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

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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

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* DOE EERE HFCIT Program Multi-year Plan for Storage

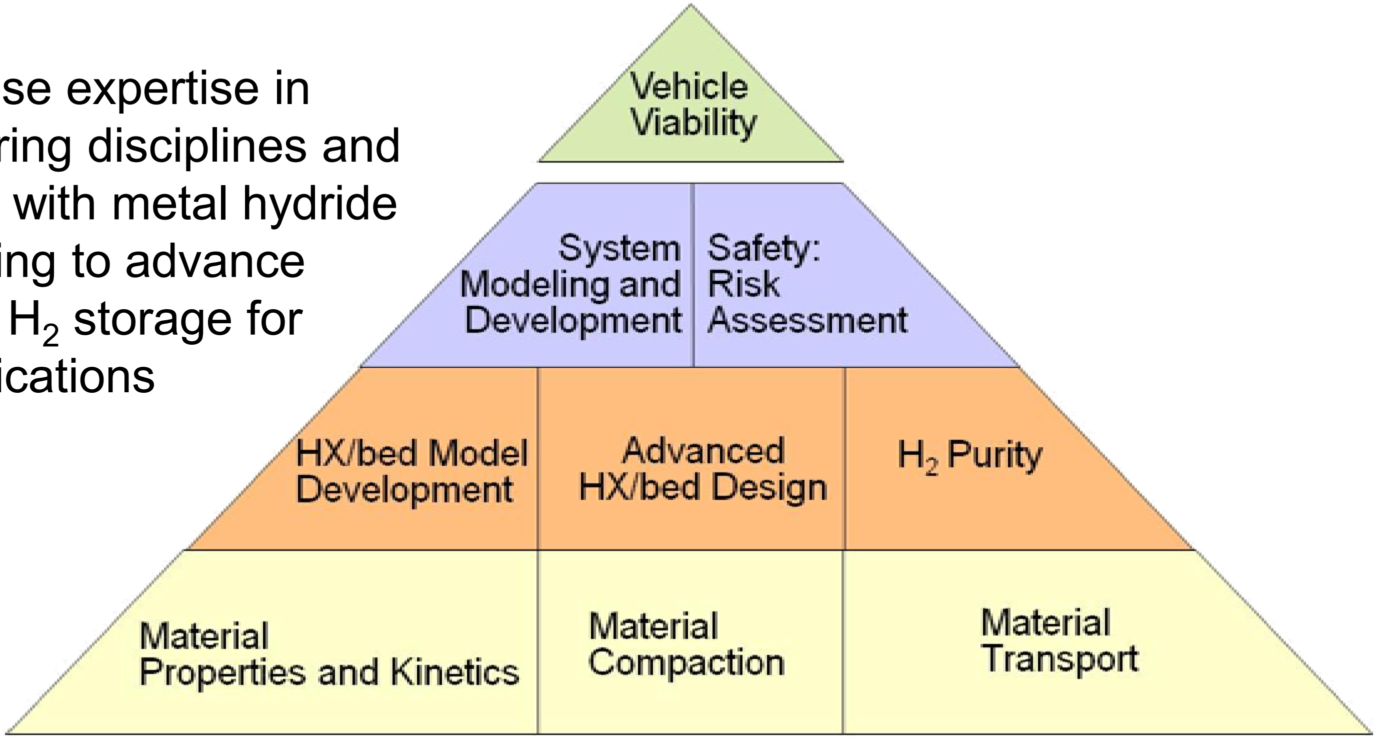
# Objectives

- 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**

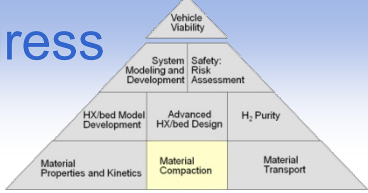
- Off-Board Rechargeable - PNNL
- On-Board Rechargeable – GM
- Power Plant – Ford

### *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

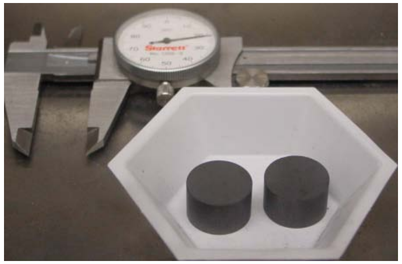
**Leading / Project Tasks**
**Additional Project Tasks**
Supporting




# Engineered Compaction

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

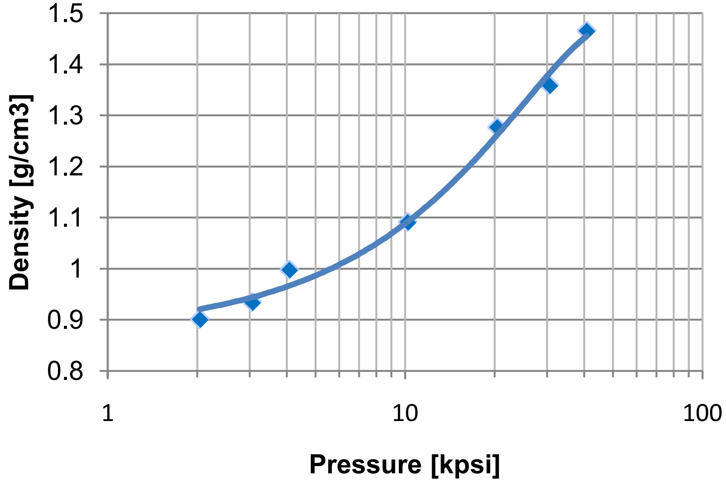

Press inside glovebox



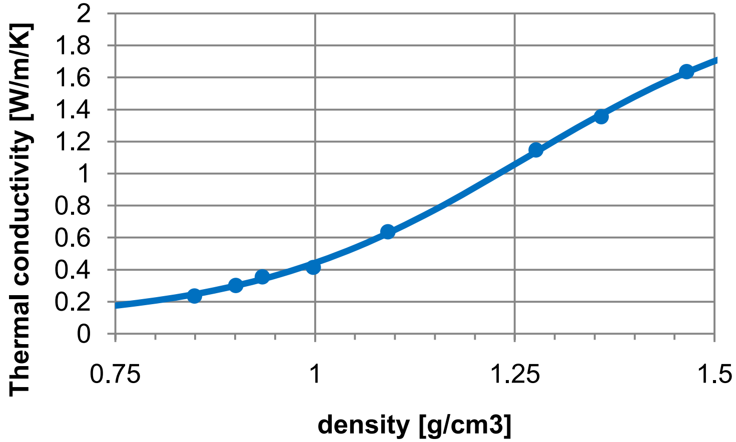
Pellets for thermal Conductivity measurements

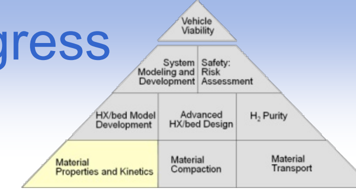
Thermal conductivity analyzer

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



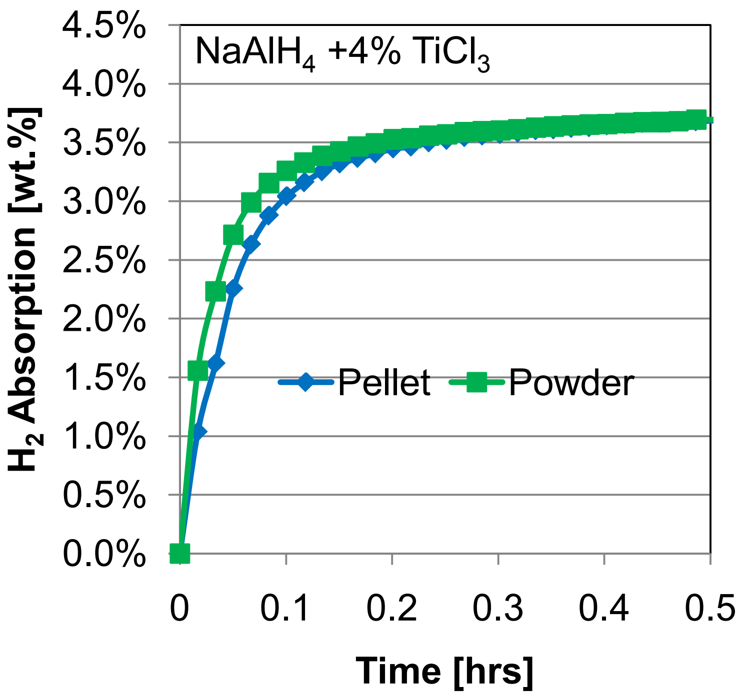

7X improvement of thermal conductivity





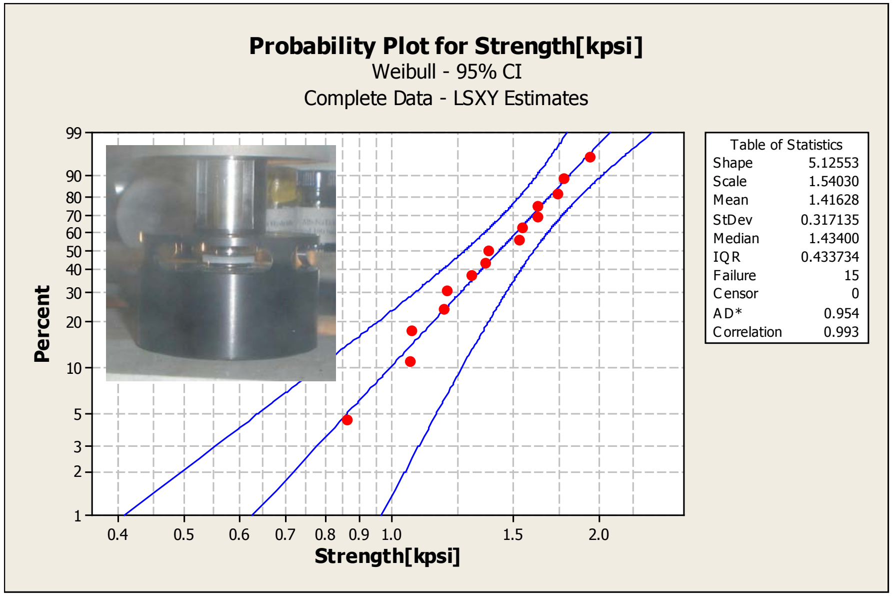

# Properties of Compacted Metal Hydride

- $H_2$ 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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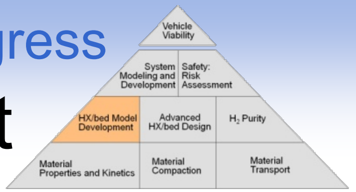
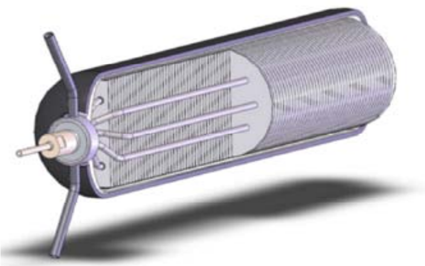
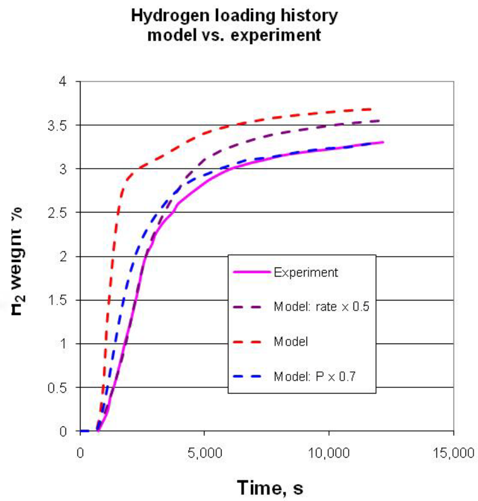


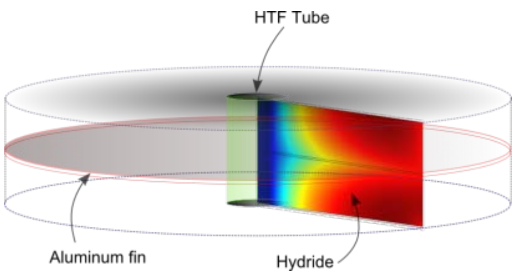

# Storage System Model and HX Development

- 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

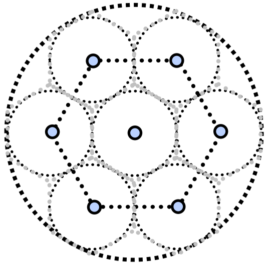


Prior UTRC prototype

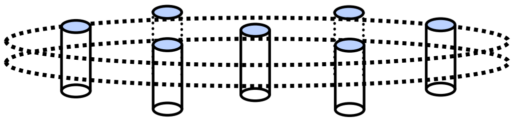



Finite element model



Parametric model



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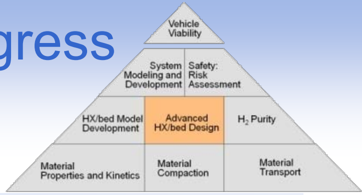
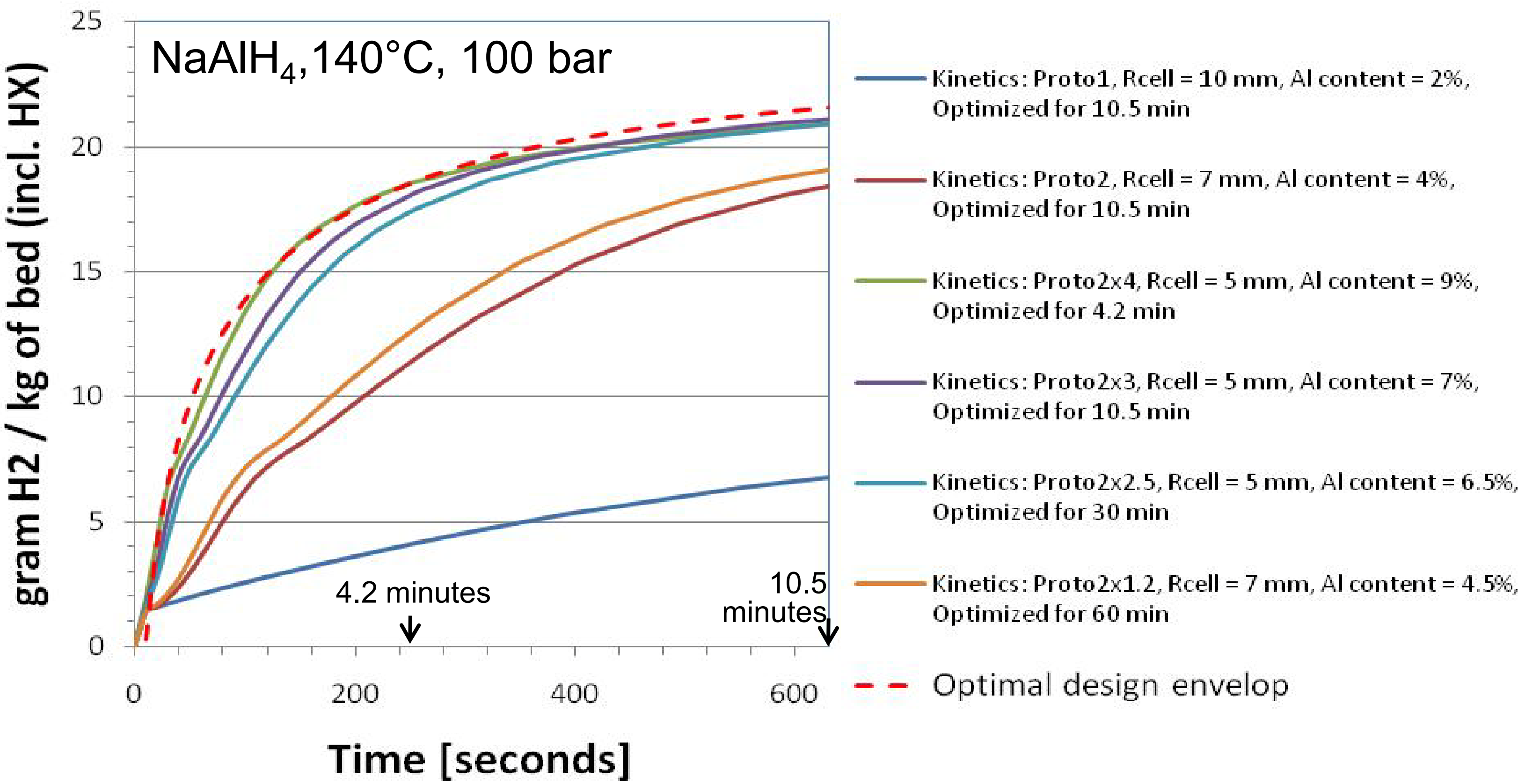
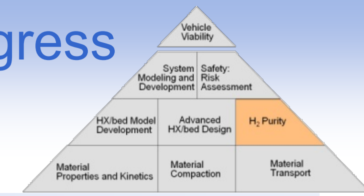



# HX Design for Fast Refueling Time

- 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

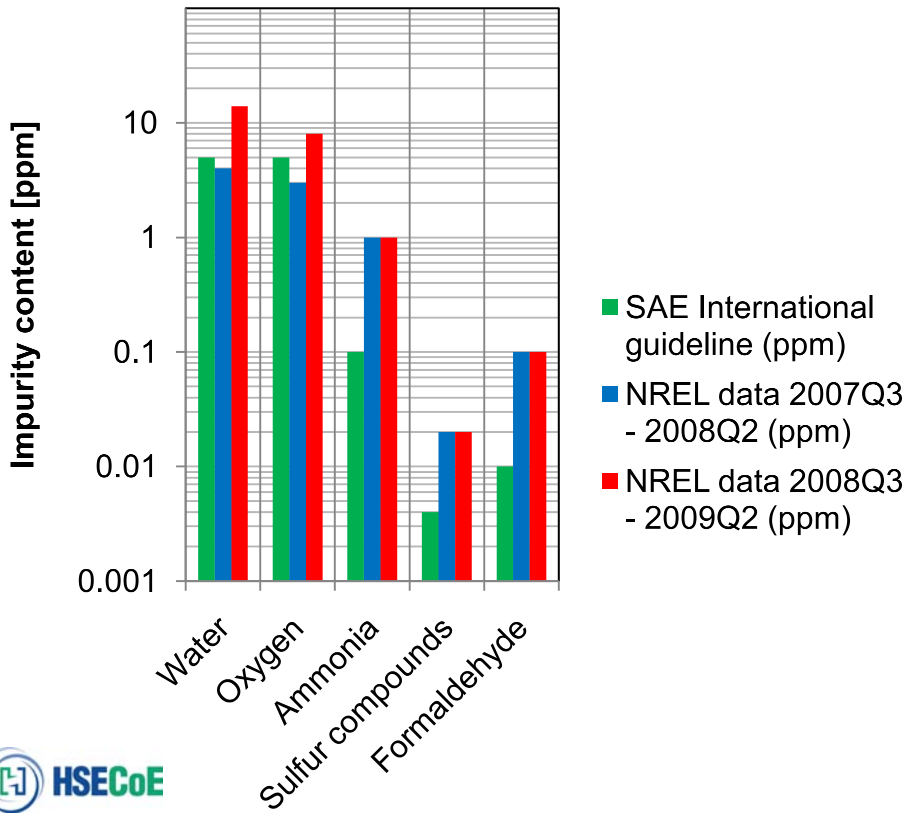



# $H_2$ Purity

- 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

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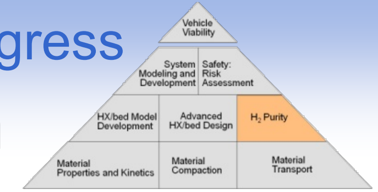
# Preliminary Purification System Comparison

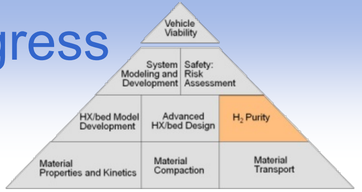



| Factor | Conventional Palladium Membrane | Regenerable Physical Adsorption | Chemical Adsorption |
|---|---|---|---|
| **Weight** | Heavy | Heavy[1)] | Light |
| **Volume** | Big | Big | Small |
| **Cost** | **Expensive** | Affordable | Affordable |
| **$H_2$ loss** | 2-5% | **High[1)]** | Low |
| **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** |

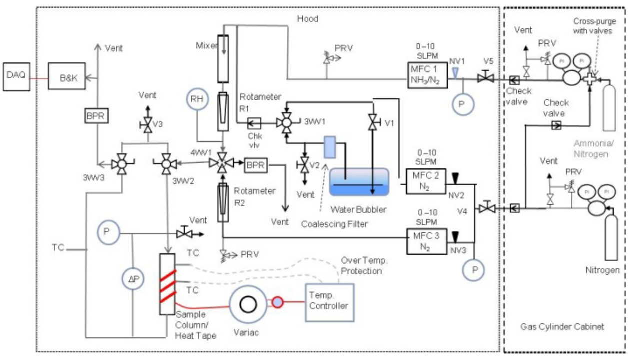
[1)] Assuming on-board regeneration

Chemical adsorption cartridge selected for Ammonia

# Adsorption System Development



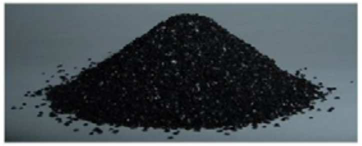

## Process Flow Diagram



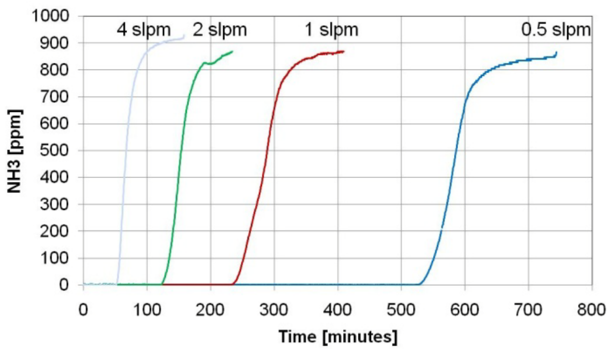

## Test apparatus

## $NH_3$ 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

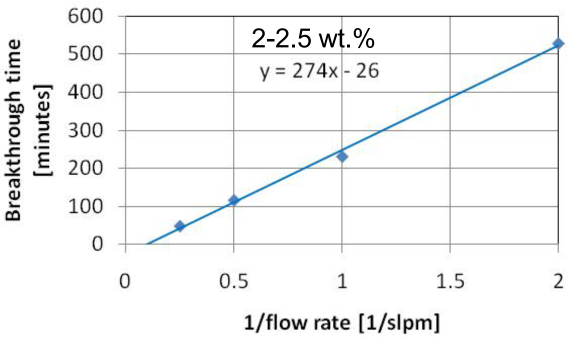


## $NH_3$ breakthrough curves

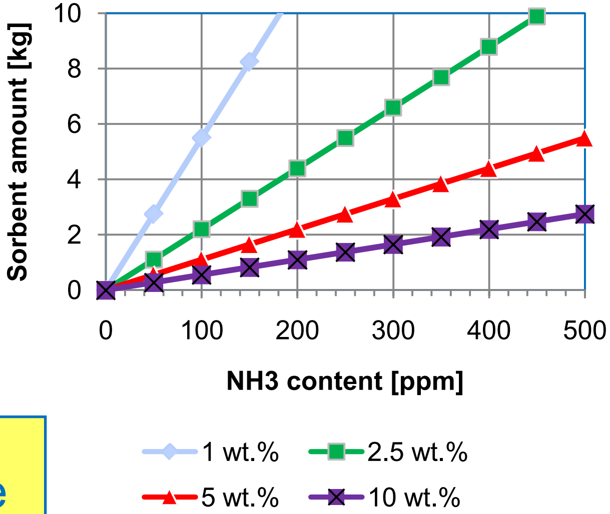



7.5 g, bed height: 12 cm, Inlet: 1000 ppm $NH_3$ in $N_2$

## 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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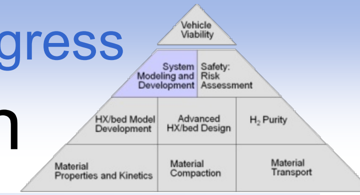
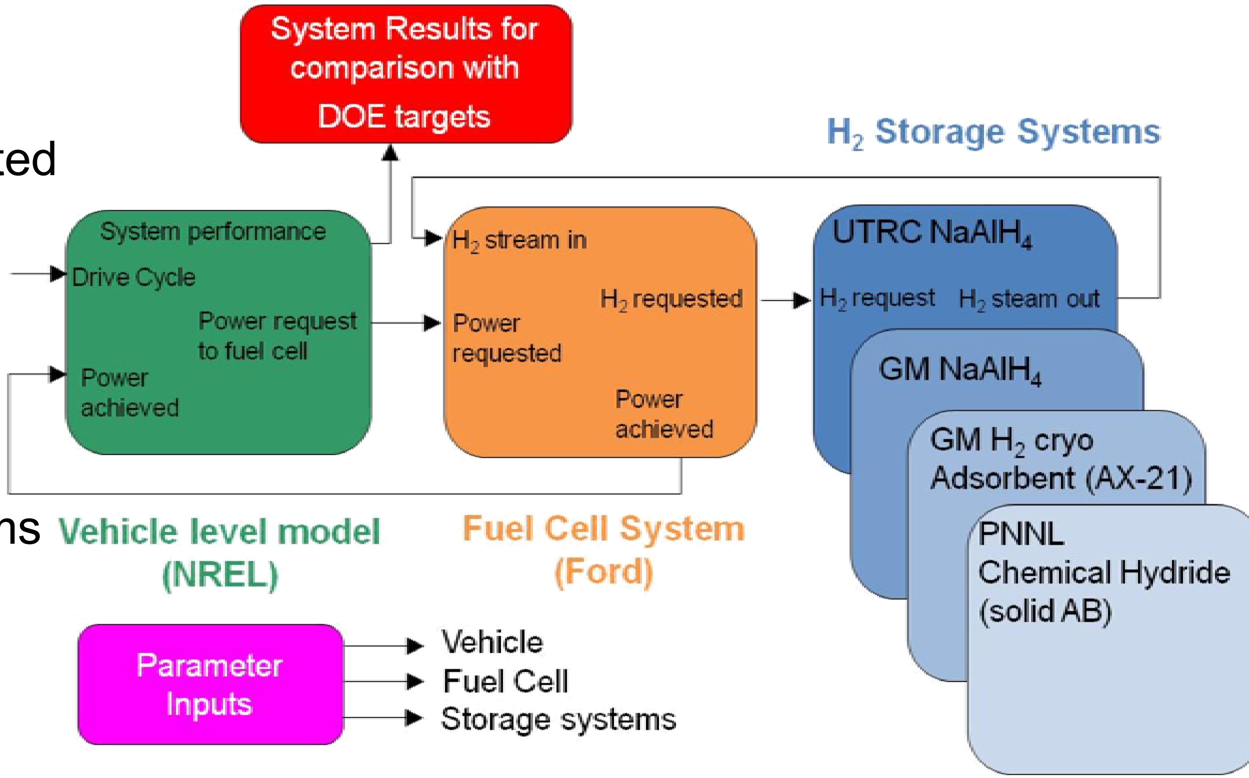


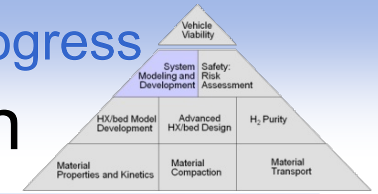

# Integrated Framework for Vehicle Simulation

- 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

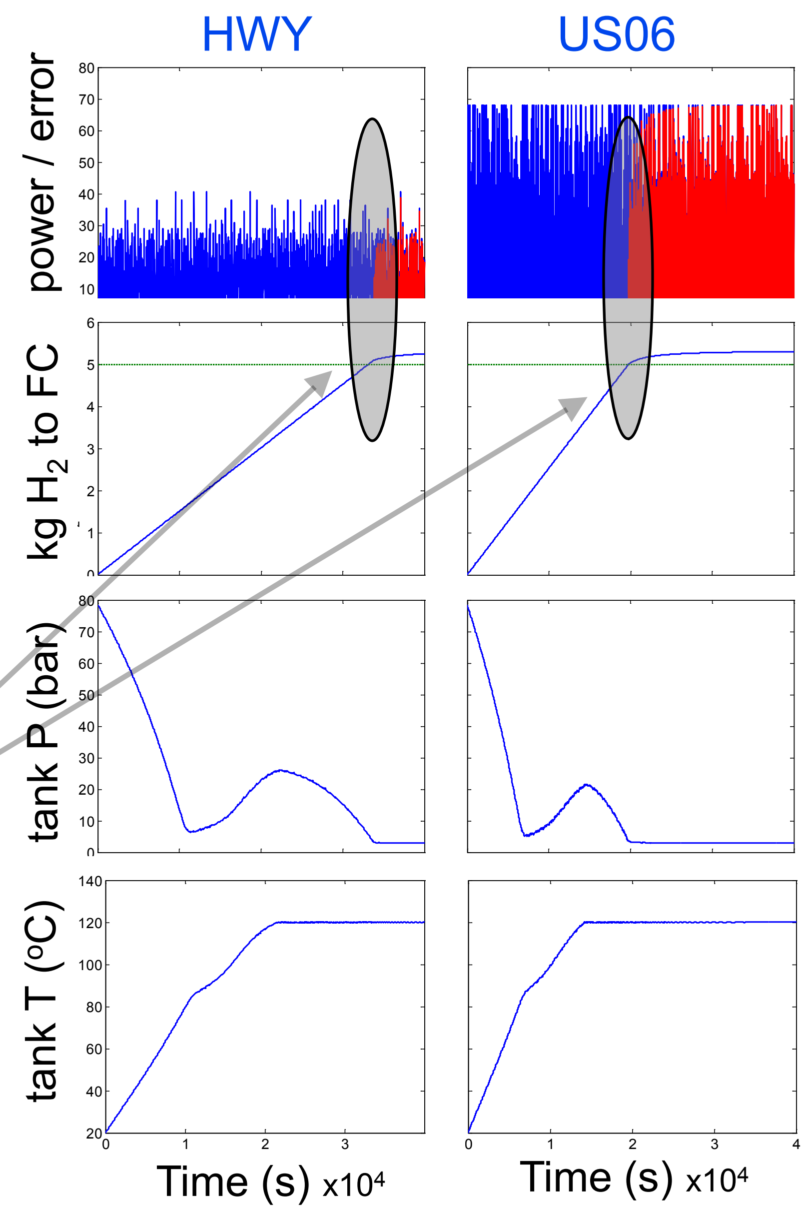



# Integrated Framework for Vehicle Simulation

## $NaAlH_4$ 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

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# 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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