Overview

Timeline
- Start: 10/1/05
- End: 9/30/06
- Percent complete: 50%

Barriers Addressed
- System Gravimetric Capacity
- System Volumetric Capacity
- Environmental, Health & Safety

Budget
- Funding received in FY05
  - $500,000
- Funding for FY06
  - $650,000

Partners
- Alfred University - microspheres
- United Technologies Corp. – alanates
- Sandia NL - system
- Brookhaven NL - alane
Objectives

- Identify rechargeable hydrogen storage media with a gravimetric capacity of 7.5 wt% or greater
  - Develop low pressure charging system for AlH₃ enabling its practical commercial utilization
  - Identify new complex compounds in the (Na,Li,Mg)Tm(AlH₄)ᵢ system through the use of Molten State Processing techniques.
  - Develop photo-enhanced hollow glass microspheres capable of storing and readily discharging hydrogen

- Develop and model the performance of gravimetrically and volumetrically efficient solid state hydrogen storage systems
  - Develop system models
  - Develop heat exchange component models
  - Develop media kinetic models and synthesis techniques
Summary

- Electrolytic charging of alane appears plausible pending analytical results of products generated.
- **Molten State Processing, MSP**, has been utilized to synthesize new compounds LiNa$_2$AlH$_6$ and K$_3$AlH$_6$
- **Photo Enhanced-Hollow Glass Microspheres, PE-HGM**, through glass composition modification established as plausible hydrogen storage methodology.
- Solid state hydrogen storage modeling and safety testing initiated to establish design concepts for the next generation storage system.
Responses to Reviewers’ Comments

- “The addition of cycling test in the next research period may help in the material selection.”

  A dehydride/rehydride cycle was added to this year’s experimental plan in response to this comment.

- “Need to soon move to materials with higher gravimetric and volumetric hydrogen densities (e.g., borohydrides, amides and AlH₃)”

  Alane work has commenced (see adjoining program outline) since the last review.
Publications


Alane Regeneration

SRNL
SAVANNAH RIVER NATIONAL LABORATORY
We Put Science To Work

R. Zidan
Approach

The objective of this research is to develop a low-cost rechargeable hydrogen storage material based on aluminum hydride having a capacity of 10wt%, cyclic stability and favorable thermodynamics and kinetics fulfilling the DOE onboard hydrogen transportation goals.

- Specific Approach
  - Based on Faraday equation:
    \[ E = -\frac{RT}{2F} \ln \left( P_{H_2} \right) \]
    
    utilizes electrolytic potential, \( E \), to increase hydrogen activity to form \( \text{AlH}_3 \).
  - Design and fabricate a novel high pressure cell to efficiently charge aluminum hydride (alane)
  - Test and evaluate feasibility of multiple cell designs for alane charging
  - Characterize and analyze charged alane materials for structure, purity and yield
Accomplishments

- Design and fabrication of a high pressure electrolytic cell capable of 200 bar operation was completed.
- Chemically prepared alane materials were characterized (SEM, XRD, TGA, TPD, TVA) as a base line.
- Electrode design and materials are under evaluation.
- Electrolyte solution and composition need to be selected to avoid electrolytic or thermal breakdown during operation.
- Safety and chemical handling procedures were established.
- High Pressure Cell testing has been initiated with promising results generated.

High pressure electrolytic cell has been designed and fabricated.

Preliminary tests resulted in anode dendrite formation.
Accomplishments

- Two ambient pressure electrolytic cell designs have been completed.
- Construction of one cell has been completed and the other is currently in process.
- Various electrode designs and materials are under evaluation.
- Electrolyte solution and composition will be selected to avoid electrolytic or thermal breakdown during operation.
- Safety and chemical handling procedures were established.

![Image of Ambient pressure electrolytic cell](image)

Ambient pressure electrolytic cell has been designed and fabricated.

SRNL
Future Work

- Perform high pressure cell testing utilizing various electrolytes and compositions to achieve optimum performance.
- Initiate ambient pressure cell testing utilizing various electrolytes and compositions to achieve optimum performance.
- Perform structural characterization and physical property analyses of both anode and cathode products to identify material purity and yield (XRD, DSC).
- Optimize cell performance to achieve efficient AlH$_3$ yield.
- Modify electrolytic charging parameters to yield alane having discharge kinetics sufficient to meet DoE 2010 targets.
- Exchange samples for additional characterization and testing with BNL, SNL and Hawaii.
High Capacity Complex Hydride “Alloying”

Material Synthesis and Modification
The SRNL Molten State Process, MSP, was used to develop new hybrid alanate compounds by combining or “alloying” together different complex hydrides compounds.

The SRNL MSP has unique operating conditions that allow these materials to interact and combine leading to a much higher probability of successful fusion over traditional ball milling and chemical processing techniques, alone.

Material Characterization
Structural characterizations and physical property analyses are employed to identify newly synthesized complex hydride phases. X-ray diffraction and PCT system are the primary tools. Other analysis are conducted in collaboration with partners.
Accomplishments

- New **Molten State Process** was successfully demonstrated.
- Kinetics of NaAlH$_4$ was enhanced due to higher catalyst homogeneity.
- Compositions of (Na,Li,Mg)AlH$_4$ synthesized
  - Elemental substitution of Na, Li & Mg demonstrated in formation of NaMgH$_3$, Na$_2$LiAlH$_6$ via MSP.
- Compositions of (Na,Li,Mg)(Ca,K)AlH$_4$ synthesized
  - Elemental substitution of Li, K, Mg was shown in formation of K$_3$AlH$_6$
- Achieving a better understanding of the mechanism of formation of these materials
Accomplishments

- Compositions of (Na,Mg,Fe)(AlH₄)ₓ, (Li,Mg,Ni)(AlH₄)ₓ were synthesized via MSP at 100bar/190°C
  - Neither Ni nor Fe were observed to react in any of the compositions
  - Intermetallic compounds Al₃Ni and Mg₂Ni
  - Li containing compounds were not observed in many of the compositions thus processed indicative of either amorphous phases or masking by other products.
Future Work

- Incorporate V, Cr & Mn into (Na,Li,Mg)AlH₄ compositions utilizing MSP.
- Complete characterization of Ni and Fe additions to (Na,Li,Mg)AlH₄.
- Extend MSP work to study quaternary “alloying” of (Na,Li,Mg)NH₄ & (Na,Li,Mg)BH₄ to determine its efficacy in these alternate complex hydride systems.
- Extend MSP work to include high pressure solute charging of alanates, boranes and amides.
Photo Enhanced Hydrogen Diffusion in Hollow Glass Microspheres

R. F. Schumacher, L.K. Heung, & G.G. Wicks
SRNL support of Alfred University to demonstrate hydrogen storage and dehydrogenation of hollow glass microspheres (HGMs) using photo-enhanced hydrogen diffusion.

Provide hydrogen filled HGMs for investigation and demonstration of the photo-enhanced dehydrogenation.
Accomplishments

- Alfred University – SRNL CRADA approved to begin work 1/24/06.
- Samples of doped HGMs and glass from Alfred University received at SRNL.
- Small stainless steel vessel designed to withstand hydrogen pressure and temperature for charging HGMs – designed and fabricated.
- Hazard Assessment Package for the task has been prepared and is waiting for approval.
Future Work

- Demonstrate safe hydrogen charging of HGMs and glass samples.
- Transfer of charged samples to Alfred University.
- Support Alfred University on the design of the demonstration device and understanding photo-enhanced hydrogen diffusion mechanisms.
Approach

- **System Modeling, Design and Evaluation**
  - Lead the MHCoE task on Engineering Analysis Design and Test, EADT.
  - Develop heat and mass transfer methods & models to design ultra-high gravimetric and volumetric density storage systems.
  - Utilize static and dynamic system models to design efficient PEMFC and ICE hydrogen fueled power generation methods.
  - Develop media process techniques to achieve large batch kinetic & capacity goals.
  - Design, build and evaluate the next generation hydrogen storage system prototype based on new metal hydride compositions developed in the CoE.

- **Solid State Hydride Safety**
  - Develop standard testing techniques to quantitatively evaluate both materials and systems.
  - Determine fundamental chemical kinetics of environmental reactivity of complex hydrides.
  - Develop amelioration methods and systems to mitigate the risks of using these systems to acceptable levels and demonstrate in prototype systems.

Increase system gravimetric efficiency from current UTRC state-of-the-art design of 19% using conventional tube/foam heat exchange through reduction of their requirement.
Accomplishments

- Baseline system models have been developed using ASPEN utilizing conventional 5 & 10 ksi pressurized hydrogen tanks.
- Mass flow models in packed hydride beds have been analyzed leading to new bed design concepts.
- Alternative solid state hydride system designs have been constructed and are currently being modeled for both volumetric and gravimetric efficiency.
Accomplishments

- Methods have been developed for the mechanico-chemical synthesis of catalyzed complex compound hydrides in ½ to 1 kg batches.
- Kinetics have been shown to be comparable to those achieved in 1 to 2 gram batches via SPEX milling.
- Temperature control has been identified as a key variable in high energy processing of large batch sized and is required to achieve kinetically active media.
Future Work

- Hydrogen Storage-Internal Combustion Engine, ICE, systems will be modeled to determine these system specific requirements.
- Novel heat and mass transfer approaches will be modeled to minimize system mass and volume.
- Solid state hydrogen storage systems incorporating leading media candidates will be modeled to optimize system performance.
- New concepts in storage system design around regenerable AlH$_3$ will be developed and modeled to take advantage if its specific attributes.
- Develop initial automobile/fueling station models to account for large heat load requirement during fueling.
- A new effort will be initiated to study the safety considerations required to utilize solid state hydrogen storage to include: empirical risk assessment, chemical kinetics, risk mitigation and subsystem prototype verification of mitigation methods.