Hydrogen Storage Engineering
CENTER OF EXCELLENCE

Chemical Hydride Rate Modeling, Validation, and System Demonstration

LANL Team

T.A. Semelsberger (P.I.) , Eric Brosha, Jose Tafoya, Gerie Purdy, Tessui Nakagawa, and Ben Davis

DOE Fuel Cell Technologies Program Annual Merit Review,
EERE: Hydrogen, Fuel Cells and Infrastructure Technologies Program
Washington, DC June 07-11, 2010
Technology Development Manager : Monterey Gardiner

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U.S. Department of Energy
Energy Efficiency and Renewable Energy
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The Institute for Hydrogen and Fuel Cell Research

Project ID: ST007

Introduction and Project Approach

Los Alamos National Laboratory's Chemical Hydride Rate Modeling, Validation, and System Demonstration Project is a newly funded DOE project under the Hydrogen Storage Engineering Center of Excellence led by Savannah River National Laboratory (SRNL). The scope of work for the Hydrogen Storage Engineering Center of Excellence are:

- **Systems engineering for hydrogen storage systems for vehicular applications**
- **Energy management. Understand impact on subsystems of required heat and/or mass transport**
- **Novel component & reactor designs. Stress conformable designs that are compact and light-weight**
- **Concept evaluation & sub-scale prototype testing**

In support of the goals and objectives of the Hydrogen Storage Engineering Center Excellence (HSECoE) , Los Alamos National Laboratory will contribute to modeling, designing, fabricating, and testing a prototype hydrogen release reactor for a hydrogen storage system based on chemical hydrides. Through these efforts, we will solve the critical issues for implementation of chemical hydrides in a hydrogen storage system and develop two key enabling technologies for other hydrogen storage system types.

Los Alamos National Laboratory work scope includes:

- **Develop fuel gauge sensors for hydrogen storage media**
- **Develop models of the aging characteristics of hydrogen storage materials**
- **Develop rate expressions of hydrogen release for chemical hydrides**
- **Develop novel reactor designs for start-up and transient operation for chemical hydrides**
- **Identify hydrogen impurities and develop novel impurity mitigation strategies**
- **Design, build, and demonstrate a subscale prototype reactor using liquid or slurry phase chemical hydrides**

LANL Project Overview

Timeline

- Project Start Date: Feb FY09
- Project End Date: FY14
- Percent Complete: 25%

Budget

- Project End Date: FY14
- Funding:
  - 2009: $578K
  - 2010: $712K

Barriers

- **Barriers Addressed**
  - *Efficiency*
  - *Gravimetric Capacity*
  - *Volumetric Capacity*
  - *Durability/Operability*
  - *H_2 Discharging Rates*
    - *Start time to full flow*
    - *Transient Response*
  - *H_2 Purity*
  - *Environmental, Health & Safety*

Project Timeline

Phase 1									Phase 2						Phase 3					
2009			2010				2011		2011		2012				2013				2014	
Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2

HSECoE Partners

SRNL
SAVANNAH RIVER NATIONAL LABORATORY

Pacific Northwest
NATIONAL LABORATORY

United Technologies
Research Center

JPL

H
HSM
SYSTEMS

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CALIFORNIA INSTITUTE OF TECHNOLOGY
1891

NREL
National Renewable
Energy Laboratory
Innovation for Our Energy Future

HRI
UQTR

LINCOLN
COMPOSITES
A Member of Hexagon Composites Group

Ford

OSU
Oregon State
UNIVERSITY

GM

BASF
The Chemical Company

LANL Project Objectives, Project Milestones & Project Go/No-Go Decision Points

	Phase 1								Phase 2						Phase 3					
	FY09				FY10				FY11				FY12				FY13			
Objectives and Tasks	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Objective 1: To Act as the Chemical Hydrogen Storage Center of Excellence (CHSCoE) Liaison																				
TASK 1.1: Identify and compile engineering modeling data for chemical hydrides						D4					D13			D18						
TASK 1.2: Provide testing protocols to CHSCoE							D6													
TASK 1.3: Identify media risks and mitigation strategies								D7						D19						
Objective 2: Develop Fuel Gauge Sensors for Hydrogen Storage Media																				
TASK 2.1: Identfiy first generation fuel gauge sensors				D1				G1												
TASK 2.2: Develop and demonstrate fuel gauge sensors									M2					D20						
Objective 3: Mathmatically Model the Aging Characteristics of Candidate Hydrogen Storage Media																				
TASK 3.1: Develop models to predict shelf-lives									M3					D21						
TASK 3.2: Provide accelerated aging testing protocols for shelf-life modeling to the HSMCoE				D2				D8												
Objective 4: Develop Rate Models for Hydrogen Release on Candidate Chemical Hydrides																				
TASK 4.1: Identify operating temperatures and hydrogen release rates				D3																
TASK 4.2: Collect kinetics data from CHSCoE and develop catalytic reaction rate models						D5														
TASK 4.3: Model reactors with release kinetics coupled with mass and heat transfer effects								M1				D14								
TASK 4.4: Provide feedback to CHSCoE with strategies on catalyst optimization and design								D9				D15								
Objective 5: Develop Novel Strategies for Start-Up and Transient Operation with Candidate Chemical Hydrides																				
TASK 5.1: Identify reaction coupling schemes that minimize reactor start-up times and maximizing energy efficiency								D10												
TASK 5.2: Examine transient effects on reactor turn-down											M5			D22						
Objective 6: Identify Hydrogen Impurities and Develop Novel Impurity Mitigation Strategies																				
TASK 6.1: Identify impurities demonstrating fuel cell degradation								D11												
TASK 6.2: Determine adsorbate-adsorbent interactions												D16								
TASK 6.3: Quantify and model hydrogen impurities demonstrating fuel cell degradation								D12				D17								
TASK 6.4: Identify novel impuritiy separation strategies									M4			G2		D23						
DOE CENTER-WIDE GO/NO-GO												**G3**								
Objective 7: Design, Build, and Demonstrate a Subscale Prototype Reactor that Releases Hydrogen using Chemical Hydrides																				
TASK 7.1: Coordinate risk assessment and mitigation strategies for demonstration																D27				
TASK 7.2: Coordinate the integration of the relevant design concepts into the prototype design											M6			D24 G4						
TASK 7.3: Coordinate the development of a logistics plan for testing and evaluating prototypes															D25					
TASK 7.4: Coordinate the development of decomissioning plans for subscale prototypes															D26					
TASK 7.5: Scale and design an optimized chemical hydride prototype													M7				D28			
TASK 7.6: Fabricate subscale system components for chemical hydride prototype															M8					
TASK 7.7: Build subscale chemical hydride test bed station																M9		D29		
TASK 7.8: Assemble and evaluate subcale chemical hydride protoype																	M10			D30
TASK 7.9: Coordinate the decommissioning of all subscale prototypes																				D31

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LANL Project Deliverables

Phase	Deliverable	Description	Delivery to	Date
Phase 1	D1	First generation fuel gauge sensor *(DEMONSTRATED)*	DOE	Q4 FY09
	D2	Testing protocols for shelf-life data acquisition *(COMPLETED)*	CHSCoE	Q4 FY09
	D3	Identify the operating conditions for rate data collection *(COMPLETED)*	CHSCoE	Q4 FY09
	D4	Identify & compile engineering data for chemical hydrides *(IN PROGRESS)*	DOE & ECoE	Q2 FY10
	D5	Collate rate data collected by the CHSCoE and develop rate model *(IN PROGRESS)*	ECoE	Q2 FY10
	D6	Provide testing protocols to CHSCoE *(IN PROGRESS)*	CHSCoE	Q3 FY10
	D7	Identify & compile chemical hydride media risks and mitigation strategies *(IN PROGRESS)*	DOE & ECoE	Q4 FY10
	D8	Update testing protocols for shelf-life data acquisition (as needed) *(IN PROGRESS)*	CHSCoE	Q4 FY10
	D9	Provide feedback to CHSCoE on potential catalyst optimization strategies *(IN PROGRESS)*	CHSCoE	Q4 FY10
	D10	Reaction coupling schemes addressing start-up and transient operation *(IN PROGRESS)*	CHSCoE, ECoE, & DOE	Q4 FY10
	D11	Identify fuel cell impurities *(IN PROGRESS)*	DOE, HSMCoE, & ECoE	Q4 FY10
	D12	Quantify minimum fuel-cell impurity level for safe operation	DOE & ECoE	Q4 FY10
Phase 2	D13	Update engineering data for chemical hydrides (as needed)	DOE & ECoE	Q3 FY11
	D14	Rate model for chemical hydride hydrogen release	DOE & ECoE	Q4 FY11
	D15	Provide update to CHSCoE on potential catalyst optimization strategies	CHSCoE	Q4 FY11
	D16	Determine fuel cell degradation via impurities	DOE & ECoE	Q4 FY11
	D17	Update on minimum fuel-cell impurity level for safe operation	DOE & ECoE	Q4 FY11
	D18	Update engineering data for chemical hydrides (as needed)	DOE & ECoE	Q2 FY12
	D19	Update chemical hydride media risks and mitigation strategies	DOE & ECoE	Q2 FY12
	D20	Working fuel gauge sensor capable of monitoring H2 levels within +/- 5%	DOE & ECoE	Q2 FY12
	D21	Shelf-life models for candidate hydrogen storage media	DOE & ECoE	Q2 FY12
	D22	Report on transient operation of novel reaction coupling schemes	DOE & ECoE	Q2 FY12
	D23	Working Impurity mitigation device with low cost, low volume & low mass	DOE & ECoE	Q2 FY12
	D24	Final prototype designs for all media types	DOE & ECoE	Q2 FY12
Phase 3	D25	Logistics plan for testing and evaluating subscale prototypes	DOE & ECoE	Q3 FY12
	D26	Decommissioning plans for SRNL, JPL, & LANL	DOE & ECoE	Q3 FY12
	D27	Report on all known risks and mitigation strategies for prototype demonstrations	DOE & ECoE	Q4 FY12
	D28	Final scaled design of all prototypes	DOE & ECoE	Q1 FY13
	D29	Test bed proper for demonstrating subscale prototype	DOE & ECoE	Q2 FY13
	D30	Final assembly and evaluation of subscale prototypes	DOE & ECoE	Q4 FY13
	D31	Prototype decommissioning	DOE & ECoE	Q4 FY13

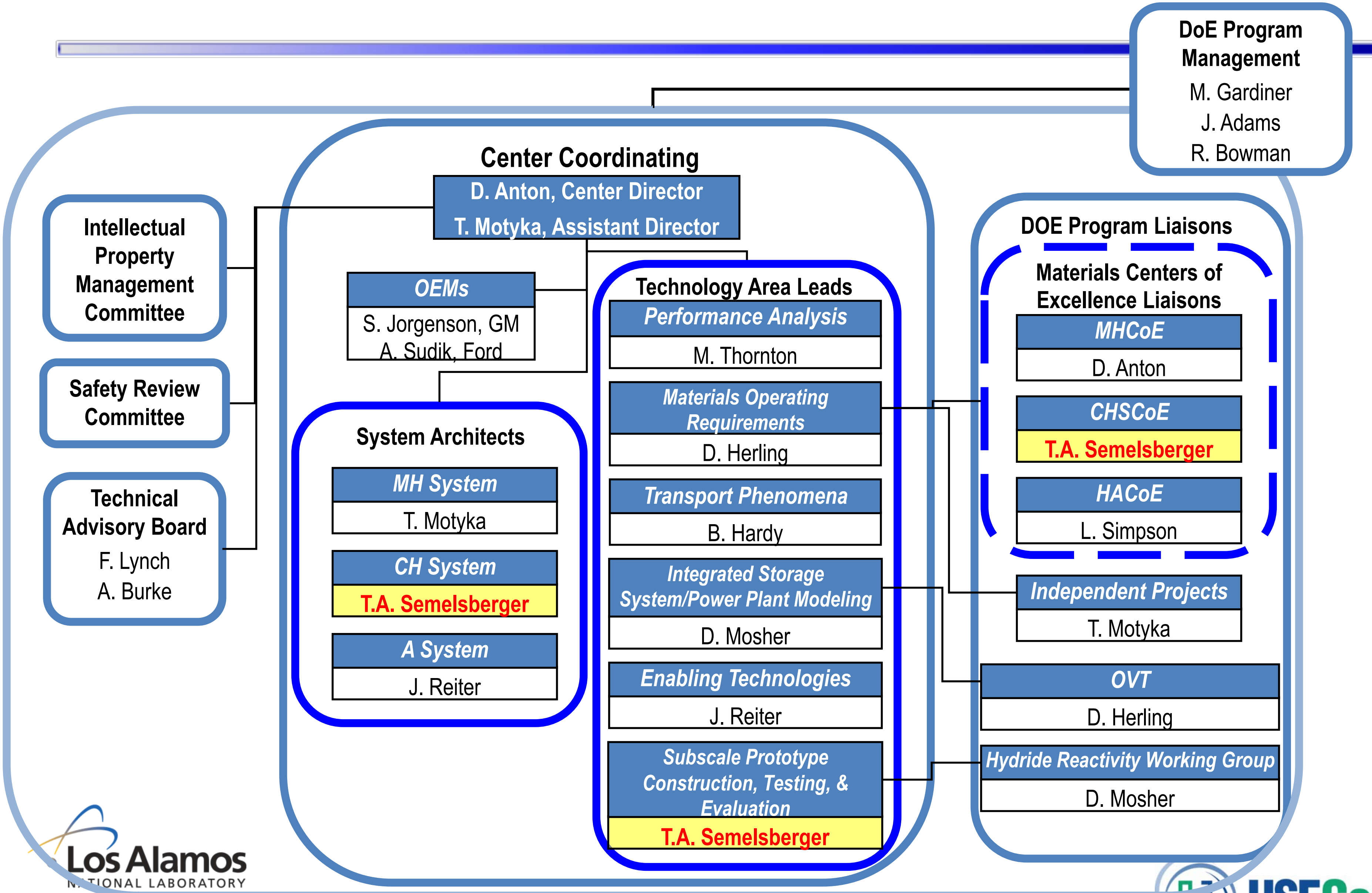
LANL Project Milestones and Go/No-Go Decisions

Phase	Milestone	Description	Dependencies	Date
Phase 1	M1	Reactor model with release kinetics coupled with heat and mass *(IN PROGRESS)*	TASKS 4.1 and 4.2	Q4 FY10
Phase 2	M2	Fuel gauge sensor development and demonstration	TASK 2.1	Q1 FY11
	M3	Shelf-life model development	TASK 3.2	Q1 FY11
	M4	Impurity mitigation strategiy development	TASKS 6.1 and 6.3	Q1 FY11
	M5	Examination of transient effects on reactor turn-down	TASK 5.1	Q3 FY11
	M6	Integration of most promising design concepts in subscale prototypes	ECoE TASKS	Q3 FY11
	M7	Scale and design chemical hydride prototype system proper	TASK 7.2	Q1 FY12
Phase 3	M8	Fabricate subscale system components	TASK 7.5	Q3 FY12
	M9	Build subscale chemical hydrided test bed station	TASK 7.6	Q4 FY12
	M10	Assemble and evaluate subscale chemical hydride prototype	TASK 7.7	Q1 FY13

Phase	Go/No-Go	Description	Criteria*	Date
Phase 1	G1	Go/No-Go Decision on fuel gauge sensor *(On Track)*	+/- 5% of H_2 Stored	Q4 FY10
Phase 2	G2	Go/No-Go Decision on viable impurity mitigation/separation strategies	mass, volume, cost	Q4 FY11
	G3	DOE Center-Wide Go/No-Go for Continuing to Phase 3	volume, cost, mass	Q4 FY11
	G4	Go/No-Go decisions on integrated design concepts for each prototype	efficiency, mass, volume, cost	Q2 FY12

** all Go/No-Go decisions will be based on the most current DOE Technical Targets; the components or designs that most favorably compare to the DOE Technical Targets will be chosen*

Overall Structure of HSECoE



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HSECoE Technology Areas (TAs)

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 (UTRC)
- Adsorption Properties (UQTR)
- Metal Hydride Properties (UTRC)
- ***Chemical Hydride Properties (LANL)***

Transport Phenomena

B. Hardy (SRNL)

- Bulk Materials Handling (PNNL)
- Mass Transport (SRNL)
- Thermal Transport (SRNL)
- Media Structure (GM)

Enabling Technologies

J. Reiter (JPL)

- Thermal Insulation (JPL)
- Hydrogen Purity (UTRC)
- ***Sensors (LANL)***
- Materials Compatibility (PNNL)
- 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 Reversible (UTRC)
- On-Board Reversible (GM)
- Power Plant (Ford)

Subscale Prototype Construction, Testing & Evaluation

T.A. 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)***

LANL Led Technology Area Team

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LANL Management Tasks in Support of HSECoE

- **Technology Area Leader** (TAL) for the Subscale Prototype Construction, Testing, & Evaluation Technology Area

- **Technology Area Team Lead for:**
  - Chemical Hydride Properties
  - Sensors
  - System Design Concepts and Integration
  - Design and Optimize Subscale Prototype
  - Fabricate Subscale System Component
  - Assemble and Demonstrate Subscale Prototypes
- **DOE Program Liaison** to the Chemical Hydrogen Storage Center of Excellence (CHSCoE)

- **Chemical Hydride System Architect**
  - Monitor progress on chemical hydrides technology across the technology areas to be sure all needed features are being advanced and that needed communication across groups and areas is occurring
  - Continually assess system for 4/40 Go/No-Go status and with the expertise of the TALs, assure that their system minimally meets requirements
  - Continually assess system for 6/50 Go/No-Go status and with the expertise of the TALs, assure that their system minimally meets requirements

LANL Management Accomplishments/Highlights

- **Technology Area Team Lead for:**
  - Chemical Hydride Properties: *Gathered pertinent thermo-physical properties and identified missing property data for chemical hydrides and identified institution for quantifying necessary data*
  - Sensors: *Developed a first generation fuel gauge sensor*
  - System Design Concepts and Integration: *Delivered preliminary design concepts*
    - *Solid chemical hydride*
    - *Liquid phase chemical hydride*

- **DOE Program Liaison** to the Chemical Hydrogen Storage Center of Excellence (CHSCoE): *Coordinated/collaborated with CHSCoE on the status of state-of-the-art chemical hydride materials*

- **Chemical Hydride System Architect**
  - ✓ *Monitored progress on chemical hydrides technology across the technology areas for needed features to be advanced and to insure needed communication across groups and areas occurs*
  - ✓ Assessed system for 4/40 Go/No-Go status:
    - *Assessment performed on solid AB*
    - *Beginning assessment on liquid AB*

LANL Primary Technical Contribution Areas

Hydrogen Storage Engineering Center of Excellence

D. Anton (SRNL)
T. Motyka (SRNL)

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D. Herling (PNNL)

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Subscale Prototype Construction, Testing & Evaluation

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- ***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)***

LANL Engineering Tasks in Support of HSECoE

LANL Engineering Tasks

Task 2: Develop Fuel Gauge Sensors for Hydrogen Storage Media (*Ahead of Schedule*)

Task 3: Develop Models of the Aging Characteristics of Hydrogen Storage Materials (*On Schedule*)

Task 4: Develop Rate Expressions of Hydrogen Release for Chemical Hydrides (*Behind Schedule*)

Task 5: Develop Novel Reactor Designs for Start-up and Transient Operation for Chemical Hydrides (*On Schedule*)

Task 6: Identify Hydrogen Impurities and Develop Novel Impurity Mitigation Strategies (*Ahead of Schedule*)

Task 7: Design, Build, and Demonstrate a Subscale Prototype Reactor Using Liquid or Slurry Phase Chemical Hydrides (*On Schedule*)

Task 2: LANL Fuel Gauge Sensor Development

✓**Relevance:**

•DOE Targets Addressed: N/A

•All commercialized vehicles necessitate a fuel gauge sensor

✓**Expected Outcomes:**

•Fuel gauge sensor for solid- and slurry-phase hydrogen storage media

✓**Tasks:**

2.1 Identify first generation fuel gauge sensors

2.2 Demonstrate fuel gauge sensor technology on candidate hydrogen storage media

❖ Deliverables

Phase	Deliverable	Description	Delivery to	Date
Phase 1	D1	First generation fuel gauge sensor *(DEMONSTRATED)*	DOE	Q4 FY09
Phase 2	D20	Working fuel gauge sensor capable of monitoring H2 levels within +/- 5%	DOE & ECoE	Q2 FY12

❖ Go/No-Go

Phase	Go/No-Go	Description	Criteria*	Date
Phase 1	G1	Go/No-Go Decision on fuel gauge sensor *(On Track)*	+/- 5% of H_2 Stored	Q4 FY10

** all Go/No-Go decisions will be based on the most current DOE Technical Targets; the components or designs that most favorably compare to the DOE Technical Targets will be chosen*

❖ Milestone

Phase	Milestone	Description	Dependencies	Date
Phase 2	M2	Fuel gauge sensor development and demonstration	TASK 2.1	Q1 FY11

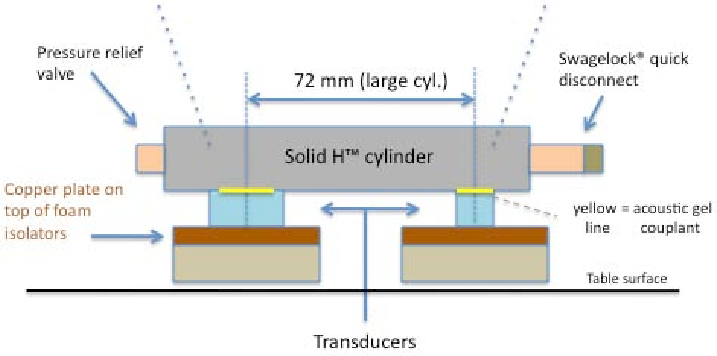
Task 2: Acoustic Fuel Gauge Sensor Proof of Concept

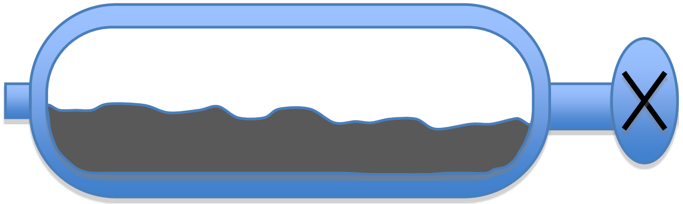
LANL developed and demonstrated a novel acoustic fuel gauge sensor on

- Three different metal hydrides
- Three different cylindrical vessels
- Metal hydride conditioning

Investigating fuel gauge sensor response as a function of

- Transducer placement
- Metal hydride compression
- Internal gas pressure in the absence of a metal hydride
  - Ar
  - H_2
- Ancillary Components
  - Valve position
  - Line attachments



- "Home made" cylinder using stainless steel vessel and Swagelok®, ¼" 316 hardware.
- Ergenics™ 208 powder free to flow and settle within container volume. Introduces "randomness" to the measurement?

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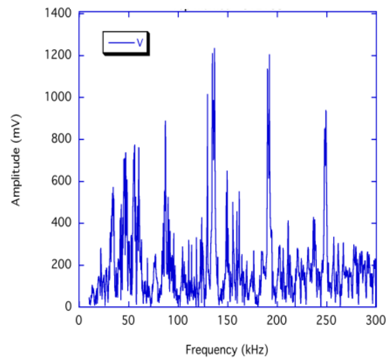
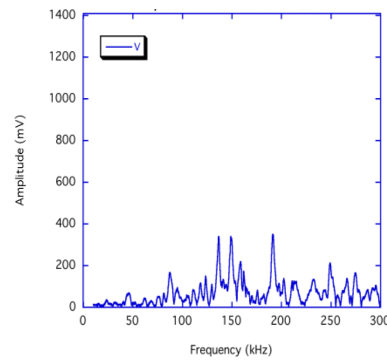
Task 2: Acoustic Fuel Gauge Sensor Proof of Concept

Solid-H™ BL-30 Hydride Storage Cylinder

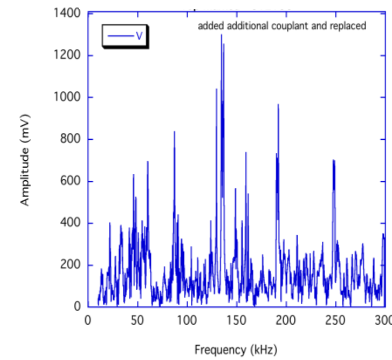
"Discharged"



"Charged"

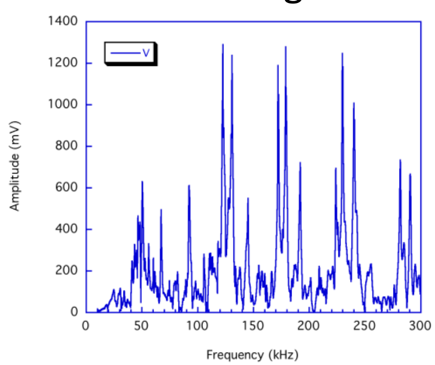


"Discharged"

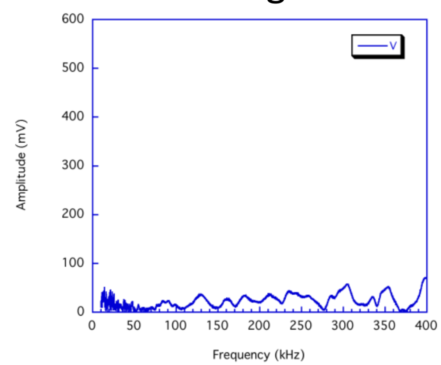


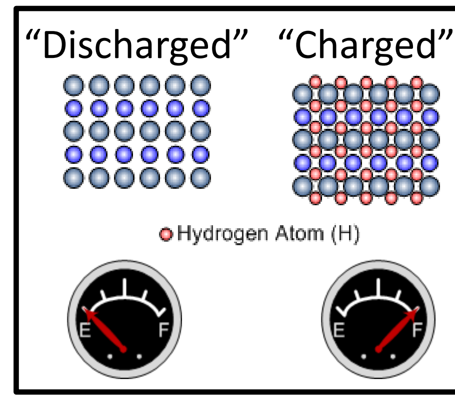
Solid-H™ Mini Hydride Storage Cylinder

"Discharged"



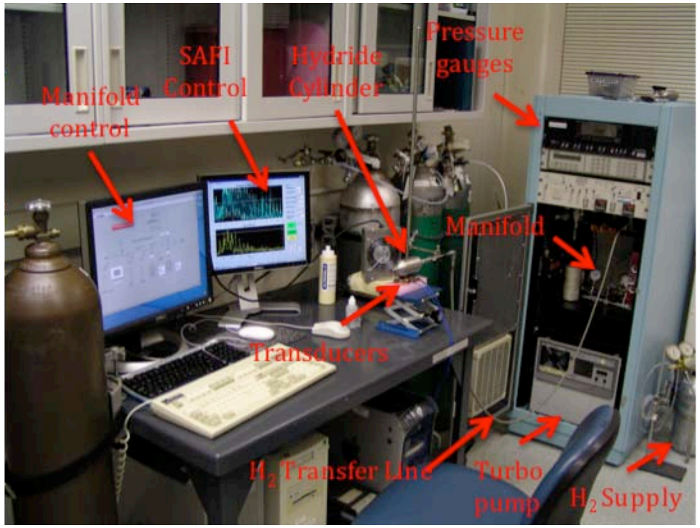
"Charged"



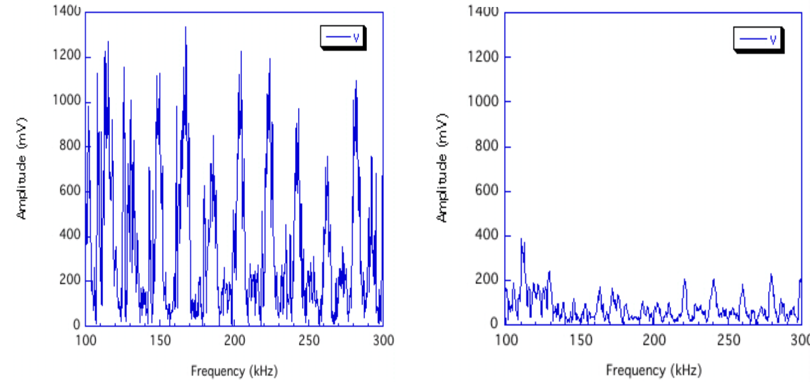


LANL Novel acoustic fuel-gauge sensor capable of accurately measuring the "charged" and "discharged" states of various metal hydrides

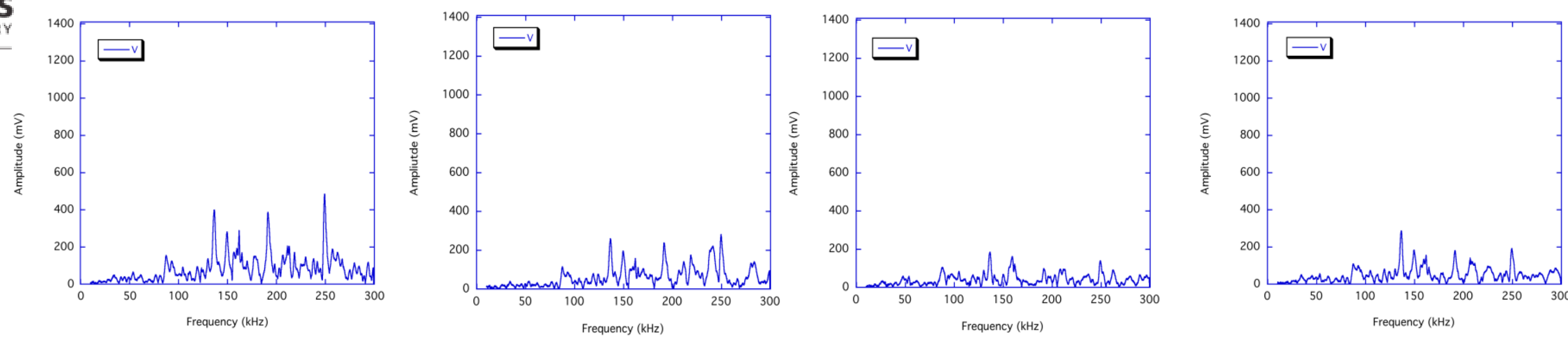
Task 2: Acoustic Fuel Gauge Sensor Proof of Concept



"Discharged" "Charged"



LANL Built $MNi_{4.5}Al_{0.5}$ Hydride Storage Cylinder



Small changes in acoustic response as function of cylinder placement observed

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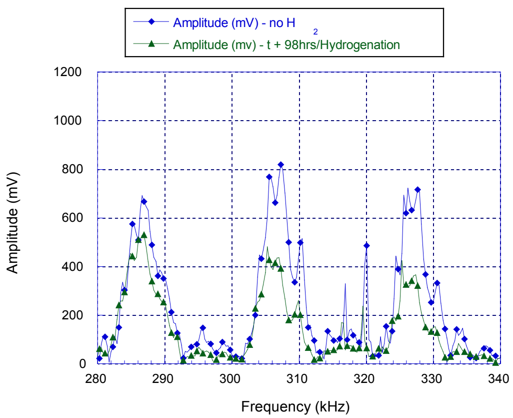
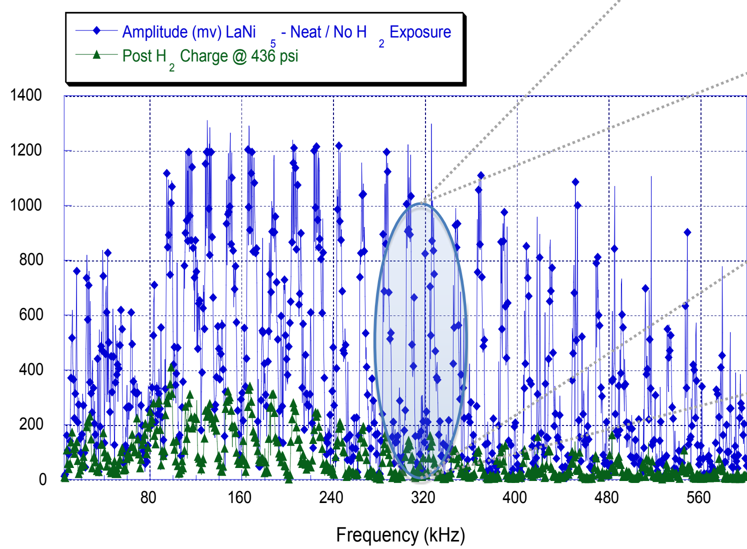
Task 2: Acoustic Fuel Gauge Sensor Proof of Concept

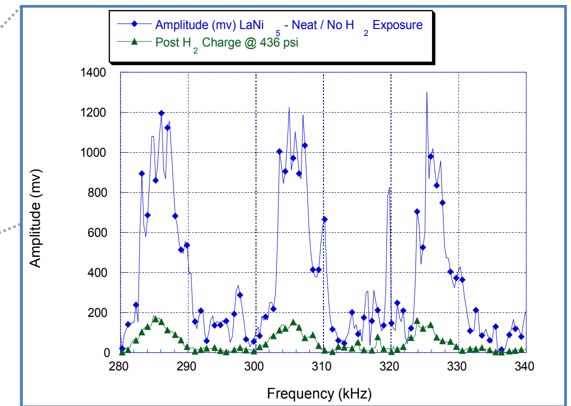
- New hydride pressurized > 300 psig. Hydride sluggish to hydrogenate
- Cylinder Temp (pre break-in) did not rise more than few degrees above ambient
- Resonance spectra changed little (superimposed on a continuous and slow decrease in P_{H2} as hydrogenation took place) unlike previous measurements made on conditioned metal hydride materials

Pre break-in





Post break-in



LANL Built $MNi_{4.5}Al_{0.5}$ Hydride Storage Cylinder

LANL Novel acoustic fuel-gauge sensor capable of tracking the progress of metal hydride charging and hydride cycling effects

Task 2 Summary: Acoustic Fuel Gauge Sensor

- Level gauge milestones for FY'10 are on track and will be met by end of Q4.
- The change in swept acoustic frequency response with metal hydride hydrogenation/dehydrogenation observed in commercially prepared metal hydride cylinders has been reproduced in simple stainless steel vessels
  - Characteristic response observed for two different metal hydride alloys
  - Ergenics™ 208 and $LaNi_5$ alloy obtained from Aldrich in different cylinder masses/volumes show same effect
- Experiments performed with neat $LaNi_5$ show transition from neat alloy to hydrided-alloy during metal hydride break in procedure.
- Experiments confirm that sound waves are coupling with, and interacting with, the metal hydride within the stainless steel pressure vessels and not due to secondary effects.
- After a prolonged, two week break-in period, the previous the characteristic acoustic behavior observed in Solid-H™ commercial metal hydride cylinders and in house-prepared, Ergenics™ 208 metal hydride based hydrogen storage systems were duplicated.
- Patent Submitted
- Acoustic sensor may be useful for Metal Hydride and Adsorbent cycling studies

LANL Demonstrated novel acoustic fuel-gauge sensor with metal hydrides

Task 2 Future Work: Acoustic Fuel Gauge Sensor

- Investigate the effects hydrogen head pressure on acoustic response
- Investigate the effects valve positioning and supply lines on acoustic response
- Perform compaction test to determine if acoustic coupling effects
- Demonstrate tracking intermediate states of hydrogen charge of the commercial hydride cylinder and look at effects of temperature on the resonance spectra.
- Begin work with other H_2 storage media

Task 3: Shelf-life Modeling

✓**Relevance:**

•DOE Targets Addressed:

- •Cost
- •Durability and Operability
- •Environmental, Health and Safety

✓**Expected Outcomes:**

•Key variables: time, temperature, pressure, humidity, and geographic location

•Updated cost models regarding production plant size, production plant storage capacity, and frequency of regeneration

✓**Tasks:**

3.1 Develop models to predict shelf lives of hydrogen storage media

3.2 Provide accelerated aging protocols for shelf life modeling to the HSMCoE

❖ Deliverables

Phase	Deliverable	Description	Delivery to	Date
Phase 1	D2	Testing protocols for shelf-life data acquisition *(COMPLETED)*	CHSCoE	Q4 FY09
	D8	Update testing protocols for shelf-life data acquisition *(IN PROGRESS)*	CHSCoE	Q4 FY10
Phase 2	D21	Shelf-life models for candidate hydrogen storage media	DOE & ECoE	Q2 FY12

❖ Milestone

Phase	Milestone	Description	Dependencies	Date
Phase 2	M3	Shelf-life model development	TASK 3.2	Q1 FY11

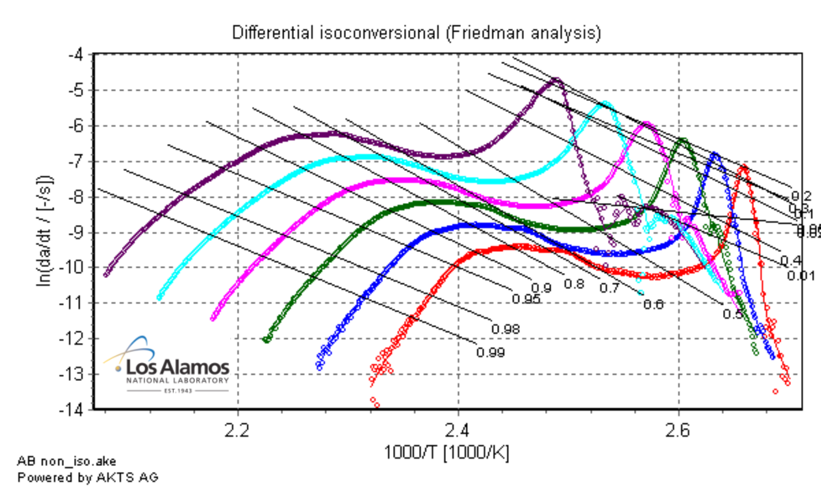
Task 3: Shelf-life Modeling of Neat AB

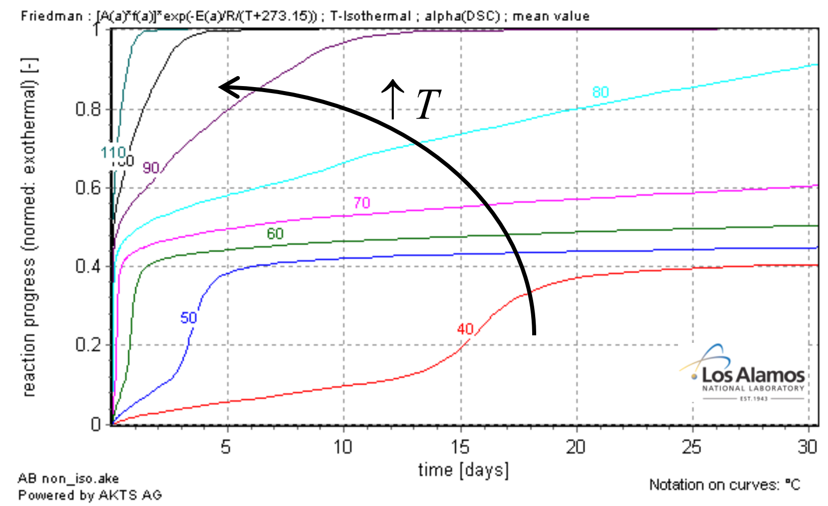
- Current Shelf-Life Model for Ammonia Borane does not agree with experiment

Down Selected Current Shelf-Life Model for Ammonia Borane (under predicts AB stability)

- Additional Experiments needed to accurately capture and predict shelf-life of Ammonia Borane
  - Liquid-Phase Ammonia Borane
  - Solid-Phase Ammonia Borane (Neat)
  - Solid-Phase Ammonia Borane (impregnated)

Need to redo the experiment with AB imbibed in methyl cellulose to eliminate foaming issues that are affecting accurate measurements

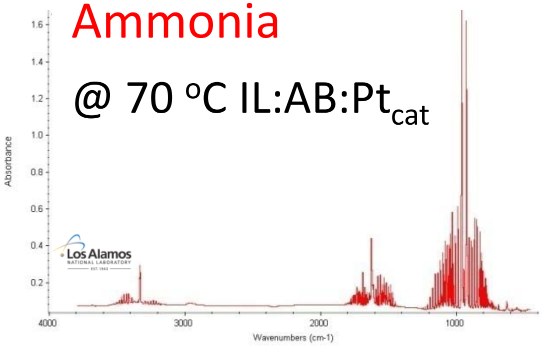


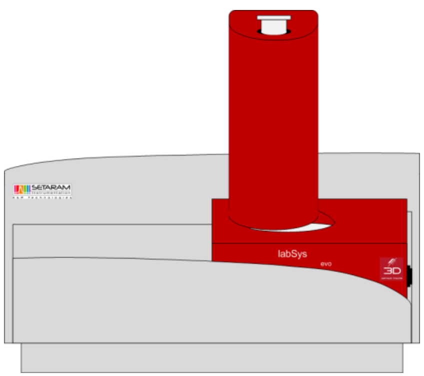


Task 3: Shelf-life Studies of Pt Catalyzed AB:IL

Ammonia

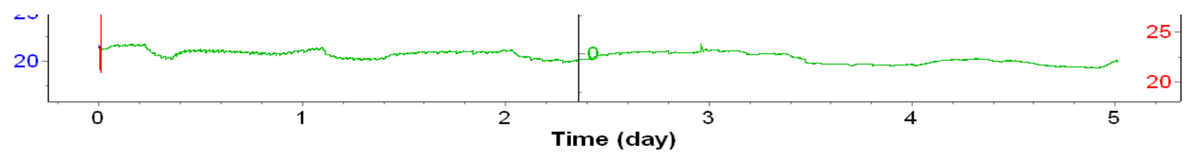
@ 70 °C IL:AB:Pt_{cat}



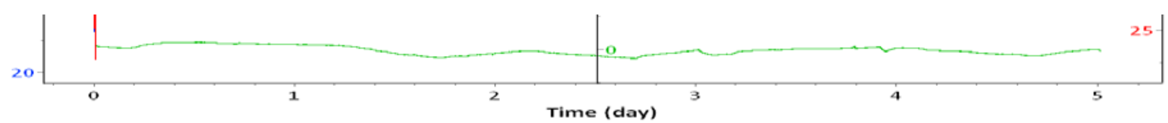


Thermal stability of IL:AB mixtures

T_{iso} = 50 ° C (Inert) $t_{online} \approx 100\ hrs$	- no change in sample mass - no detectable gas phase products via IR
T_{iso} = 50 ° C (air) $t_{online} \approx 100\ hrs$	- no change in sample mass - water was observed in gas phase due hygroscopic nature of IL (chloride is hydroscopic)



T_{iso} = 60 ° C (air) $t_{online} \approx 100\ hrs$	- no change on mass of sample for over 100 hours but slight changes in gas above sample



Only ammonia is observed in the gas phase at 70 C with catalyst, but long term stability of samples at 60 ° C still needs to be addressed

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Task 3 Summary and Future Work: Shelf-Life Studies

Summary

- Developed and updated testing protocols for accurate shelf-life data acquisition
- Collected shelf-life data for neat AB
  - Shelf-life model for neat AB under predicts stability because of foaming issues; resulting in inaccurate DSC, TGA, DTA, & Calorimeter data
- Preliminary shelf-life data collected for a liquid AB formulation
  - Liquid-AB formulations stable for 100 hrs @ 60°C; need to measure shelf-life for extended time periods (>1000 hrs)

Future Work

- Collect shelf-life data (DSC, TGA, DTA, & Calorimeter) on AB with anti-foaming agent
  - Develop shelf-life model for solid-AB formulation
- Collect a complete set of shelf-life data on liquid-AB formulations
  - Develop shelf-life model for liquid-AB formulation
- Update experimental setup and protocols as needed to ensure accurate data for model development
- Verify model accurately predicts shelf-life models for extended time periods

Task 4: Develop Reaction Rate Models for H_2 Release on Candidate Chemical Hydrides

✓**Relevance:**

- DOE Targets Addressed:
    - Charging/Discharging Rates
    - Efficiency
    - Cost
    - Hydrogen Purity
    - Gravimetric and Volumetric Capacity

$$V_{reactor} = F_{A_o} \int_0^X \frac{dX}{-r_A}$$

✓**Expected Outcomes:**

- Rate models for reactor design and operation

✓**Tasks:**

4.1 Identify operating conditions and H_2 release rates for the state-of-the-art catalysts
4.2 Collate kinetics data from CHSCoE and develop rate models
4.3 Model reactors with coupled heat, mass, momentum, and kinetics
4.4 Provide feedback to CHSCoE with strategies on catalyst optimization and design

Task 4: Develop Reaction Rate Models for H_2 Release on Candidate Chemical Hydrides

	Phase 1								Phase 2						Phase 3					
	FY09				FY10				FY11				FY12				FY13			
Objectives and Tasks	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Objective 4: Develop Rate Models for Hydrogen Release on Candidate Chemical Hydrides																				
TASK 4.1: Identify operating temperatures and hydrogen release rates for the state-of-the-art catalysts				D3																
TASK 4.2: Collect kinetics data from CHSCoE and develop catalytic reaction rate models						D5														
TASK 4.3: Model reactors with release kinetics coupled with mass and heat transfer effects								M1				D14								
TASK 4.4: Provide feedback to CHSCoE with strategies on catalyst optimization and design								D9				D15								

❖ Deliverables

Phase	Deliverable	Description	Delivery to	Date
Phase 1	D3	Identify the operating conditions for rate data collection *(COMPLETED)*	CHSCoE	Q4 FY09
	D5	Collate rate data collected by the CHSCoE and develop rate model	ECoE	Q2 FY10
	D9	Provide feedback to CHSCoE on potential catalyst optimization strategies	CHSCoE	Q4 FY10
Phase 2	D14	Rate model for chemical hydride hydrogen release	DOE & ECoE	Q4 FY11
	D15	Provide update to CHSCoE on potential catalyst optimization strategies	CHSCoE	Q4 FY11

❖ Milestone

Phase	Milestone	Description	Dependencies	Date
Phase 1	M1	Reactor model with release kinetics coupled with heat and mass	TASKS 4.1 and 4.2	Q4 FY10

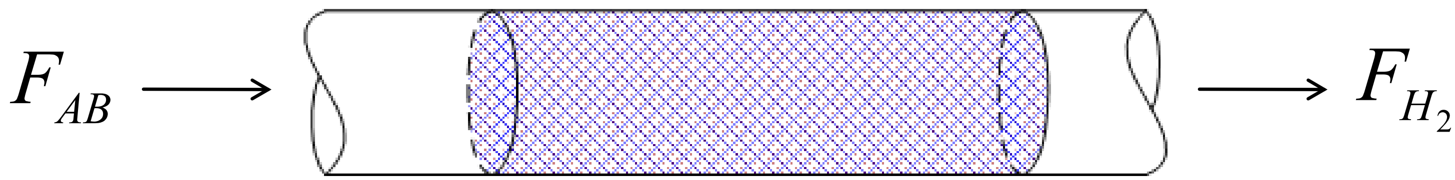
Task 4: Develop Reaction Rate Models for H_2 Release on Candidate Chemical Hydrides

Objective: To develop a liquid phase reactor capable of fast start-up and transient response

- Modeling Assumptions
  - Plug Flow Reactor (PFR)/Packed Bed Reactor (PBR)
  - Adiabatic (non-isothermal)
  - Steady-State
  - 0.8 mol H_2 / s (equivalent to full power demand for an 80 kW Fuel Cell Stack
  - Hydrogen Selectivity equal to one
  - No Catalyst Deactivation
  - First Order Rate Law with respect to Ammonia Borane
  - Constant Heat Capacities
  - Reactants and Products are liquids (exception is H_2)
  - Solvent is Inert/non-hydrogen bearing

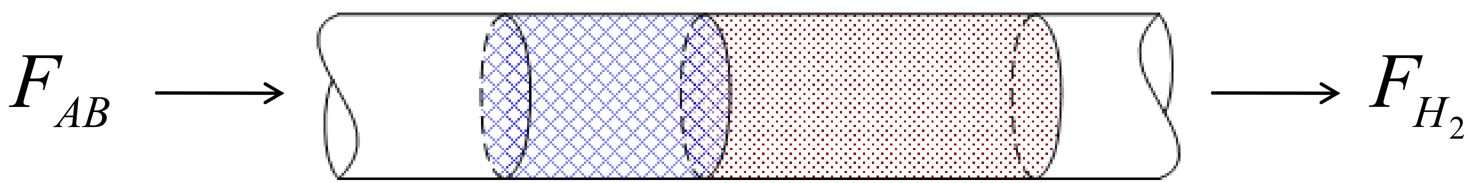
Task 4: Develop Reaction Rate Models for H_2 Release on Candidate Chemical Hydrides

CASE 1: Homogeneous Dual Catalyst Bed **(No-Go)**



Catalyst α + Catalyst β

CASE 2: Segregated Dual Catalyst Bed



Catalyst α Catalyst β

Task 4: Develop Reaction Rate Models for H_2 Release on Candidate Chemical Hydrides

Reactions

Low Temperature Catalyst (Room Temperature)

$$NH_3BH_3 \xrightarrow[Cat\ \alpha]{k_1} P_1 + H_2$$

High Temperature Catalyst (T >90°C)

$$NH_3BH_3 \xrightarrow[Cat\ \beta]{k_2} P_2 + H_2 \xrightarrow[Cat\ \beta]{k_3} P_3 + H_2$$

Energy Balance

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + \sum_{i,j}(-r_{i,j})\left[-\Delta H_{rxn\ i,j}(T)\right]}{\sum_j F_j C_{p\ j}}$$

Adiabatic Operation

$$Ua(T_a - T) = 0$$

Task 4: Develop Reaction Rate Models for H_2 Release on Candidate Chemical Hydrides

Rate Expressions

$$-r_{1A} = k_1 C_A \qquad -r_{2A} = k_2 C_A$$

$$-r_{3P_2} = k_3 C_{P_2}$$

$$k_i(T) = A_i e^{\left(\frac{-E_{ai}}{RT}\right)}$$

Mole Balances

$$\frac{dF_A}{dV} = (-r_{1A}) + (-r_{2A}) \qquad \frac{dF_{P_3}}{dV} = (-r_{3P_2})$$

$$\frac{dF_{P_1}}{dV} = (-r_{1A}) \qquad \frac{dF_H}{dV} = (-r_{1A}) + (-r_{2A}) + (-r_{3P_2})$$

$$\frac{dF_{P_2}}{dV} = (-r_{2A}) - (-r_{3P_2}) \qquad \frac{dF_I}{dV} = 0$$

Required Data

- Rate Expressions*

$$-r_i = A_i e^{\left(\frac{-E_{ai}}{RT}\right)} [C_{AB}]^{\gamma_i}$$

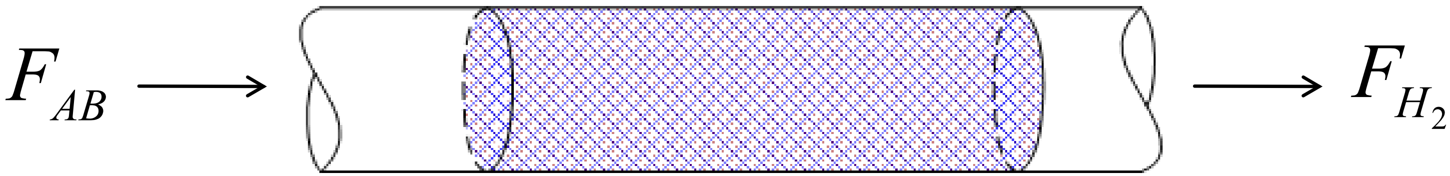
- Heat Capacities[a] (C_{pi})
- Heats of Reaction[a] (ΔH_{rxn})
- Solubility of AB in Solvent[a]

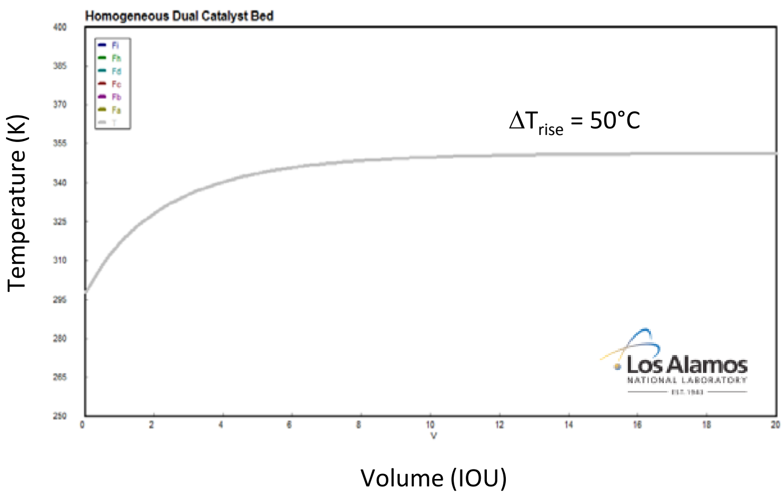
** complete set reaction kinetics are still needed from the CHSCoE*

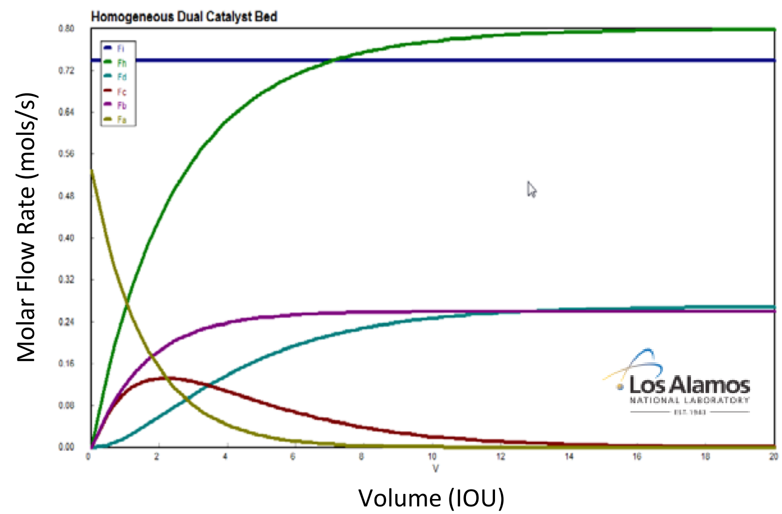
[a] measurements still needed

Task 4: Develop Reaction Rate Models for H_2 Release on Candidate Chemical Hydrides

CASE 1: Homogeneous Dual Catalyst Bed







- Solvent heat capacity can moderate adiabatic temperature rise
  - Temperature rise strong function of solvent heat capacity and AB solubility
- AB solubility is critical to gravimetric and volumetric capacity

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Task 4 Summary: Develop Reaction Rate Models for H_2 Release on Candidate Chemical Hydrides

- Solvent Heat Capacity can moderate adiabatic temperature rise
- AB Solubility is critical to gravimetric capacity
- Need to tighten up governing rate equations/kinetics wrt
  - Order of reaction
  - Selectivities (i.e., impurities)
  - Operating temperatures (broader temperature range)
  - AB concentration
  - Catalyst durability
  - Mass and heat transfer
  - Flow systems
- Rate of H_2 Production for the Low Temperature Catalyst is too fast, thus decreases the overall hydrogen production efficiency (i.e., η=0.4, η_{max}=1) with the **homogeneous dual catalyst bed design**
  - Need to maximize hydrogen production efficiency while maintaining necessary exotherm to drive High Temperature Catalyst Route

→ No-Go on Homogeneous Dual Catalyst Bed Design (Case 1)

Task 4 Future Work: Reactor Design and Modeling

- Acquire complete set of kinetics data (i.e., Selectivity, Conversion, etc.)
  - Low temperature catalyst route
    - ✓Hydrogen bearing solvents
    - ✓Non-hydrogen bearing solvent
  - High temperature catalyst route
    - ✓Hydrogen bearing solvents
    - ✓Non-hydrogen bearing solvent
- Focus on segregated dual catalyst bed (Case 2) Design
  - Mass transfer limited case
  - Kinetics limited case
- Incorporate transient behavior into reactor design model [in collaboration with B. Hardy (SRNL)]

Task 5: Novel Reactor Designs for Startup and Transient Operation

✓**Relevance:**

•DOE Targets Addressed:

- •Charging/Discharging Rates
- •Efficiency
- •Cost
- •Hydrogen Purity
- •Gravimetric and Volumetric Capacity

✓**Tasks:**

5.1 Identify reaction coupling schemes that minimize reactor start-up times and maximize energy efficiency

5.2 Examine transient effects on reactor turn-down

✓**Expected Outcomes:**

•Novel reactor designs addressing startup and transient operation

❖ Deliverables

Phase	Deliverable	Description	Delivery to	Date
Phase 1	D10	Reaction coupling addressing start-up and transient operation	CHSCoE, ECoE, & DOE	Q4 FY10
Phase 2	D22	Report on transient operation of novel reaction coupling schemes	DOE & ECoE	Q2 FY12

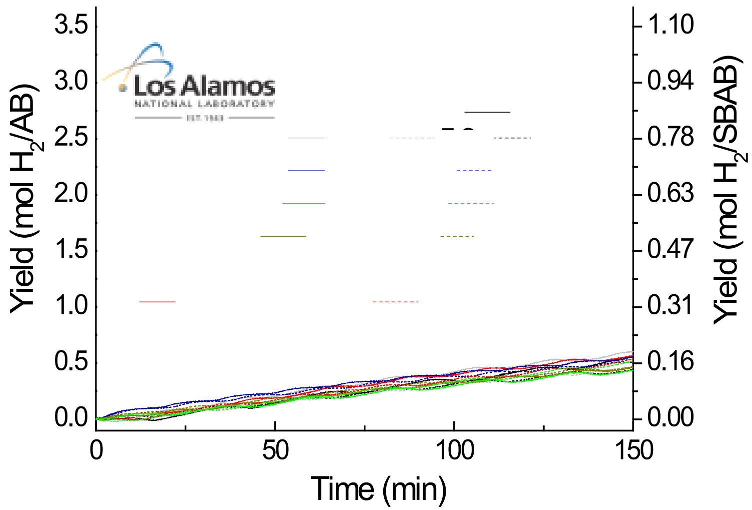
❖ Milestone

Phase	Milestone	Description	Dependencies	Date
Phase 2	M5	Examination of transient effects on reactor turn-down	TASK 5.1	Q3 FY11

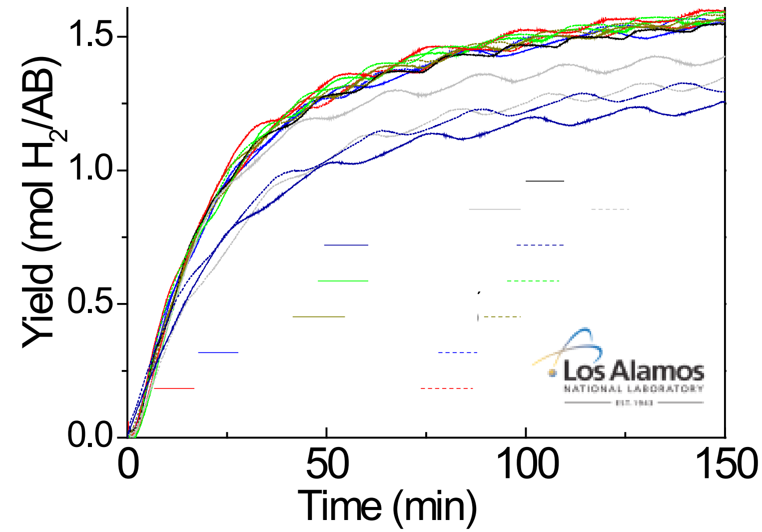
Task 5: Low Temperature Dehydrogenation Catalysts for Startup and Transient Operation

Objective: develop a low temperature catalyst (coupled with novel reactor designs) for start-up and transient operation for on-board hydrogen delivery in order to eliminate auxiliary heating devices

Liquid AB, T = 60°C



Liquid AB, T = 90°C



➢LANL has developed and screened a number of catalysts for the low-temperature (room temperature) dehydrogenation of liquid AB solutions-all have been unsuccessful

Task 5 Summary and Future Work: Low Temperature Catalysts for Startup and Transient Operation

Summary

- Screened approximately 20 catalysts for room temperature activity
  - reactor tested catalysts cannot meet the startup requirement needed for an on-board hydrogen delivery system
- We do have homogeneous catalysts that release one-equivalent of H_2 at room temperature
- Novel reactor designs (without auxiliary heating sources) addressing start-up and transient operation require the development of novel heterogeneous catalysts that are active at room temperature

Future Work

- Continued efforts will focus on converting the room temperature homogeneous catalysts into heterogeneous form while maintaining room temperature activity

Task 6: Hydrogen Impurities and Mitigation

✓**Relevance:**

- DOE Targets Addressed:
  - Cost
  - Durability and Operability
  - Environmental, Health and Safety
  - Fuel Purity

✓**Expected Outcomes:**

- Impurities demonstrating fuel cell degradation for all candidate storage materials
- Strategies for impurity mitigation/separation

✓**Tasks:**

6.1 Identify impurities demonstrating fuel cell degradation

6.2 Determine adsorbate-adsorbent interactions

6.3 Quantify and model hydrogen impurities demonstrating fuel cell degradation

6.4 Identify novel impurity separation/mitigation strategies

✓**Go/No-Go Decision Criterion:**

- DOE Technical Target of 99.99% H_2 purity (Q4 FY11)

❖ Deliverables

Phase	Deliverable	Description	Delivery to	Date
Phase 1	D11	Identify fuel cell impurities	DOE, HSMCoE, & ECoE	Q4 FY10
	D12	Quantify minimum fuel-cell impurity level for safe operation	DOE & ECoE	Q4 FY10
Phase 2	D16	Determine fuel cell degradation via impurities	DOE & ECoE	Q4 FY11
	D17	Update on minimum fuel-cell impurity level for safe operation	DOE & ECoE	Q4 FY11
	D23	Working Impurity mitigation device with low cost, low volume & low mass	DOE & ECoE	Q2 FY12

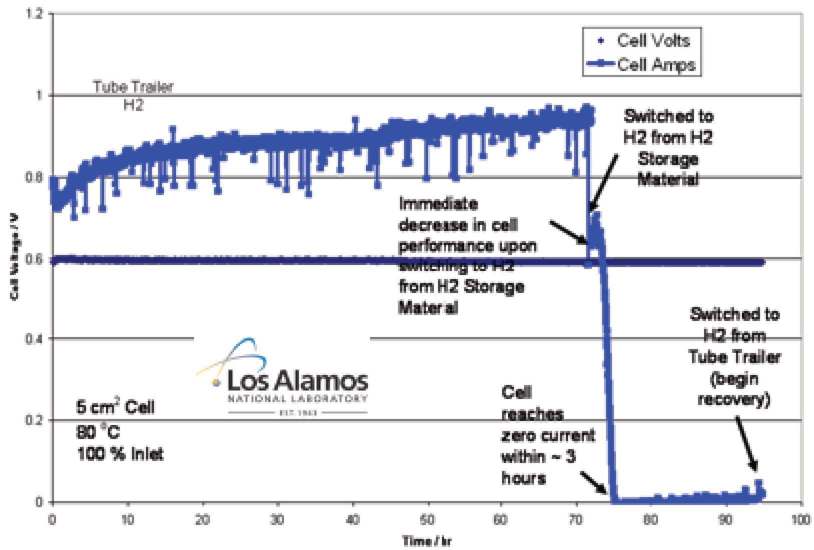
❖ Milestone

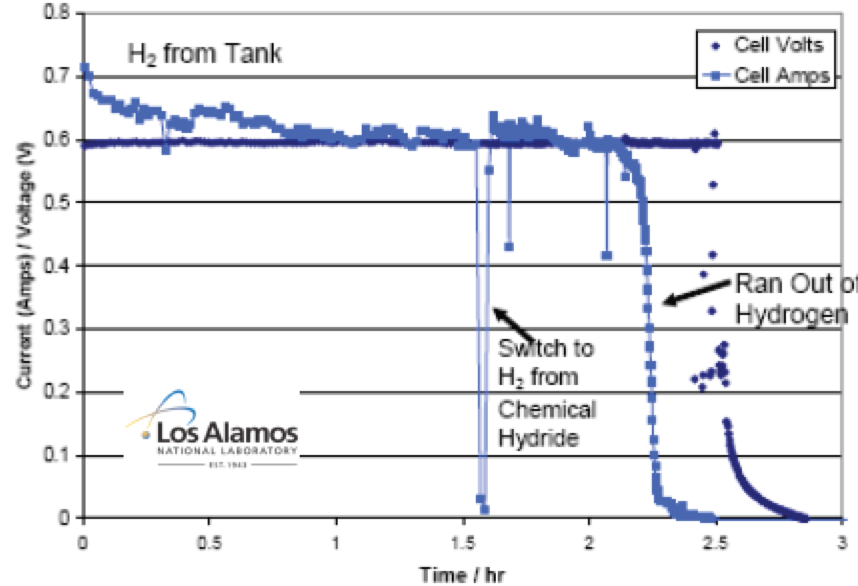
Phase	Milestone	Description	Dependencies	Date
Phase 2	M4	Impurity mitigation strategy development	TASKS 6.1 and 6.3	Q1 FY11

❖ Go/No-Go

Phase	Go/No-Go	Description	Criteria	Date
Phase 2	G2	Go/No-Go Decision on viable impurity mitigation/separation strategies	mass, volume, cost, purity	Q4 FY11

Task 6: Hydrogen Impurities and Mitigation





Raw H_2 from thermal treatment of AB contains borazine, which is known to poison Pt fuel cell catalyst

Simple inline filter removes borazine, FC performance unaffected

Fuel cell recovered under clean hydrogen and analysis indicates catalysis was poisoned, not the membrane.

- Future Test hydrogen release systems H_2 purity using long term fuel cell operation

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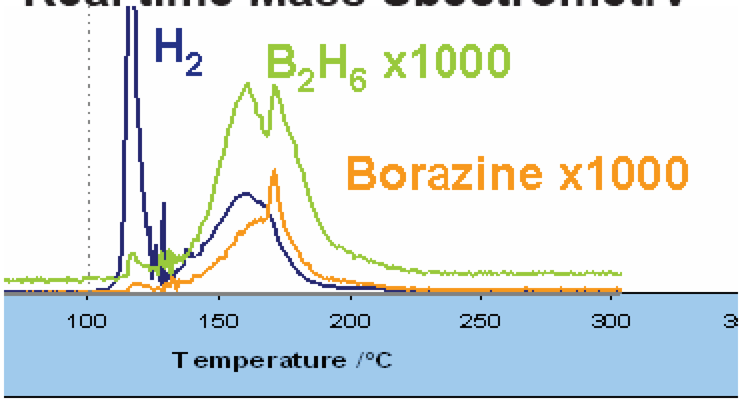
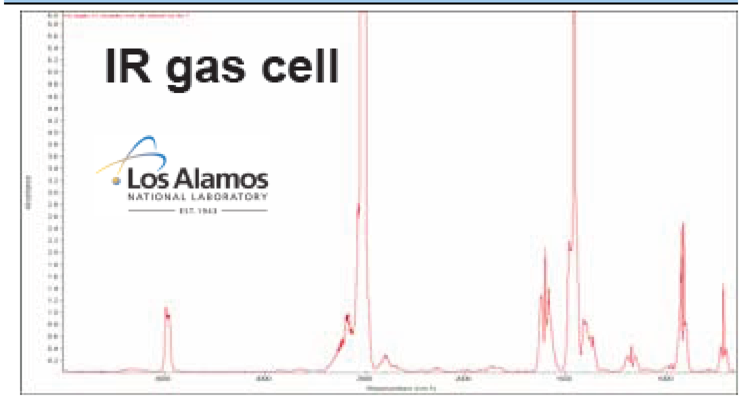
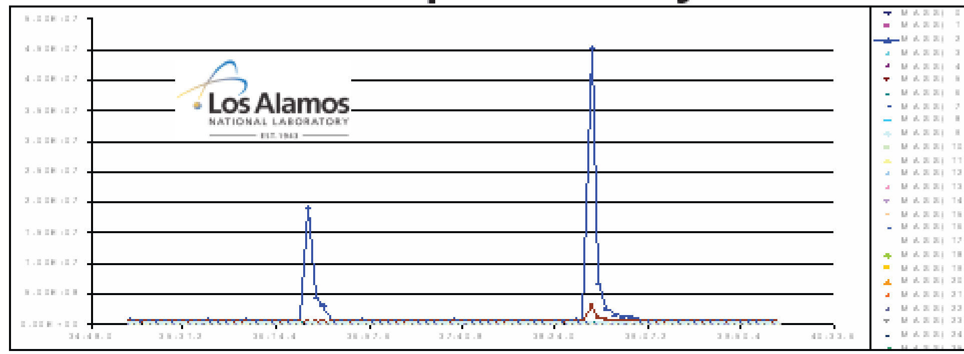
Task 6: Hydrogen Impurities and Mitigation

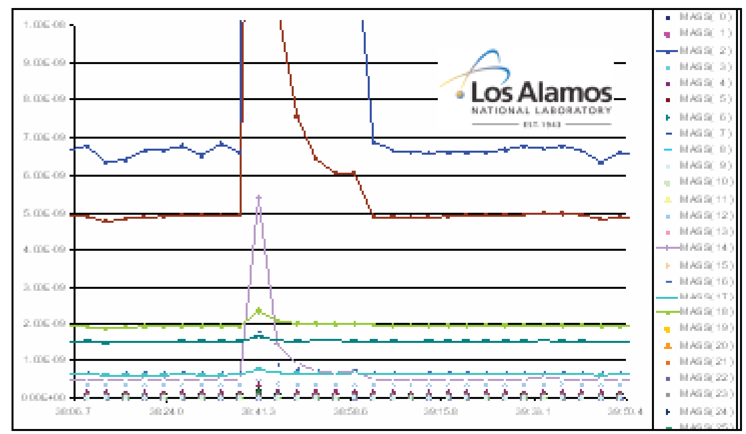
Real time Mass Spectrometry





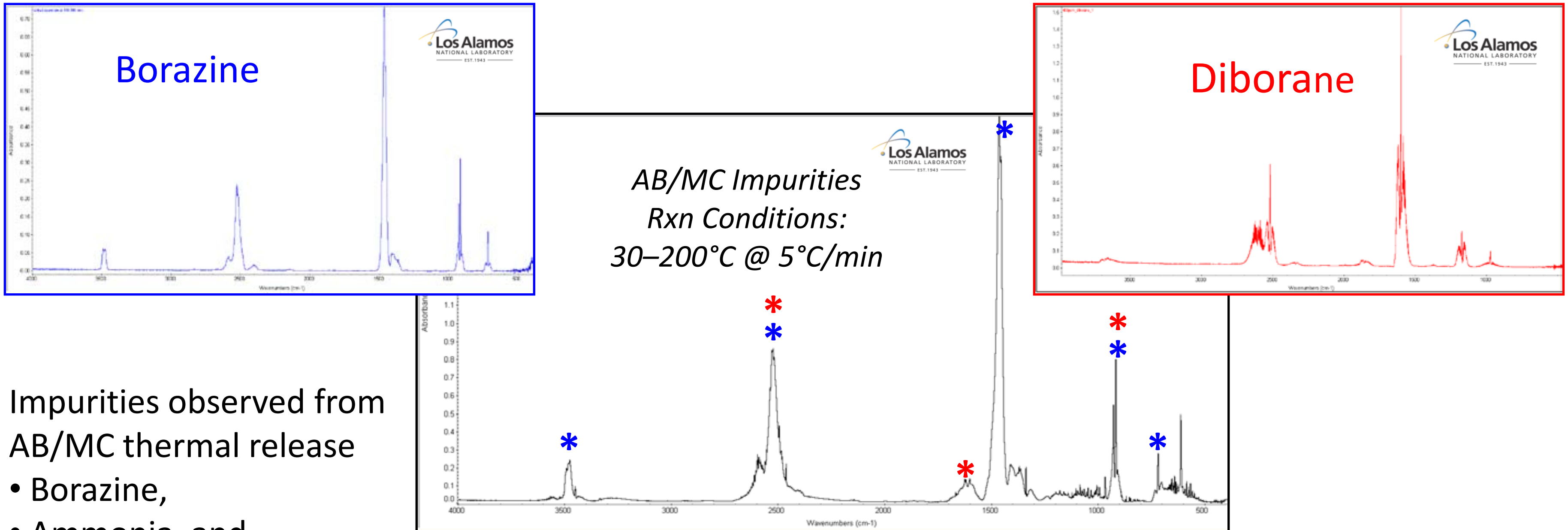
Mass Spectrometry





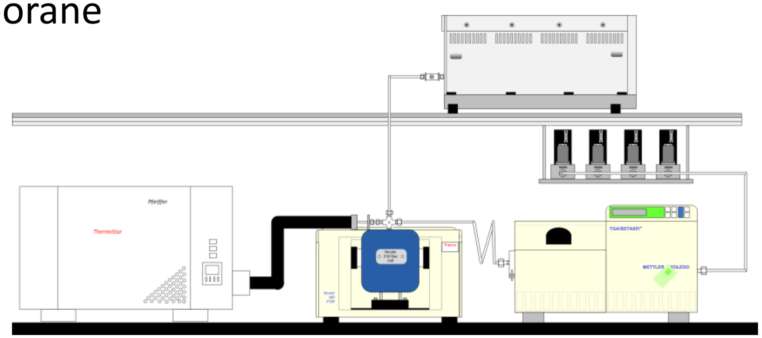
We can use spectroscopy and spectrometry for determining H_2 purity
But what about effects of very small, perhaps undetectable contaminants over long operating times?

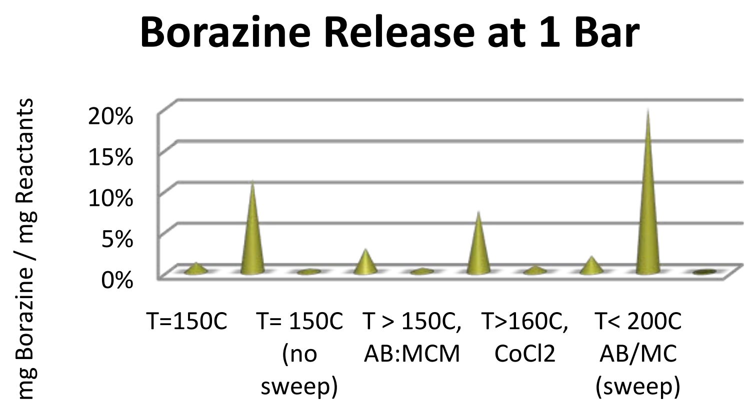
Task 6: Hydrogen Impurities and Mitigation (solid AB)



Impurities observed from AB/MC thermal release

- Borazine,
- Ammonia, and
- Diborane





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Task 6: Hydrogen Impurities and Mitigation (solid AB)

- **Experimental Data**

AB/MC Borazine Production

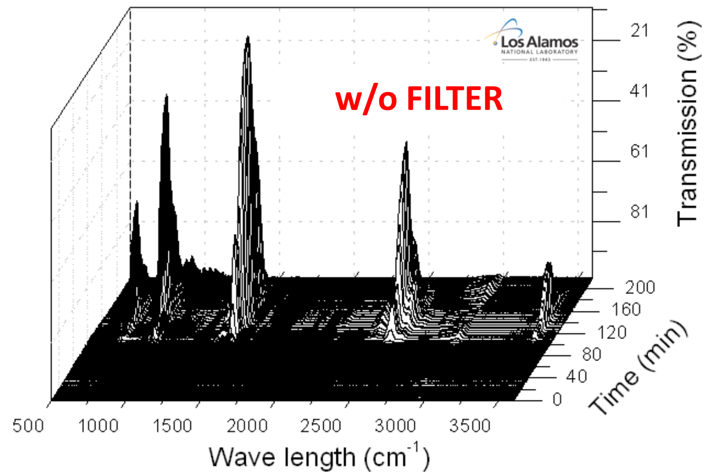
$0.2\ mg_{Borazine} / mg_{AB/MC\ Reacted}$

Reaction Conditions: 30-200°C @ 5°C/min

Borazine Sorption Capacity

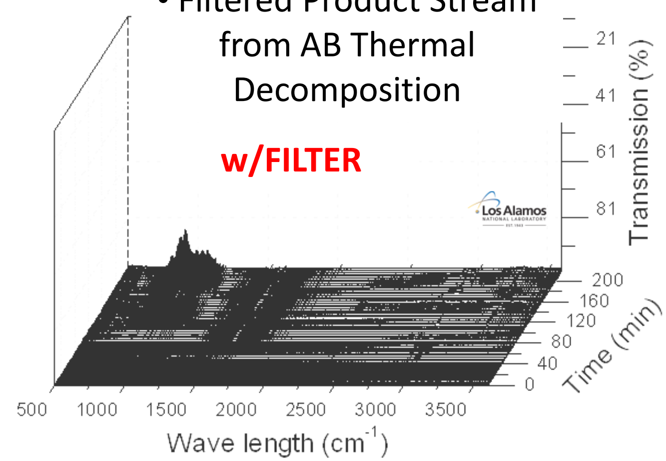
Activated Carbon (ACN-210-15):

$0.26\ mg_{Borazine} / mg_{Carbon}$



- Raw Product Stream from AB Thermal Decomposition

- Filtered Product Stream from AB Thermal Decomposition



- **Carbon Sorbent Scaleup**
  - 5kg of H_2 results in 37kg of AB/MC (2.5 moles H_2/mole AB)

➡ 6.2 kg of borazine produced per fuel tank

➡ 24 kg of carbon per fuel tank

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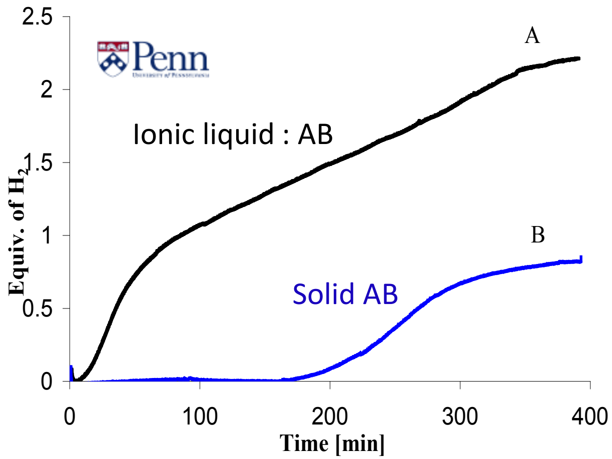
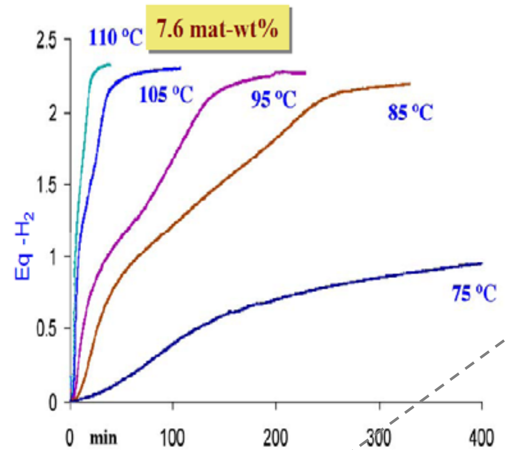
Task 6: Hydrogen Impurities and Mitigation (AB:IL Liquid phase-Thermal Release)

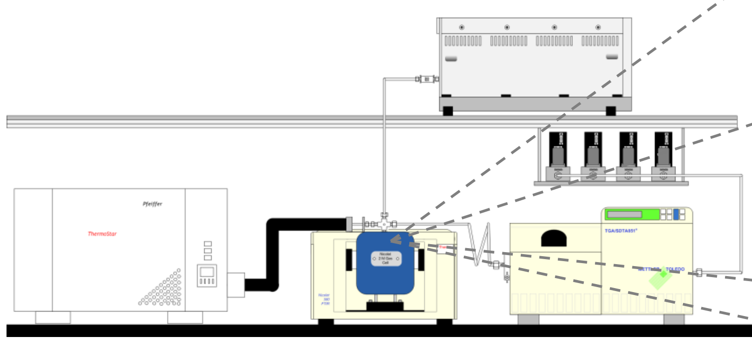


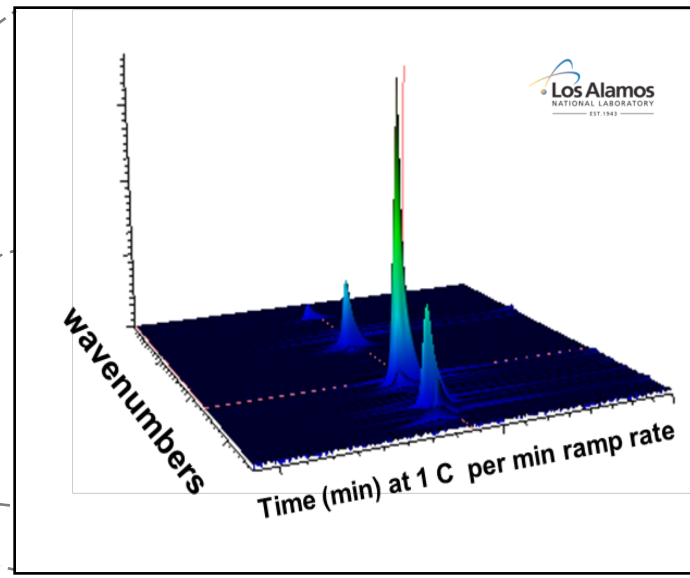


Impurities Observed AB: IL

- Borazine
- Ammonia

✓Quantification of impurities are in progress





Impurities still present in hydrogen from thermal release, but no diborane!

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Task 6 Summary: Gas Phase Impurities & Mitigation

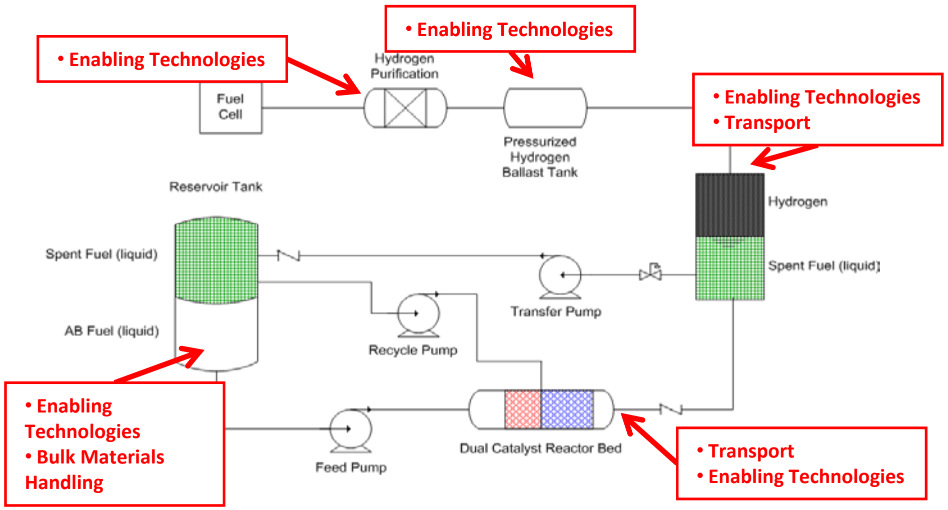
- Impurities generated from Ammonia Borane are detrimental to fuel cell performance
- Ammonia borane imbibed methyl cellulose and neat ammonia borane produce identical impurities
  - Amount of impurities is a function of temperature and heating rate
  - ⇒ Mitigation strategies include increased control of reaction (i.e., thermal management, reactor design)
- Ammonia borane in current ionic liquid demonstrated a decreased production of borazine and no diborane
- Suppression of impurity generation can be achieved via catalytic routes of hydrogen release from liquid phase ammonia borane
- Borazine can be scrubbed using activated carbon @ 0.26 $mg_{Borazine}$/ mg_{Carbon}
- Completed IR calibrations for diborane, borazine, and ammonia @ the ppb levels
- Accurate borazine and diborane measurments are nontrivial, extreme care and caution are required to quantify these impurities accurately

Task 6 Future Work: Gas Phase Impurities & Mitigation

- In collaboration with LANL CHSCoE, quantify impurities from liquid AB formulations as a function of temperature ramp
  - in the presence of catalysts
  - in the absence of catalysts
- In collaboration with PNNL CHSCoE, quantify impurities from solid AB formulations as a function of temperature ramp
  - in the presence of catalysts/additives
  - in the absence of catalysts/additives
- In collaboration with MHSCoE, quantify impurities from candidate metal hydrides formulations as a function of temperature ramp
  - in the presence of catalysts/additives
  - in the absence of catalysts/additives
- In collaboration with UTRC, explore and test possible alternative scrubbing technologies for ammonia, diborane and borazine

- *If Funding available, quantify the minimum acceptable levels of borazine and diborane for the safe operation of a fuel cell*

Task 7: LANL Liquid Phase Chemical Hydride Preliminary System Designs



Unit Operations of Liquid AB System

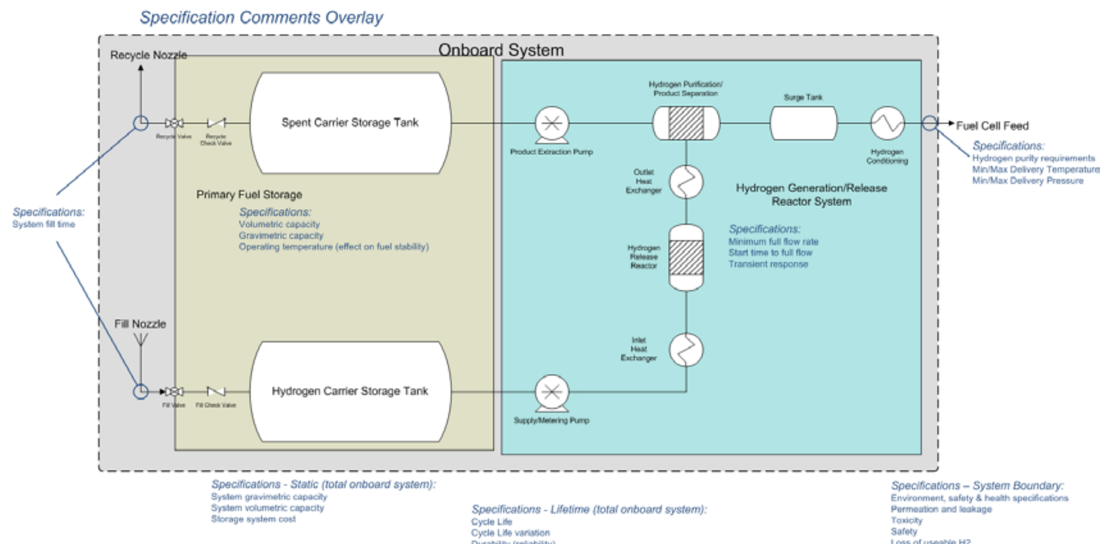
- Heterogeneous Catalytic Reactor (*Transport*)
- Gas-Liquid Separator (*Enabling Technologies, Transport*)
- Hydrogen Purifier (*Enabling Technologies*)
- Heat Exchanger (*Enabling Technologies*)

BOP Components of Liquid AB System

- Pumps
- Storage Tank(s) (*Enabling Technologies*)
- Fuel/Spent Fuel
- Ballast Tank

Critical Aspects of Liquid AB System

- Solvent
  - Physical properties
  - Boiling pt, freezing pt
  - Viscosities
  - Heat capacities, etc
- Gas-liquid separator
- Hydrogen selectivities
- Heterogeneous catalytic reactor
  - Deactivation
  - Low temperature startup



Task 7 Future Work: System Designs (System Architect)

- **Solid AB System: PNNL**
  - Physical properties of solid AB
  - Demonstration/validation of bulk handling/reactor unit
    - Impurities
    - Feasibility/reliability

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- **Liquid AB: LANL**
  - System sizing (Q3 FY10)
    - Spider chart

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  - Demonstration/validation of heterogeneous catalytic reactor (milestone Q1-2 FY11)
    - Kinetics
    - Catalyst deactivation
    - Impurities
    - Low temperature startup

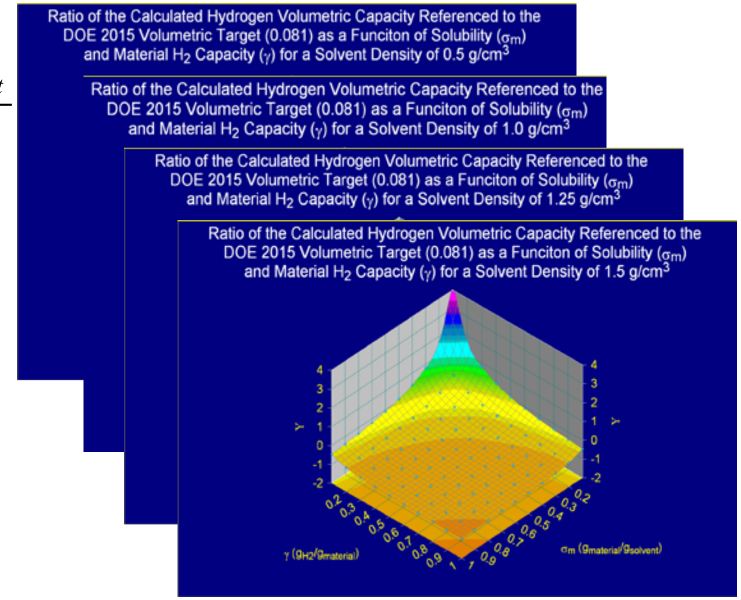
Aspects of Liquid AB System

$$\gamma^* \equiv \frac{m_{H2}}{m_{system}} = \frac{\sigma_m \gamma}{1+\sigma_m}$$

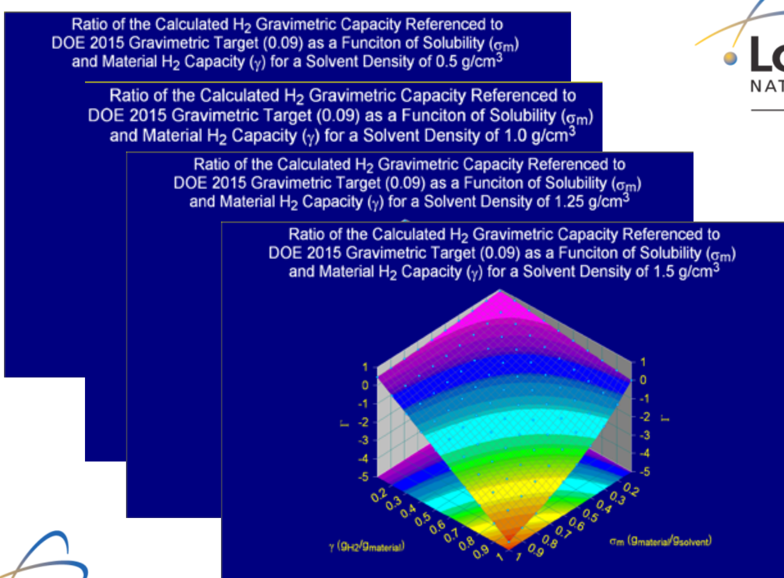
$$\sigma_m \equiv \frac{m_{material}}{m_{solvent}}; (0 \le \sigma_m \le 1)$$

$$\gamma \equiv \frac{m_{H2}}{m_{material}}; (0 \le \gamma \le 0.5)$$

$$\Upsilon \equiv \frac{\upsilon^* - DOE_{Vol\ target}}{DOE_{Vol\ target}}$$



$$\Gamma \equiv \frac{DOE_{grav\ target} - \gamma^*}{DOE_{grav\ target}}$$



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$$\upsilon^* \equiv \frac{m_{H2}}{V_{system}} \approx \frac{m_{H2}}{V_{solvent}} = \sigma_v \gamma = \rho_{solvent} \sigma_m \gamma = \rho_{solvent} \gamma^* (1+\sigma_m)$$

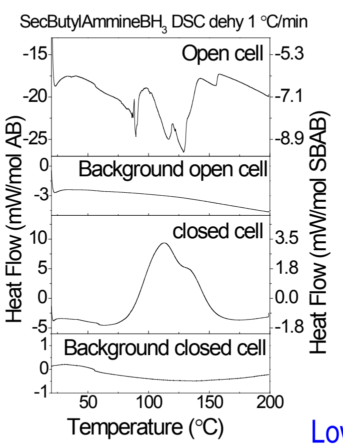
$$\sigma_v \equiv \frac{m_{material}}{V_{solvent}}; (0 \le \sigma_m \le 1)$$

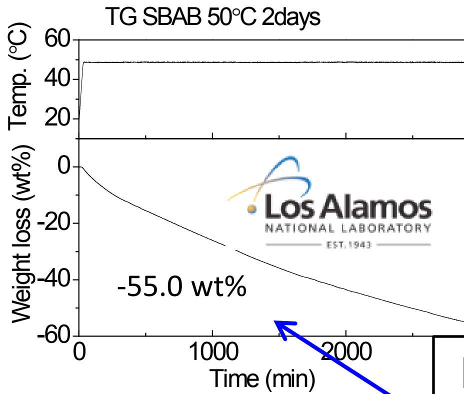
$$\gamma \equiv \frac{m_{H2}}{m_{material}}; (0 \le \gamma \le 0.5)$$

$$\rho^*_{system} = \frac{\upsilon^*}{\gamma^*} = \frac{\sigma_v \gamma}{\left[\frac{\sigma_m \gamma}{1+\sigma_m}\right]}$$

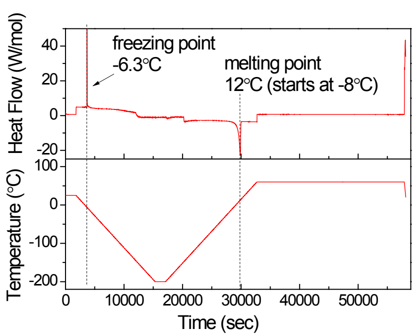
Materials Operating Requirements: SecButyl Amine Borane(SBAB) Solvent for Liquid AB Systems

Pure SBAB Solvent





Low temperature (-77K) DSC



Physical Properties of SBAB Solvent

$$T_{boiling\ onset} \approx 73-85^{\circ}C$$

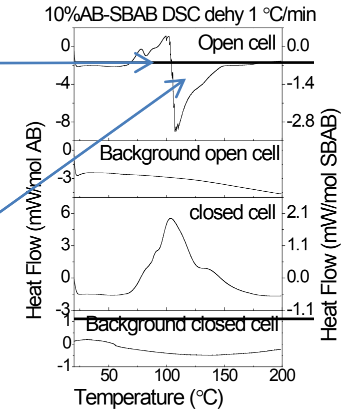
$$T_{mpt} \approx \left(-6.3^{\circ}C\right)-\left(-8^{\circ}C\right)$$

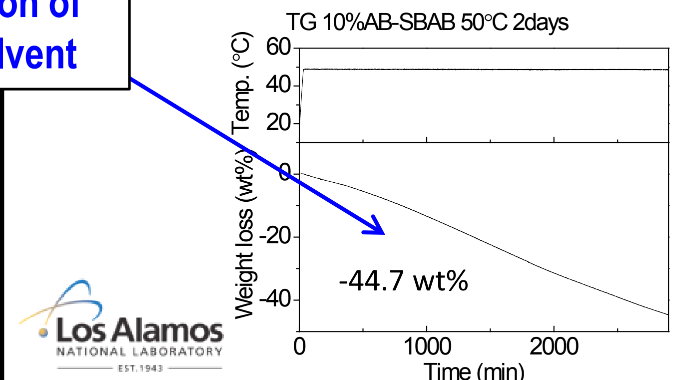
Mass loss due to evaporation of SBAB solvent

Liquid AB/SBAB Fuel

AB Dehydrogenation Exotherm

SBAB Boiling Endotherm





SBAB has low boiling point (high vapor pressure), slow H_2 release kinetics and low H_2 yields; Collaborated with CHSCoE in the decision to discontinue SBAB work

Acknowledgements

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