in hydrogen gas during periodic recharging will have an impact on the hydrogen loading capacities due to surface or bulk effects.

Approach

- **Perform long-term thermal cycling and aging experiments of catalyzed Li-based complex hydrides to evaluate degradation of the hydriding/dehydriding properties. These experiments will be conducted with the addition of controlled amount gaseous impurities in the charged UHP hydrogen. Samples will be obtained from MHCoE partners (Main focus)**

- **In-situ determination (hydrogen pressure and temperature as variables) of thermodynamic and structural properties by neutron scattering and X-ray Photoelectron Spectroscopy (XPS). These characterizations will be performed before and after thermal cycling/aging to determine the effect of gaseous impurities**

- **Perform calorimetric experiments to determine phase transitions and heat evolved/absorbed during hydriding/dehydriding.**

- **Understand the role of catalyst, surface or bulk effects during hydrogen sorption by Transmission Electron Microscopy (TEM) (limited experiments in collaboration with Uni. of Illinois).**

Technical Approach – 1

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- **Materials Selection**

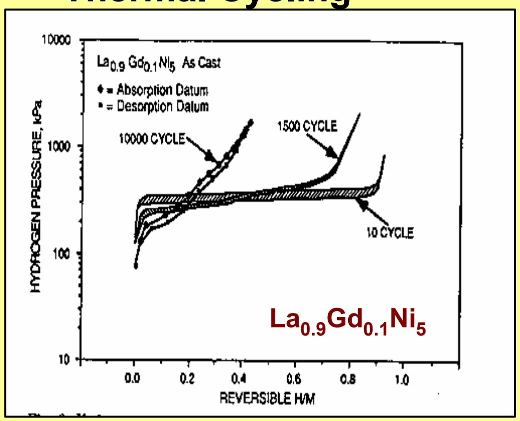
  - **The long term thermal cycling and aging experiments at UNR will be performed on primarily on materials (Li-based Complex Hydrides) supplied by SNL and other partners at MHCoE.**
  - **However, UNR will also synthesize some samples of catalyzed Li-based complex hydrides for comparison purposes. We will add catalysts such as activated TiN nanopowders, and others via ball milling.**

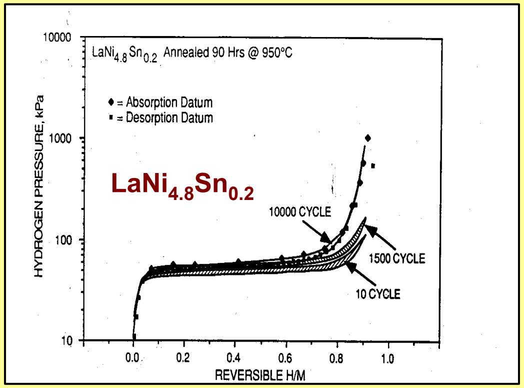
Technical Approach – 2

• Long-term Thermal Cycling and Aging Studies

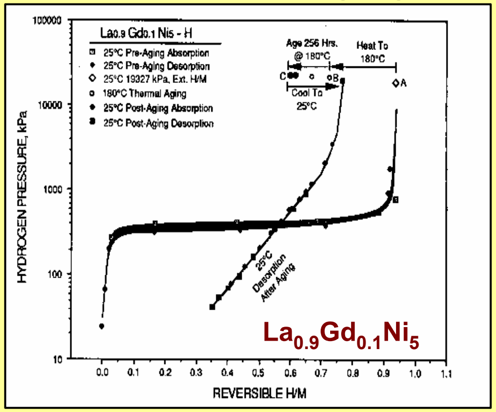
Example of Previous Work on Intrinsic Degradation of Classical La-Ni Based Hydrides

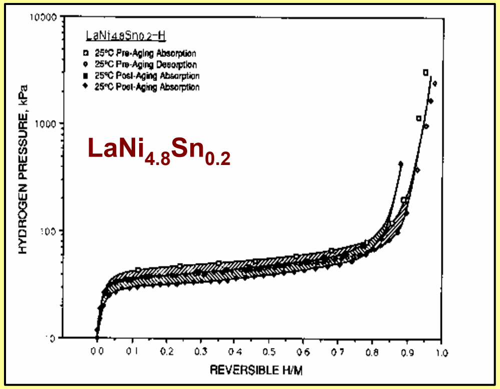
Thermal Cycling





Thermal Aging





➢ **The PC Isotherms shown on the left are for classical hydrides to study intrinsic degradation; i.e. recycle the desorbed hydrogen in a closed system.**

➢ **It is evident that $LaNi_{4.8}Sn_{0.2}$ does not show any significant degradation during both Thermal Cycling and Aging whereas $La_{0.9}Gd_{0.1}Ni_5$ degrades significantly (UNR-HCI NASA Spons. Studies)**

➢ ***Long-term Thermal Cycling and Aging (Accelerated Testing) Experiments are extremely useful to understand the long-term reliability of hydrides. These approaches may be extended to Complex hydrides .***

Technical Approach – 3

• Extrinsic Degradation Li-based Complex Hydrides

- Extrinsic thermal cycling and aging studies will be performed on Li-based Complex Hydrides after necessary modifications of the fully automated Sievert's Apparatus at UNR is completed.

- From our previous intrinsic studies on classical hydrides, it was found that thermal aging at a critical pressure and temperature will give the degradation behavior as a function time within approximately two to four weeks. These short term thermal aging results are comparable with long term 10,000 cycles (approx. 1.5 years or so of thermal cycling; please see slide No.7).

- It is expected that the extrinsic behavior due to addition of gaseous impurities such as O_2, H_2O, CO etc. in ppm/ppb levels in UHP H_2 during each recharge will provide information that extrapolated for long term stability after numerous refill cycles (~1500 cycles, DOE goal).

- The number of cycles and aging time will be decided in collaboration with MHCoE Partners for a particular type of complex hydride.

Fully Automated Sievert's Apparatus at UNR to be Modified for Thermal Cycling

Technical Approach – 4

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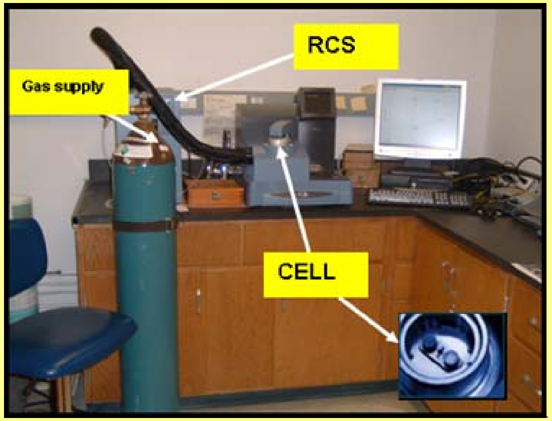
• Thermal Analysis of Li-based Complex Hydrides

- Phase transitions and heat evolution/absorption due to hydriding reactions can be determined by performing Differential Scanning Calorimetry (DSC).

- A pressure cell for use with Hydrogen will be designed and fabricated.



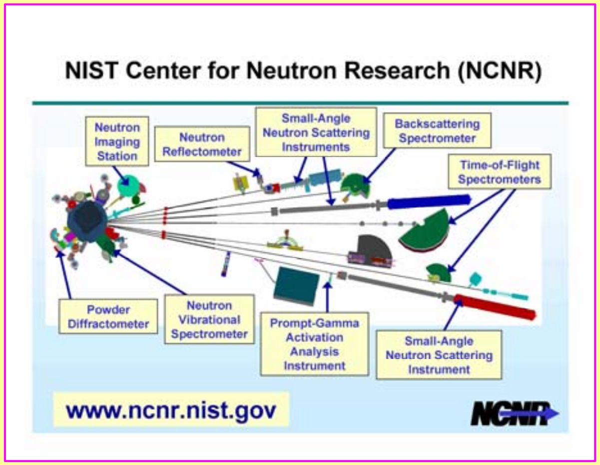
State-of-the-art DSC Q100 Instrument at UNR to be modified for use with Hydrogen

Technical Approach – 5

- **Characterization of Catalyzed Li-based Hydrides before and after Thermal Cycling/Aging**

- **In-situ neutron diffraction experiments during thermal cycling will be performed at NCNR, NIST to determine if there is a formation/dissolution of any intermediate phases during the cycling process. The changes in crystal structure will be also be determined continually throughout the cycling process. These experiments will be conducted in both UHP H_2 and UHP H_2 mixed with predetermined levels of gaseous contaminants.**
- **Elastic and Inelastic Neutron Scattering will be performed on materials before and after thermal cycling/aging. These experiments will provide information about the distribution of the impurities in the host lattice.**
- **The XPS experiments using depth profile analyses will provide information about the surface and bulk effects of catalysts and impurities during the thermal cycling process.**

UNR Portable Fully Automated Sievert's Apparatus



Facilities for Neutron Experiments at NIST (Taken from NIST Website)

Technical Approach – 6

- **TEM Characterization of Catalyzed Li-based Hydrides before and after Thermal Cycling/Aging**

➢**Exploratory TEM experiments will be conducted in collaboration with Univ. of Illinois to study intermediate phase formation in low hydrogen pressures, after addition gaseous impurities.**

➢***In-situ experiments will provide simultaneous information on the kinetics and structural changes during hydriding.***

Plan for Current Fiscal Year FY05

- **To modify the existing Sievert's Apparatus (stationary as well as portable) at UNR to perform Thermal Cycling and Aging Experiments for extrinsic degradation behavior studies - main focus.**

- **To select complex hydrides in collaboration with SNL and MHCoE Partners and determine the levels (ppm/ppb) of gaseous impurities (H_2O, O_2, CO etc.)to be mixed with UHP Hydrogen.**

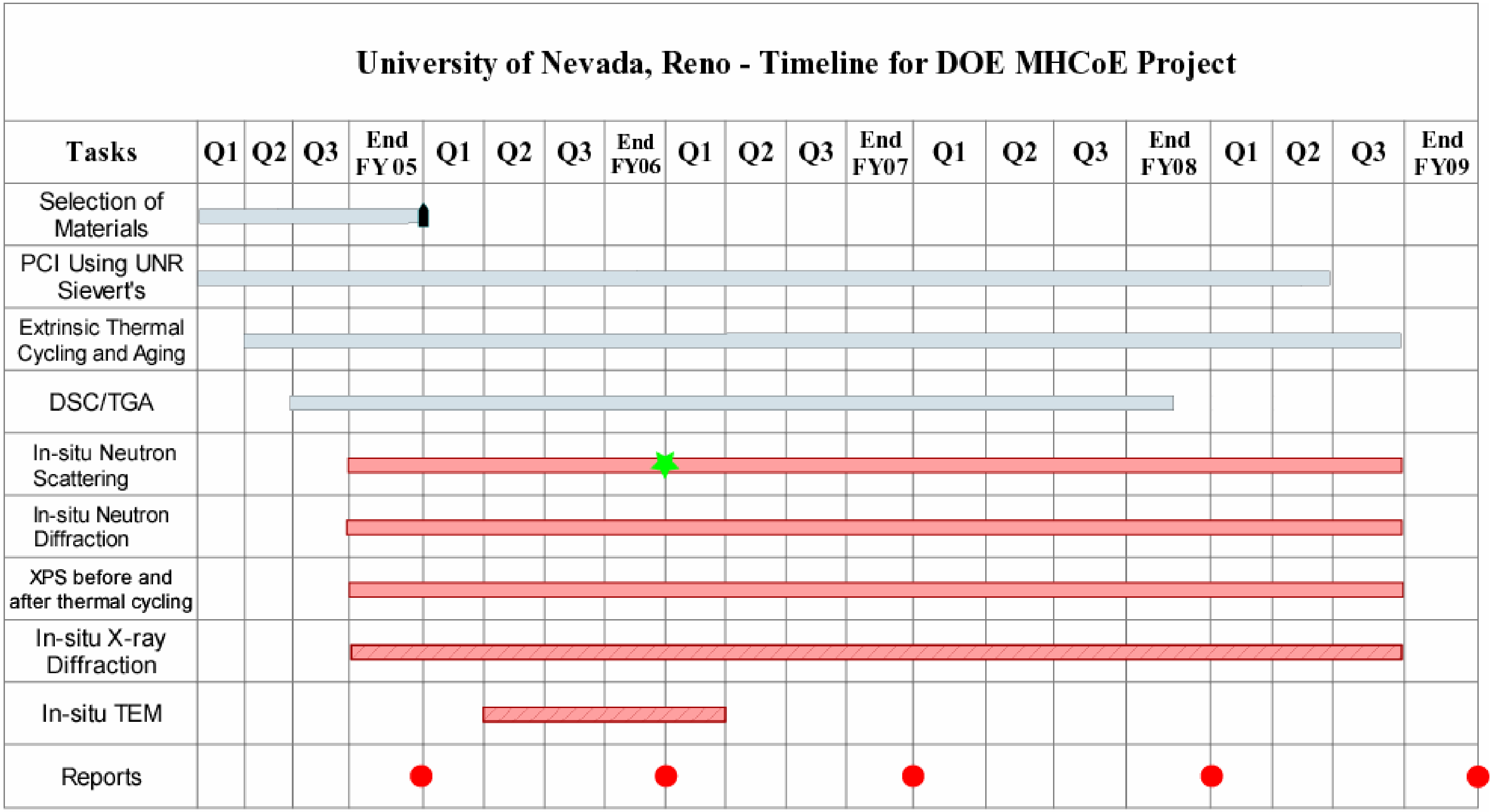
- **UNR will also synthesize catalyzed Li-based hydrides with solid state addition of catalysts, nanopowders of TiN, V etc.**

- **Baseline experiments have been initiated at Los Alamos National Laboratory (LANL) on Li_3N and Li_2NH to reproduce PCI reported in literature. The necessary equipment (Glove box, a Spex ball mill 8000) has already been set up by the PI Prof. Chandra (March '05) and will be available for future use.**

Technical Progress

- The process of modifying the Sievert's Apparatus at UNR is underway to accommodate Thermal Cycling and aging.
- A dedicated station with the necessary equipment (glove box with H_2O/O_2 control, recirculation of gases through a gettering system and UNR Spex Ball Mill 8000) has been set up at Tritium Science & Engineering Laboratory at LANL (March '05). This facility will be available for future use for our project.

Work Plan FY05 to FY09



● Annual Reports ✶ All the materials, catalysts, and the levels of contaminants will be chosen by FY06 for the final phase of the project

A go/no-go decision on the the materials obtained from SNL and other MHCoE partners for impurity testing.

Go/No-Go Criteria: (a) Unable to reversibly hydride a compound under high pressure conditions
(b) Material unable to withstand impurities that are reasonably expected in practical systems
(c) Final Go/No-Go based on the DOE/FreedomCAR target of acheiving 6.0 wt% by 2010