Advancement of Systems Designs and Key Engineering Technologies for Materials Based Hydrogen Storage

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United Technologies Research Center

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Annual Merit Review
Washington, DC
June 8, 2010

Project ID: ST006

Overview

- **Timeline**
  - Start: February 2009
  - End Phase 1: July 2011
  - End Phase 2: July 2013
  - End Phase 3 / Project: July 2014
  - Percent complete: 18.0% (spending)
- **Budget**
  - $6.86M Total Program
    - $5.32M DOE
    - $1.55M (22.5%) UTRC
  - FY09: $350k DOE
  - FY10: $870k DOE
- **Barriers***
  - A – J
  - A. System Weight & Volume
  - E. Charging / Discharging Rates
  - J. Thermal Management
- **Targets***
  - All
- **HSECoE Partners**

Pacific Northwest National Laboratory, SRNL Savannah River National Laboratory, Los Alamos National Laboratory, Lincoln Composites (A Member of Hexagon Composites Group), HRI UQTR, GM, Ford, BASF The Chemical Company, OSU Oregon State University, JPL, California Institute of Technology, NREL National Renewable Energy Laboratory

* DOE EERE HFCIT Program Multi-year Plan for Storage

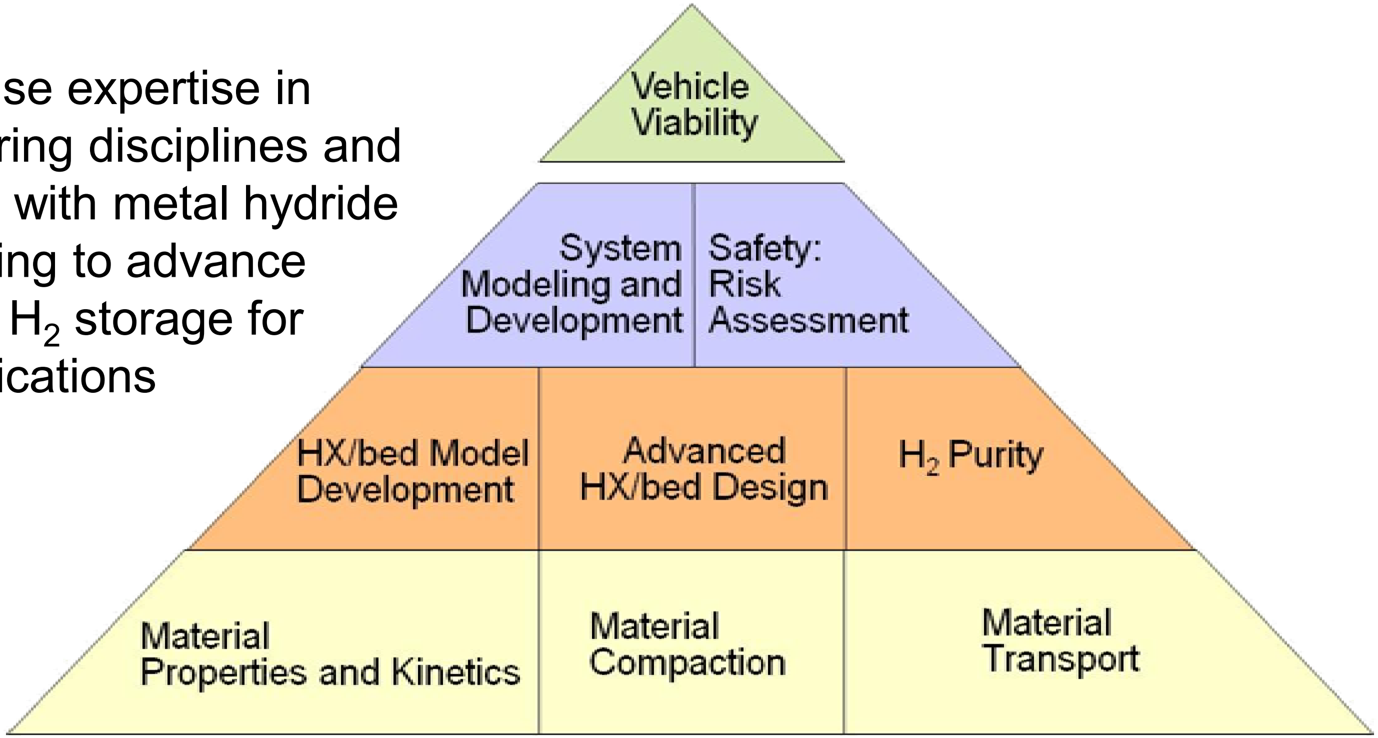
Objectives

- Design of materials based vehicular hydrogen storage systems that will allow for a driving range of greater than 300 miles
- H_2 storage system focus:
  - Metal hydride
  - Chemical hydride
  - H_2 cryo-sorption materials
- Target examples:

Performance Measure	Units	2010	2015	Ultimate
System Gravimetric Capacity	g H_2 /kg system	45	55	75
System Volumetric Capacity	g H_2 /L system	28	40	70
System fill time (for 5 kg H_2)	minutes	4.2	3.3	2.5
Fuel Purity	% H_2	SAE J2719 guideline (99.97% dry basis)		

Approach

- Leverage in-house expertise in various engineering disciplines and prior experience with metal hydride system prototyping to advance materials based H_2 storage for automotive applications



Month/Year	Go/No-Go Decision
Apr-11	Provide a system model for each material sub-class (metal hydrides, adsorption, chemical storage) which shows:
	● 4 of the DOE 2010 system storage targets are fully met
	● Status of the remaining targets must be at least 40% of the target or higher

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Center Structure – Roles & Collaborations

Hydrogen Storage Engineering Center of Excellence

D. Anton, SRNL
T. Motyka, SRNL

Materials Operating Requirements

D. Herling, PNNL

- Materials Centers of Excellence Collaboration – SRNL, LANL, NREL
- **Reactivity & Compatibility – UTRC**
- Adsorption Properties – UQTR
- **Metal Hydride Properties – SRNL**
- Chemical Hydride Properties – LANL
- Media Structure - GM

Transport Phenomena

B. Hardy, SRNL

- **Bulk Materials Handling – PNNL**
- Mass Transport – SRNL
- Thermal Transport – SRNL

Enabling Technologies

J. Reiter, JPL

- Thermal Insulation – JPL
- **Hydrogen Purity – UTRC**
- Sensors – LANL
- **Thermal Devices - OSU**
- Pressure Vessels - PNNL

Performance Analysis

M. Thornton, NREL

- Vehicle Requirements– NREL
- Tank-to-Wheels Analysis – NREL
- **Forecourt Requirements - UTRC**
- Manufacturing & Cost Analysis - PNNL

Integrated Power Plant / Storage System Modeling

D. Mosher, UTRC

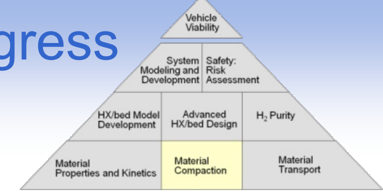
- Off-Board Rechargeable - PNNL
- On-Board Rechargeable – GM
- Power Plant – Ford

Subscale Prototype Construction, Testing & Evaluation

T. Semelsberger, LANL

- **Risk Assessment & Mitigation – UTRC**
- **System Design Concepts and Integration - LANL**
- Design Optimization & Subscale Systems – LANL, SRNL, UQTR
- Fabricate Subscale Systems Components – SRNL, LANL
- Assemble & Evaluate subscale Systems – LANL, JPL, UQTR

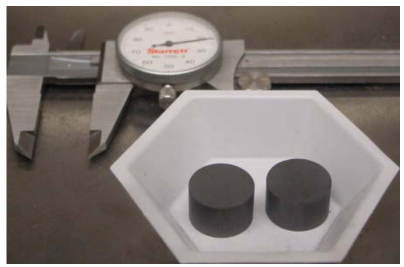
Leading / Project Tasks
Additional Project Tasks
Supporting



Engineered Compaction

- Objective: Improve volumetric capacity and thermal conductivity through powder compaction
- Coordinated through GM

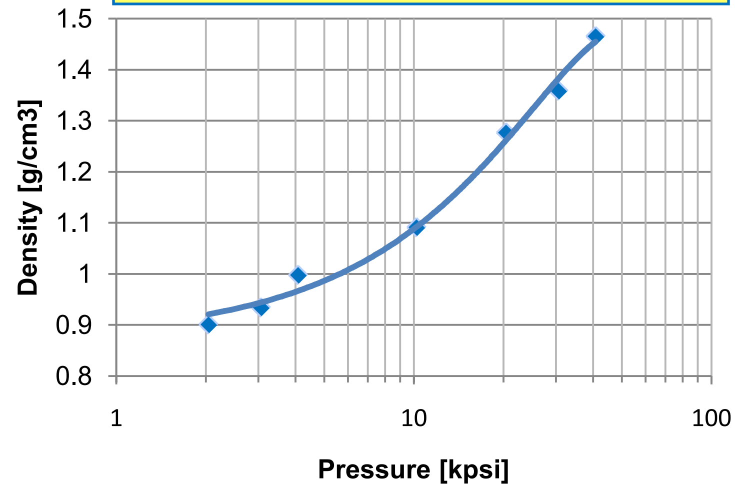
Press inside glovebox



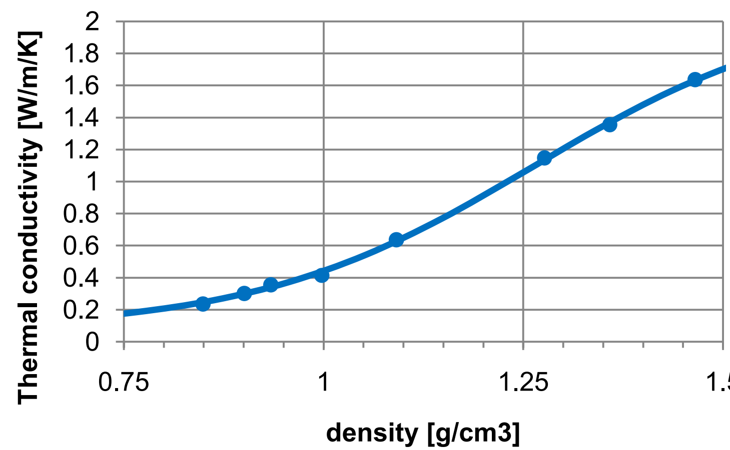
Pellets for thermal Conductivity measurements

Thermal conductivity analyzer

Density increased by 63% (39% reduction in volume)



7X improvement of thermal conductivity



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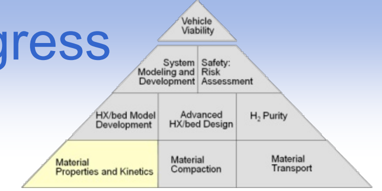
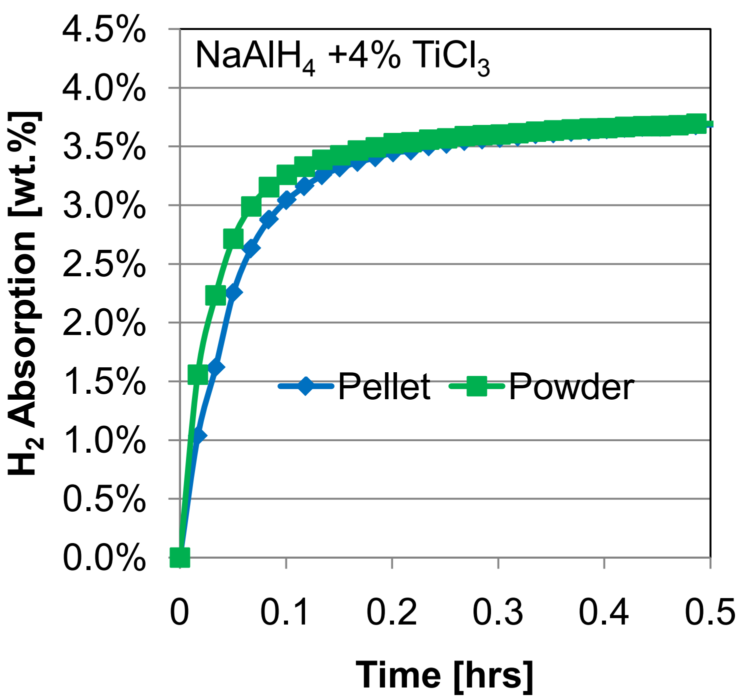


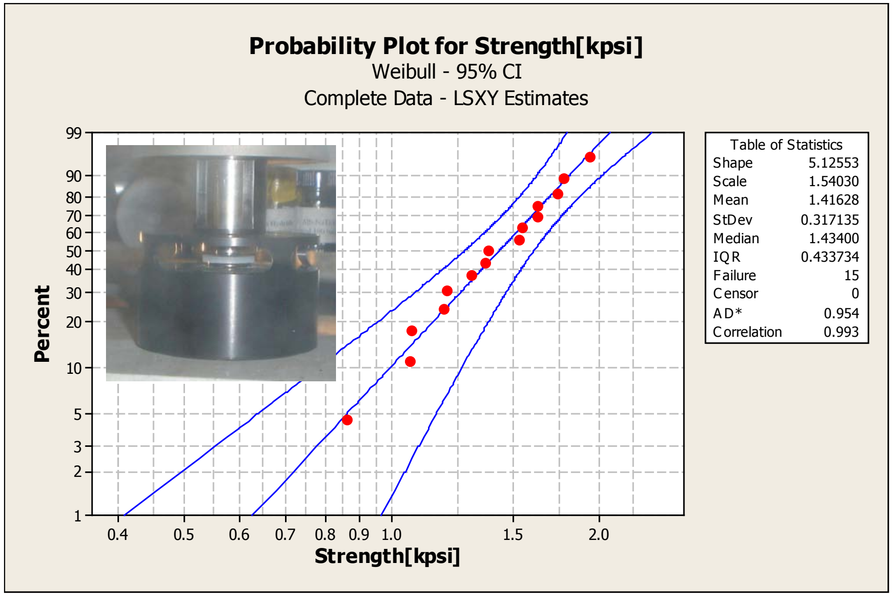
Properties of Compacted Metal Hydride

- H_2 Absorption (120°C, 110 bar)



Comparable H_2 absorption and desorption rate before and after compaction

- Biaxial flexure screening test for compressed pellets



Reinforced $NaAlH_4$

Integrating pellet reinforcement and thermal conductivity enhancement in compacted material

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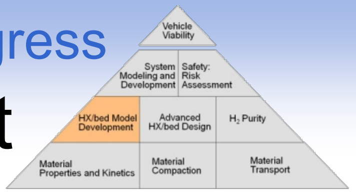
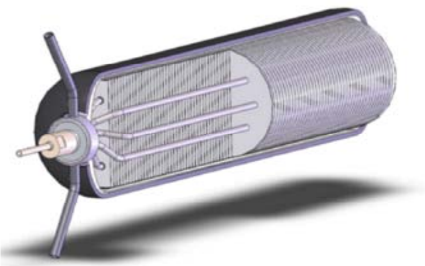
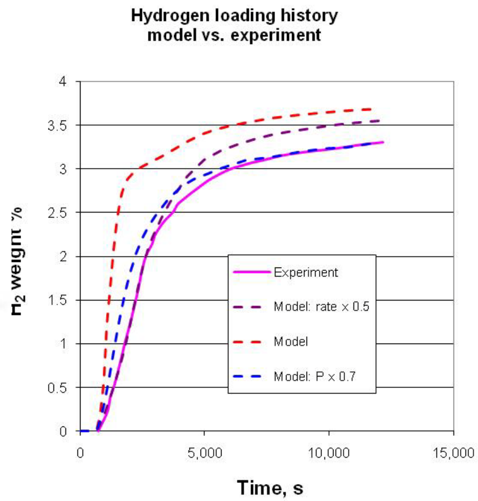


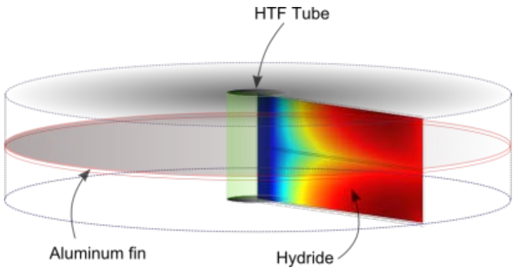
Storage System Model and HX Development

- Objective: Optimization of hydrogen storage system heat exchanger for fast refueling time
- Approach:
  - Co-developed and validated COMSOL™ model of $NaAlH_4$ bed with SRNL
  - Incorporated improved material properties after compaction (ρ, k)
  - Performed parametric study to optimize heat exchanger design for fast refueling time
  - Developed lumped parameter model for System Level Modeling

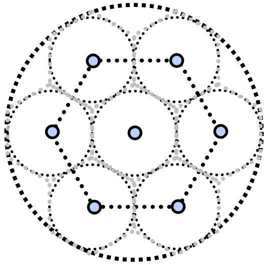


Prior UTRC prototype

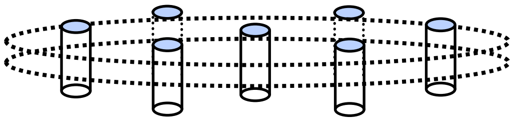


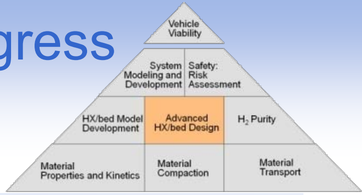


Finite element model



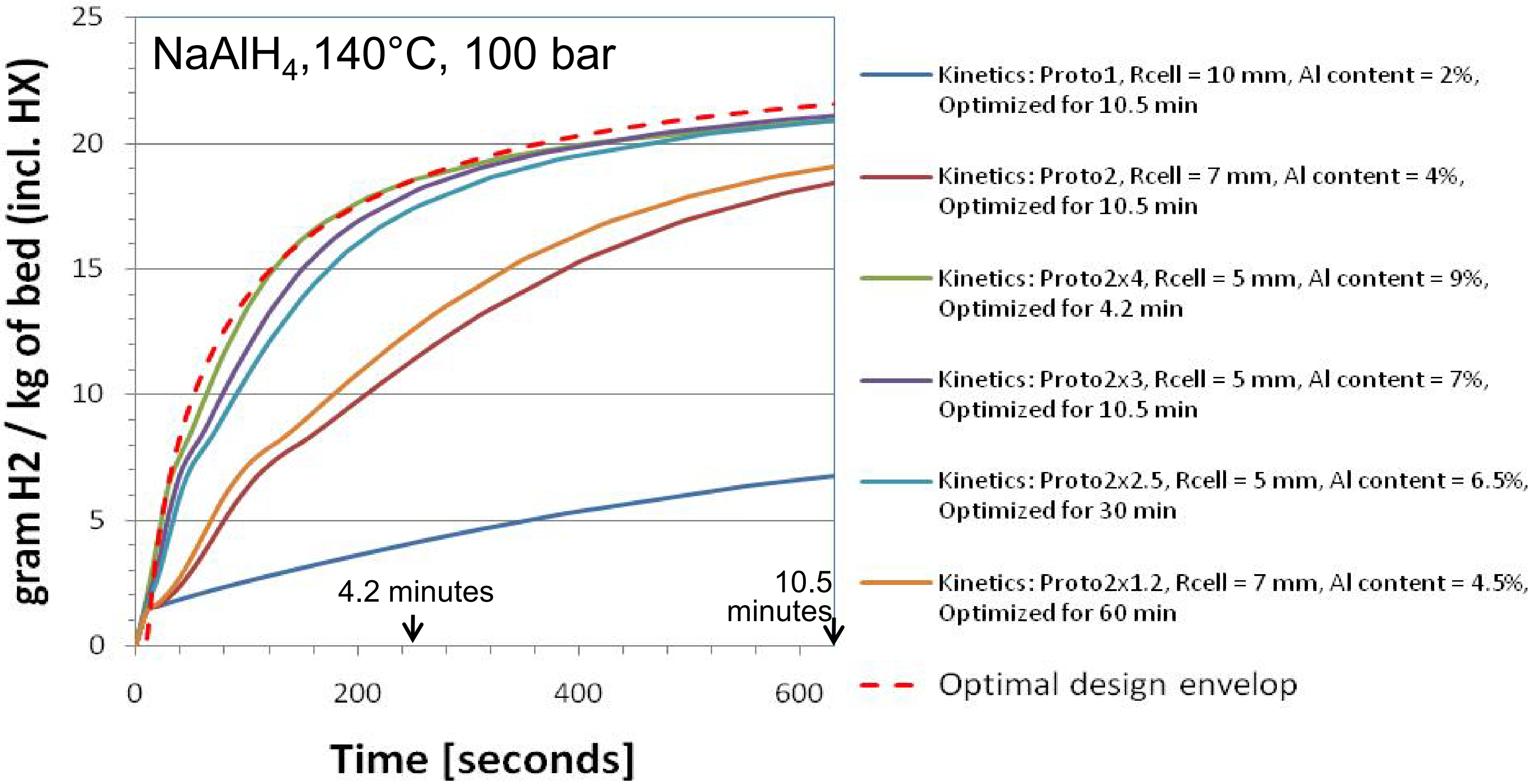
Parametric model



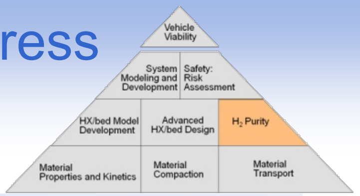


HX Design for Fast Refueling Time

- Different bed designs are optimal for specific refueling times



$NaAlH_4$ is a good model material for designing engineering tools but can not achieve gravimetric capacity targets at fast refueling times

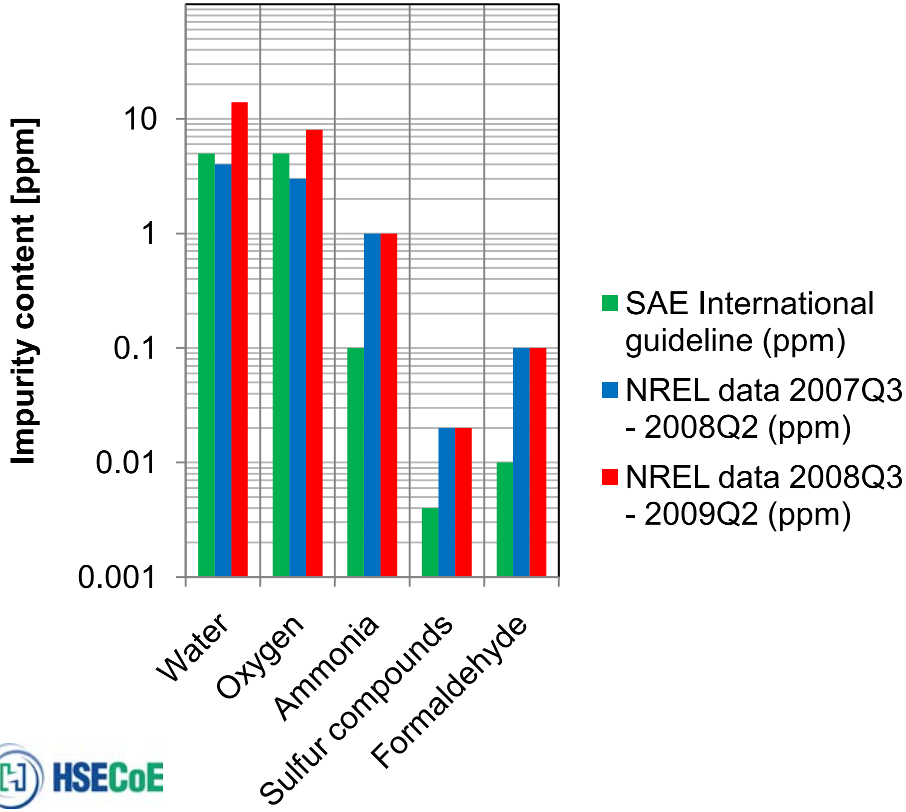


H_2 Purity

- Objective: Develop system methods to improve discharged hydrogen purity / quality for acceptable PEM fuel cell durability

Impurities of Concern:

- NREL H_2 Forecourt



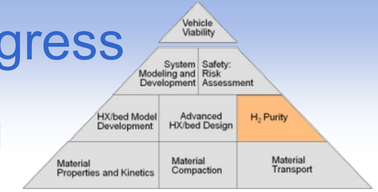
- Based on HSECoE Tier 1 & 2 Materials

Storage material	Impurity	SAE guideline	HSECoE Estimate
Ammonia Borane	Borazine	???	0.4-3.0%*
	Diborane	???	1-5 ppm
	Ammonia	0.1 ppm	20-200 ppm
Metal Amides	**Ammonia**	0.1 ppm	200-800 ppm

*LANL: 0.01-0.08 mol Borazine/ mole of AB reacted

Initial focus on Ammonia

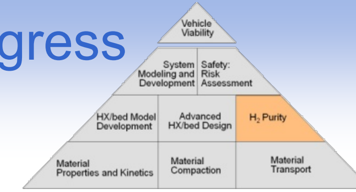
Preliminary Purification System Comparison



Factor	Conventional Palladium Membrane	Regenerable Physical Adsorption	Chemical Adsorption
Weight	Heavy	Heavy[1)]	Light
Volume	Big	Big	Small
Cost	**Expensive**	Affordable	Affordable
H_2 loss	2-5%	**High[1)]**	Low
Pressure	>50 psig	High pressure preferred	Atmospheric or high pressure
Temperature	300-400ºC	RT	RT<T<150ºC
Purity	99.9999999%	99.97%	99.97%
Life expectancy	>5 years	>2 years	**3 month replacement**

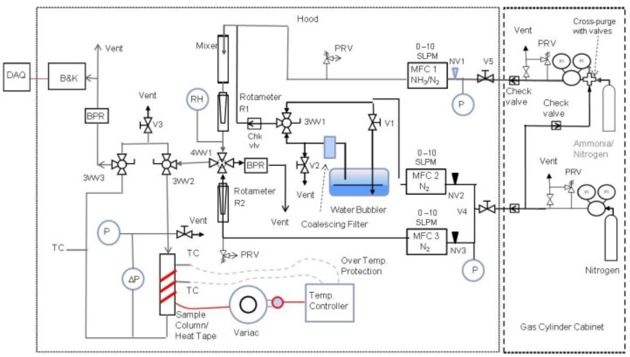
1) Assuming on-board regeneration

Chemical adsorption cartridge selected for Ammonia



Adsorption System Development

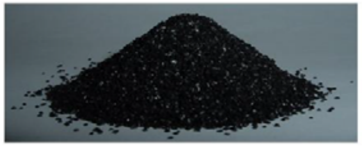
Process Flow Diagram



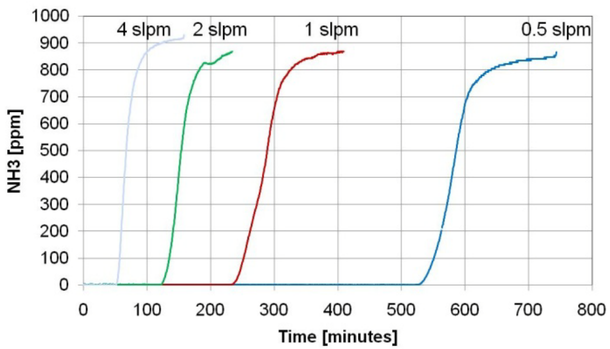
Test apparatus

NH_3 adsorbent

- Mesh size: 20x30 mesh (0.84x0.60 mm)
- Tap Density: 0.673 g/cm^3
- BET surface area: 673 m^2/g
- Pore volume: 0.338 cm^3/g
- Average Pore Diameter (4V/A by BET): 20.1 Å

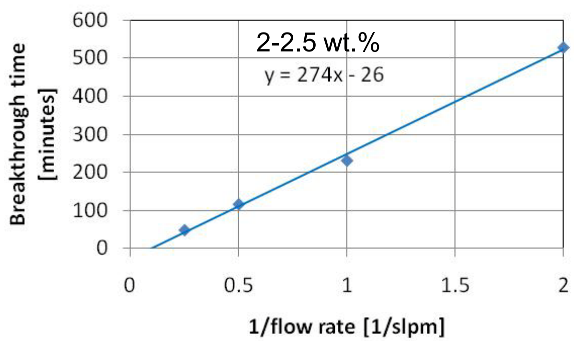


NH_3 breakthrough curves

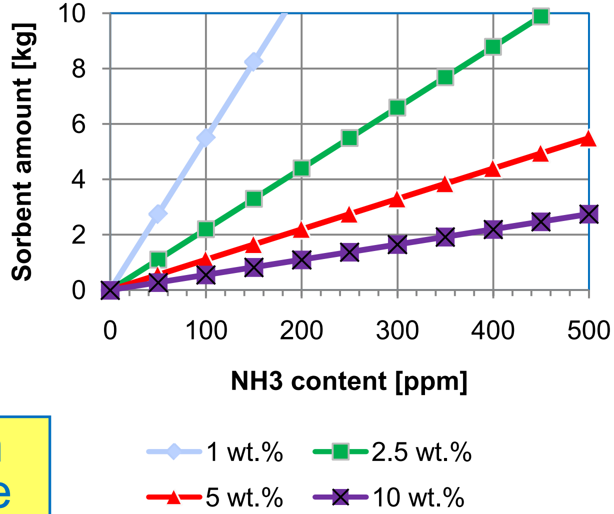


7.5 g, bed height: 12 cm, Inlet: 1000 ppm NH_3 in N_2

Flow rate dependence NH_3 breakthrough time



Cartridge weight for 3-month replacement interval



Adsorbent based H_2 purification cartridge for NH_3 appears viable

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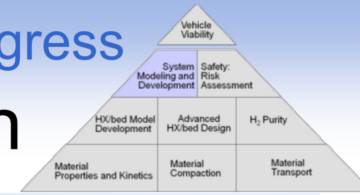
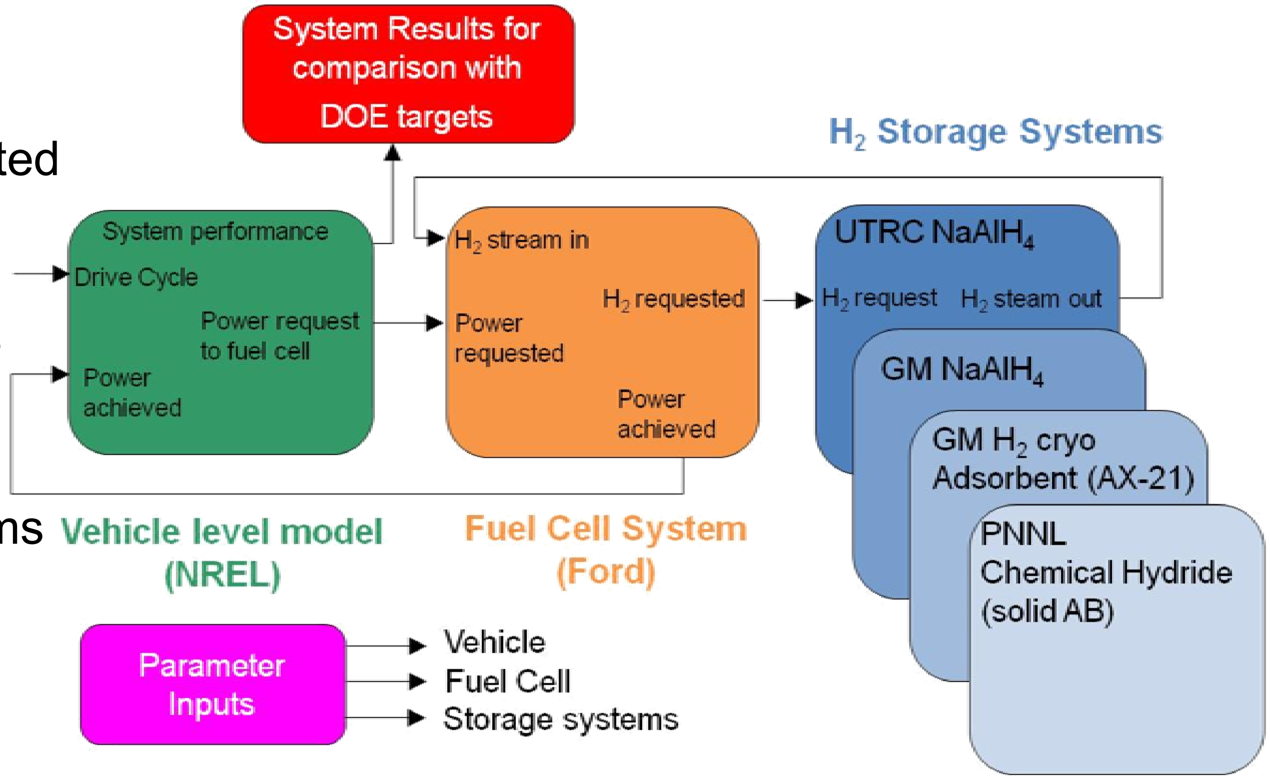


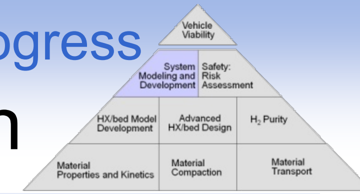
Integrated Framework for Vehicle Simulation

- Objective: Evaluate combined power plant / storage system configurations to determine hydrogen storage system requirements and predict overall performance

- Progress:
  - Framework structure developed and implemented in Simulink™
  - Different storage system types coexist within same framework
  - Results generated for comparing storage systems against DOE targets on a common basis



UTRC leading IPP/SSM technical area and providing support to all partners for implementing their contributions

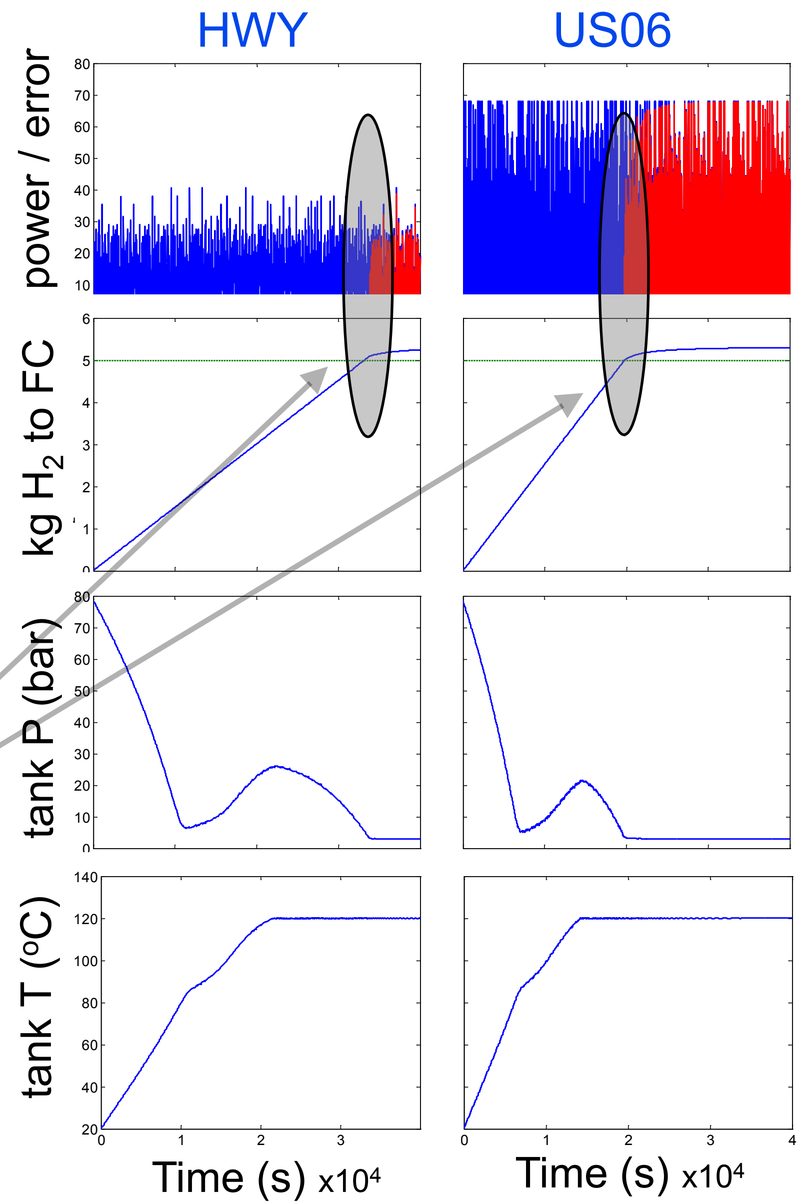


Integrated Framework for Vehicle Simulation

$NaAlH_4$ system example:

- Power demand curves from HSSIM (NREL)
- Lumped heat transfer model parameters from COMSOL™ model of $NaAlH_4$ bed
- Single "cold start" from 20°C:
  - H_2 stored in free volume is burned to raise temperature
- Drive cycle repeats indefinitely
  - Drive cycles were not designed for vehicles with materials based H_2 storage systems
- Minimum delivery pressure: P_{min}= 3 bar
- Results show drive cycle is tracked correctly until **after** 5kg H_2 have been delivered to the fuel cell.
- More details in presentation by GM

Performance comparison of all three hydrogen storage systems on a common basis



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FY10 and FY11 Plan

	FY10		FY11		
	3Q	4Q	1Q	2Q	3Q
Improve properties through compaction with reinforcing material					
Quantify impact of pressure gradients inside consolidated metal hydride powder on H_2 absorption and desorption kinetics					
Evaluate small test article with structured media					
Evaluate alternative reversible metal hydride materials in common H_2 storage framework with current engineering tools					
Improve capacity of on-board H_2 purification cartridge for ammonia					
Develop and assess methods for removing boron containing species					
Qualitative risk assessments of novel systems					
Improve definition of Balance of Plant (BOP) components in system model and establish a common bill of materials					
Implement initial cost model library for storage systems					
Identify technology gaps and prioritize concepts					
Quantify hydrogen storage system performance against DOE targets for Go/No-Go decision on April 30, 2011					☆

☆ Go/No-Go Decision

Summary

Relevance: Design of materials based vehicular hydrogen storage systems that will allow for a driving range of greater than 300 miles

Approach: Leverage in-house expertise in various engineering disciplines and prior experience with metal hydride system prototyping to advance materials based H_2 storage for automotive applications

Technical Accomplishments and Progress:

- Developed method that improved volumetric capacity and thermal conductivity through compaction
- $NaAlH_4$ is a good model materials but can not achieve gravimetric capacity targets at fast refueling times
- Hydrogen purification cartridge for adsorbing NH_3 appears viable
- Established Simulink™ framework that enables performance comparison of all three hydrogen storage materials against DOE targets on a common basis

Collaboration: Active collaboration with all partners in center, for instance between Ford, GM, PNNL and NREL on system level modeling

Future Work: Work towards milestones on quad charts of each of the technical areas and technical teams and towards Go/No-Go decision on April 30, 2011

Acknowledgements

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