Development of Complex Hydride Hydrogen Storage Materials and Engineering Systems

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<th>Objectives</th>
<th>Hydrogen Storage Engineering Systems Research</th>
<th>Complex Hydride Hydrogen Storage Materials Research</th>
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<tr>
<td>✚ Develop 1-D, 2-D and 3-D models for metal and complex hydride hydrogen storage systems</td>
<td>✚ Study effect of metal dopants, proprietary additive, and Al powder on dehydrogenation and rehydrogenation of NaAlH₄</td>
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<td>✚ Calibrate models using Savannah River Technology Center metal hydride hydrogen storage system</td>
<td>✚ Compare dehydrogenation kinetics of un-doped and Ti-doped NaAlH₄, LiAlH₄, and Mg(AlH₄)₂.</td>
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<td>✚ Develop user friendly software package for metal hydride hydrogen storage system design optimization and scale-up</td>
<td>✚ Initiate Raman and other spectroscopic and molecular modeling analyses for fundamental understanding of dopant and other additives.</td>
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2004 FY Budget

- Total Funding (18 mo Period Beginning 06/06)
  - $335,000 + $83,759 cost share

- Personnel
  - PI: 1.35 academic and 2 summer months
  - Research Professor: 8.5 calendar months
  - Postdoctoral Associate: 9 calendar months
  - Two PhD Students plus Tuition: 36 calendar months

- Travel

- Materials and Supplies
Technical Barriers and Targets

Hydrogen Storage Material and System

DOE Targets:

2005 – 1.5 kWh/kg (4.5 wt %), 1.2 kWh/L, $6/kWh
2010 – 2 kWh/kg (6 wt %), 1.5 kWh/L, $4/kWh
2015 – 3 kWh/kg (9 wt %), 2.7 kWh/L, $2/kWh

Technical Barriers:

- higher system weight, high volume
- high cost of storage
- durability of at least 1500 cycles
- lower than expected energy efficiency
- long refueling time
- lack of availability of codes and standards
- no life cycle and efficiency analyses
Approach

- Synthesis and analysis of new and improved complex hydrides for hydrogen storage
  - effect of various preparation methods (e.g. ball milling), additives and metal dopants on the hydrogenation/dehydrogenation performance of these materials

- Mathematical model development for metal and complex hydride hydrogen storage systems
  - develop models of varying degree of complexity for accurately predicting hydrogen charge and discharge behavior from the storage bed.
  - study various geometric configurations for improving design and performance of the storage vessel
Project Safety

Complex Hydrides Synthesis

- Sodium alanate is highly flammable material. It readily reacts, with water generating flammable and explosive hydrogen gas
- Storage under nitrogen, away from air mandatory $\Rightarrow$ synthesis carried out inside nitrogen glove-box
- Recent minor incident with Ti-doped NaAlH$_4$ at SNL, even when inside and Ar glove-box, reiterates the sensitivity of this material with exposure to water

Hydrogen Storage Systems Research

- Mischmetal alloy based hydride used for this study very stable at room temperature. Auto-ignition temperature above 500 °C. It is non-explosive at room temperature, but other metal hydrides can be explosive.
- Hydride particles undergo expansion and contraction during charge and discharge cycles. Vessel of high of enough material strength is used to withstand this stress.
Phase I: Complete analysis on the reversibility of the Ti-doped LiAlH$_4$ system

Phase II: Complete analysis on the reversibility of the Ti-doped Mg(AlH$_4$)$_2$ system

Phase III: Complete Raman and molecular modeling analyses on the Ti-doped NaAlH$_4$ system

Phase IV: Complete analysis on the Ti-doped NaAlH$_4$ system with proprietary additive

Phase V: Complete analysis on the effect of high temperature and pressure ball milling of complex hydrides

Phase VI: Complete analysis on long-term cycling and scale-up of promising complex hydrides
Effect of Additive Concentration on Dehydrogenation of 2% Ti-NaAlH₄

At 90°C, 10 wt% additive produces six fold increase in kinetics!

Best kinetics observed so far for this widely studied complex hydride!
Effect of Cycling on Dehydrogenation of 2% Ti-NaAlH₄ with 10 wt% Additive and 5 wt% Al

Addition of Al reduces cycling losses, while additive improves kinetics!

Qualitative Kinetics of the H₂ Charge and Discharge Process for 2% Ti-NaAlH₄ with 10 wt% Additive and 5 wt% Al

Charge rates of H₂ much faster than discharge rates, due to substantial driving force.

Excellent charge rates even at 80°C!
Industrial Fuel Cell Vehicle Program

**Partnership**
- **Industrial:** John Deere
- **Government:** WSRC/DOE
- **University:** USC

**WSRC Metal Hydride Vessel Schematic***
- **Side view:**
  - Aluminum Foam
  - Container Wall
  - Porous Media Filter
  - Metal hydride particles occupying the void space of the aluminum foam
  - Dividers
  - Thermal insulation
- **End view:**
  - H₂ in/out
  - Coolant in
  - Coolant out
  - Dividers
  - Cooling tube

*Patented

Modeling and experiments based on commercially viable \( \text{L}_{0.06} \text{Ni}_{4.96} \text{Al}_{0.04} \) metal hydride system.

**Mathematical Models**

**Six Systematically More Realistic Models**
- isothermal equilibrium model (analytical)*
- one dimensional axial-flow*
- one dimensional axial-flow, radial-energy model (AFRE)
- AFRE model with variable conductivity
- two-dimensional
- three-dimensional


**Experimental Hydrogen Storage Test Facility Layout**

- **Atmospheric vent**
- **Mass flow meter**
- **To vacuum pump**
- **H₂ tank**
- **Pressure Transducer**
- **Thermocouple Locations**

One of these tubes in the USC facility.
3-D model Predictions of the Temperature Profile Variation During Discharge

30 SLPM of hydrogen discharging from 24 atm to 1 atm in 0.65 hrs from initial temperature of 295; 295 K cooling water flowing at 0.5 gpm.
3-D Model Predictions of the Loading Profile During Discharge

30 SLPM of hydrogen discharging from 24 atm to 1 atm in 0.65 hrs from initial temperature of 295; 295 K cooling water flowing at 0.5 gpm.
Interactions and Collaborations

- Dr. Ragaiy Zidan, Hydrogen Technology Laboratory, Savannah River Technology Center
- Dr. Maximilian Fichtner, Karlsruhe Research Center, Germany
- Dr. Jacque Huot, Hydro-Quebec, Canada
- Professor Alexander Angerhofer, Chemistry Department, University of Florida
- Professor Ruhullah Massoudi, Chemistry Department, South Carolina State University
Fundamental Hydrogen Storage
Materials Issues Being Researched

- fundamental understanding of the roles of the Ti dopant, its interaction with the additive and even the presence of adding additional Al

  What else can be added and why?

- reproducible processing, i.e., ball milling is more of an art than a science

  Is there a better way?

- extension of the NaAlH$_4$ research to other complex hydrides

How much effort should be devoted to what systems?
Fundamental Hydrogen Storage Systems
Issues Being Researched

* thermoconductivity of the metal hydride as a function of hydrogen loading and temperature

How do you predict this important property, especially when coupled with the metal foam?

* thermoconductivity of the metal (Al) foam heat transfer insert

Are there better materials or structures to improve heat transfer?

* fundamental design of the metal hydride bed

How many heat transfer tubes, in what configuration and whether to operate multiple beds in series or parallel?