Clean Energy Research

Project III: Hydrogen Storage Using Chemical Hydrides

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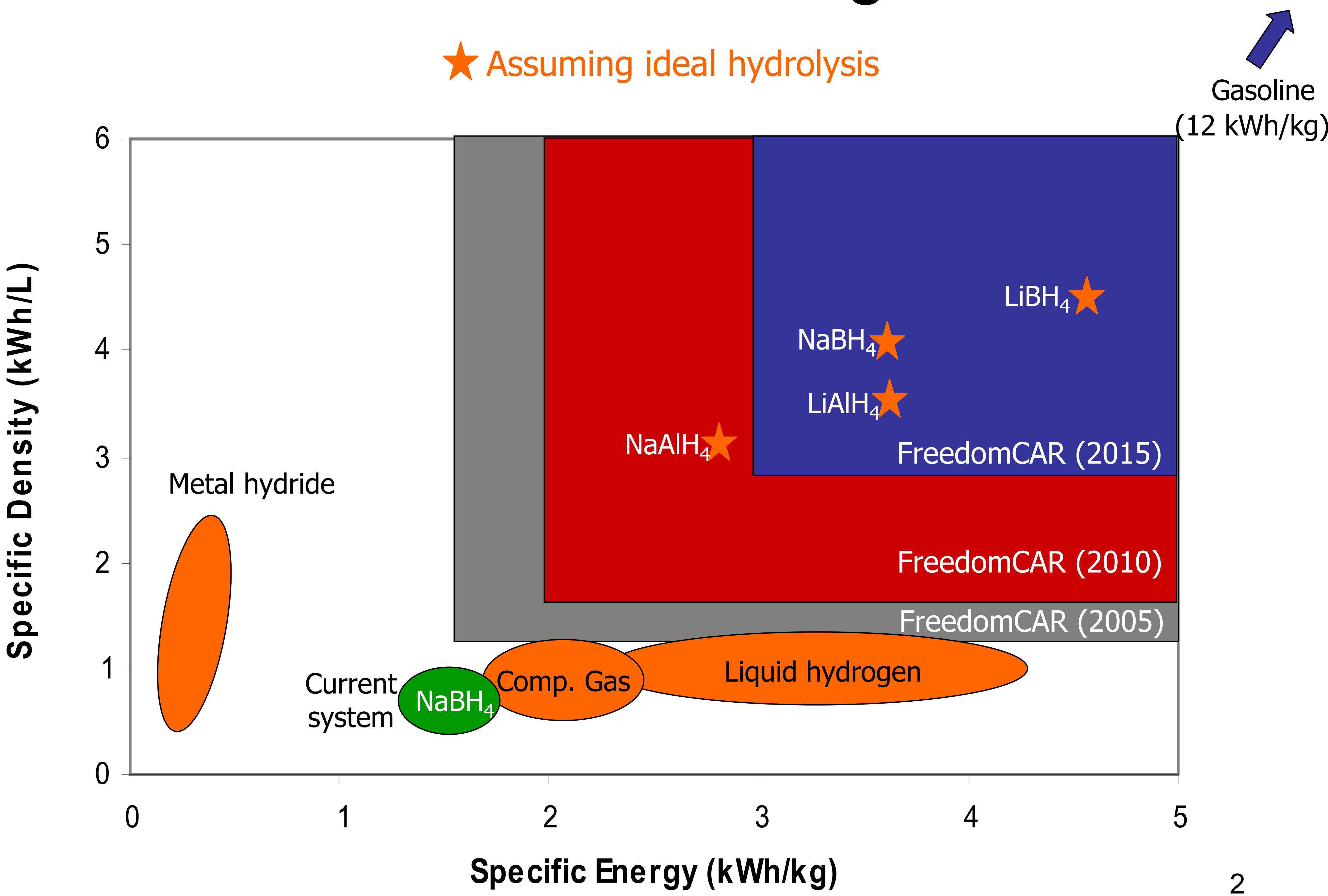
STP56

Current Technologies



Hydrogen Storage Using Chemical Hydrides

Objectives

- **Develop hydrogen storage and delivery technology based on steam + chemical hydrides for automotive fuel cell applications**

  - Evaluate novel steam + solid chemical hydride reaction as basis for on-demand production of hydrogen

  - Compare experimental data to FreedomCAR targets
    - Mass efficiency of reaction (8MAA)
    - Hydrogen production rate / kinetic data (12MAA)
    - Analysis of water utilization of reactor and characterization of hydration characteristics of products (14MAA)
    - Prototype design development (16 MAA)

DOE FreedomCAR Technical Targets

Year	2005	2010	2015
Usable Specific Energy from Hydrogen			
Target (kWh/kg system)	1.5	2.0	3.0
Target (kg H_2/kg system)	0.045	0.06	0.09
Usable Energy Density from Hydrogen			
Target (kWh/L system)	1.2	1.5	2.7
Target (kg H_2/L system)	0.036	0.045	0.081

*http://www.eere.energy.gov/hydrogenandfuelcells/pdfs/freedomcar_targets_explanations.pdf

DOE FreedomCAR Technical Targets

Year	2005	2010	2015
Fuel Cost [$ per gasoline equiv. at pump]			
Target	3	1.5	1.5
Projection	2.5	1.8	1.8
Minimum full-flow rate [g/sec/kW]			
Target	0.02	0.02	0.02
Projection	0.025-0.03	0.025-0.03	0.025-0.03

*http://www.eere.energy.gov/hydrogenandfuelcells/pdfs/freedomcar_targets_explanations.pdf

Gravimetric Efficiency (kg H_2/kg reactants) Fuel Only

Hydride	*x*=0	*x*=1	*x*=2	*x*=3
$NaBH_4$	**0.108**	**0.087**	**0.073**	**0.063**
$LiBH_4$	0.139	0.106	0.085	0.072
$LiAlH_4$	0.108	0.087	0.073	0.063
$NaAlH_4$	0.089	0.074	0.063	0.056

decrease →

$$MAH_4 + (2+x)H_2O \rightarrow 4H_2\,(g) + MAO_2 \cdot x\, H_2O$$

$x = 3$ is the lowest excess hydration factor obtained so far in our lab; optimization continues.

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If x=3, mass allowed for reactor=

-0.429 kg reactor/kg system

Not possible to meet 2015 target

0.05 kg reactor/kg system

To meet 2010 target for

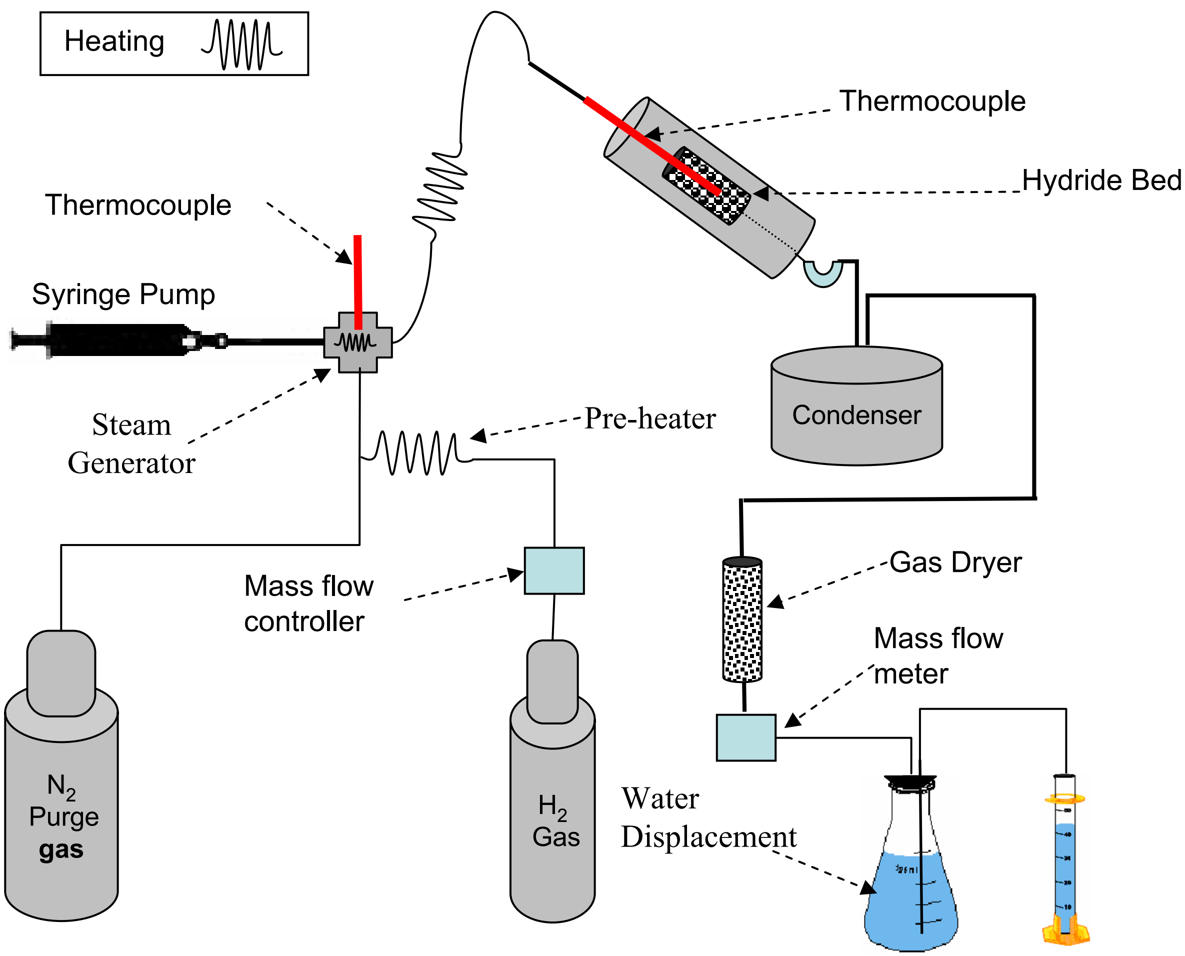
0.286 kg reactor/kg system

To meet 2005 target

Approach

- Hydrolyze chemical hydrides with dry steam, rather than aqueous catalytic process
  - Chemically simple reaction
  - Humid H_2 gas product
  - Hydride reactants and products are dry
  - Minimal water inventory in the reactor
  - Autothermal integration: use heat of reaction to produce steam
- Operate reactor at low temperatures (100 ^{O}C – 150 ^{O}C) and pressures
- Conduct basic research on the reaction to utilize water efficiently and maximize H_2 delivery rate
  - Translate results to prototype design via mathematical model

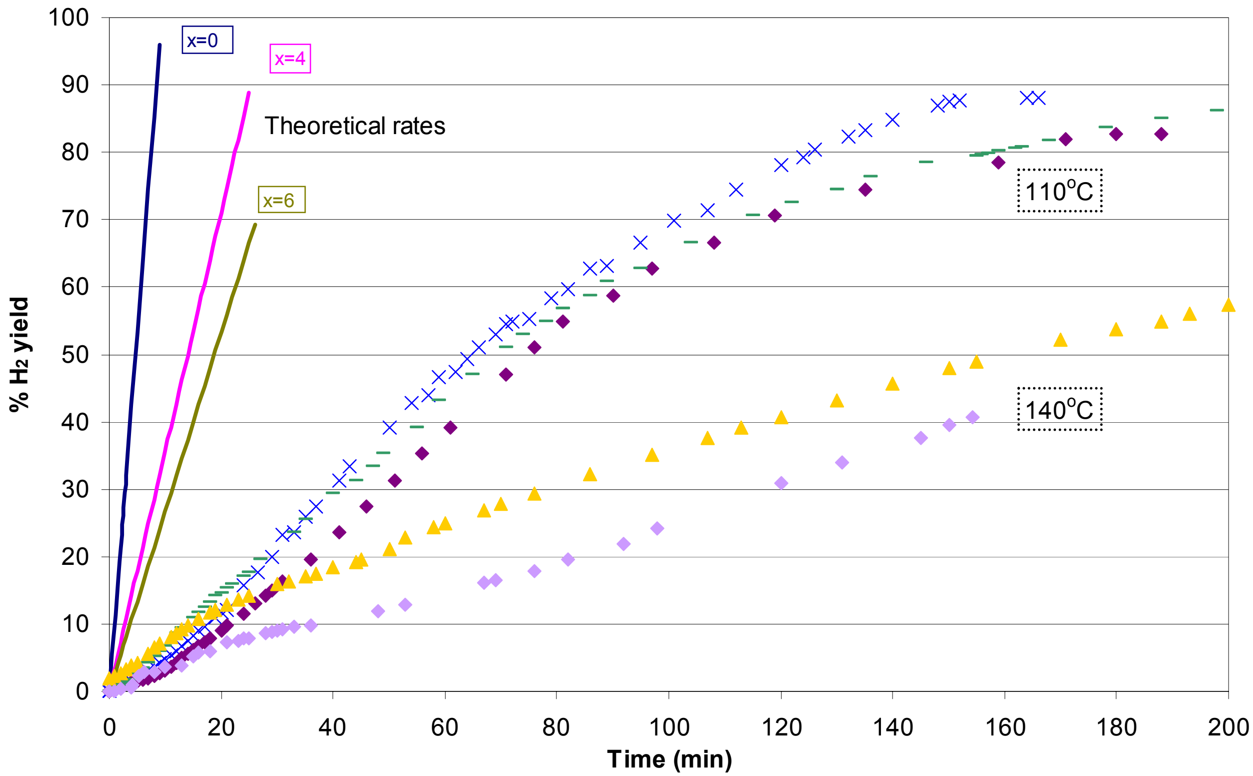
Data Collection From First Generation Screening Reactor



- Advantages
  - Screen different chemical hydrides
  - Investigate reactant preparation methods
- Disadvantages
  - Significant dead volume
  - Limited control over steam flow rate
  - Insufficient reactant contact
  - Channeling

$NaBH_4$ Powder Reacts Slowly

$$NaBH_4 + (2+x)H_2O \rightarrow 4H_2(g) + NaBO_2 \cdot x\,H_2O$$



- Good yields, low rates at 110 °C (x > 10)
- Poor yield and rates at 140 °C likely related to $NaBO_2 \cdot xH_2O$ by-product

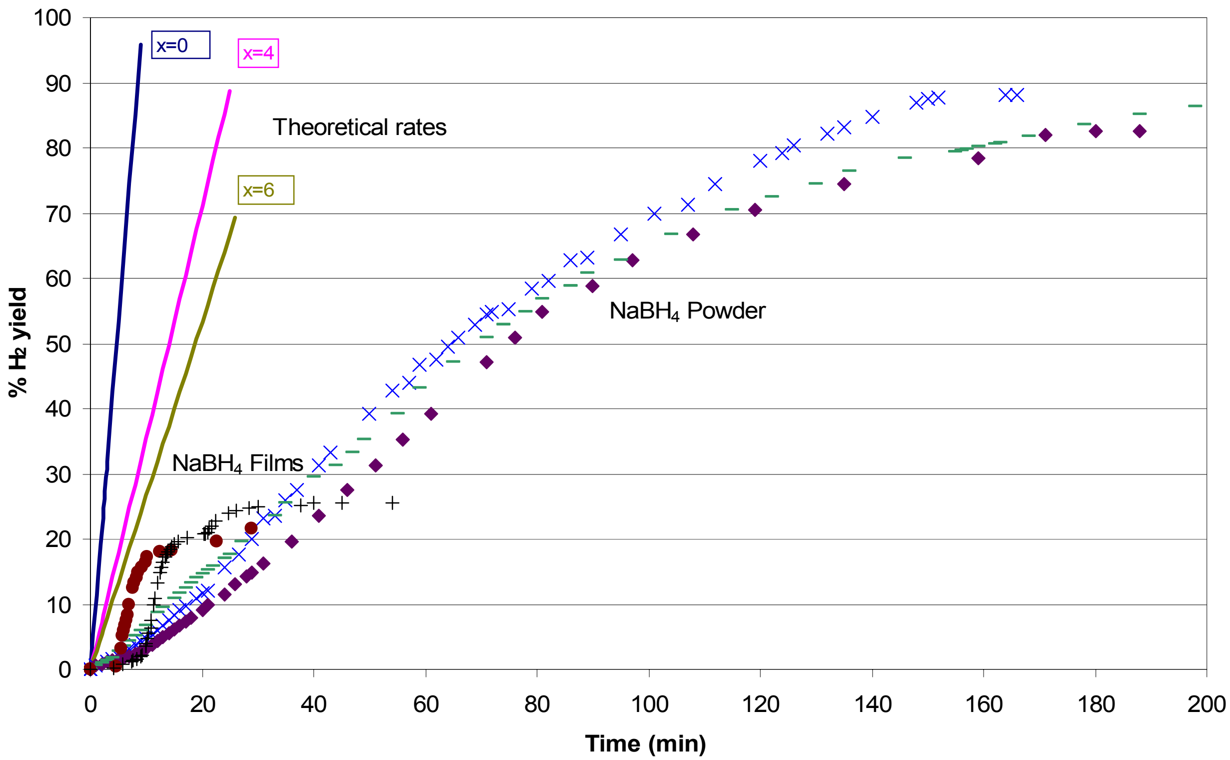
FreedomCar Gravimetric Efficiency

	Target (wt%)	Equiv. x
2005	4.5	4
2010	6.0	3
2015	9.0	1

x is the "excess hydration factor," representing the degree of hydration of the borate products

Films of Recrystallized $NaBH_4$ Give Improved Initial Rates

$$NaBH_4 + (2+x)H_2O \rightarrow 4H_2(g) + NaBO_2 \cdot x\,H_2O$$



x is an indirect measurement of the efficiency of water utilization of the reaction

- Thin films give higher initial rates (*x* = 2-3)
- Decreased yields are attributable to channeling within reactor and insufficient reactant contact at longer times.

FreedomCar Gravimetric Efficiency

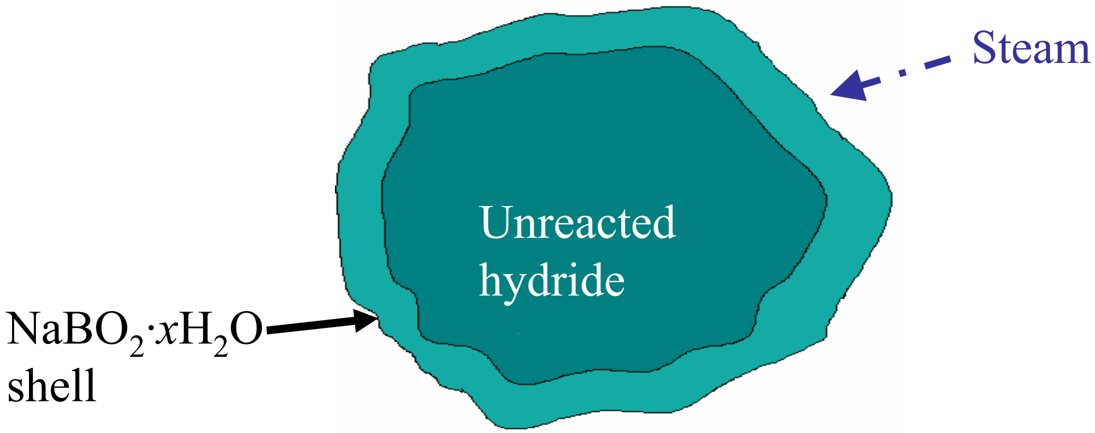
	Target (wt%)	Equiv. *x*
2005	4.5	4
2010	6.0	3
2015	9.0	1

Summary of Steam-Solid Hydrolysis Data From Screening Reactor

Description	T (°C)	Max Slope (mol/kg$_{NaBH4}$*min)	% of Theo. H_2 Yield
$NaBH_4$ powder	110	1.018	88.2
$NaBH_4$ powder	110	0.870	82.7
$NaBH_4$ powder	110	0.825	94.0
$NaBH_4$ powder	140	0.628	67.1
$NaBH_4$ powder	140	0.327	40.8
$NaBH_4$ film	110	4.42	19.7
$NaBH_4$ film	110	5.14	22.9
Theoretical Values (assuming instantaneous rxn)	11.1 (x=0)		100
	3.70 (x=4)		100
	2.78 (x=6)		100

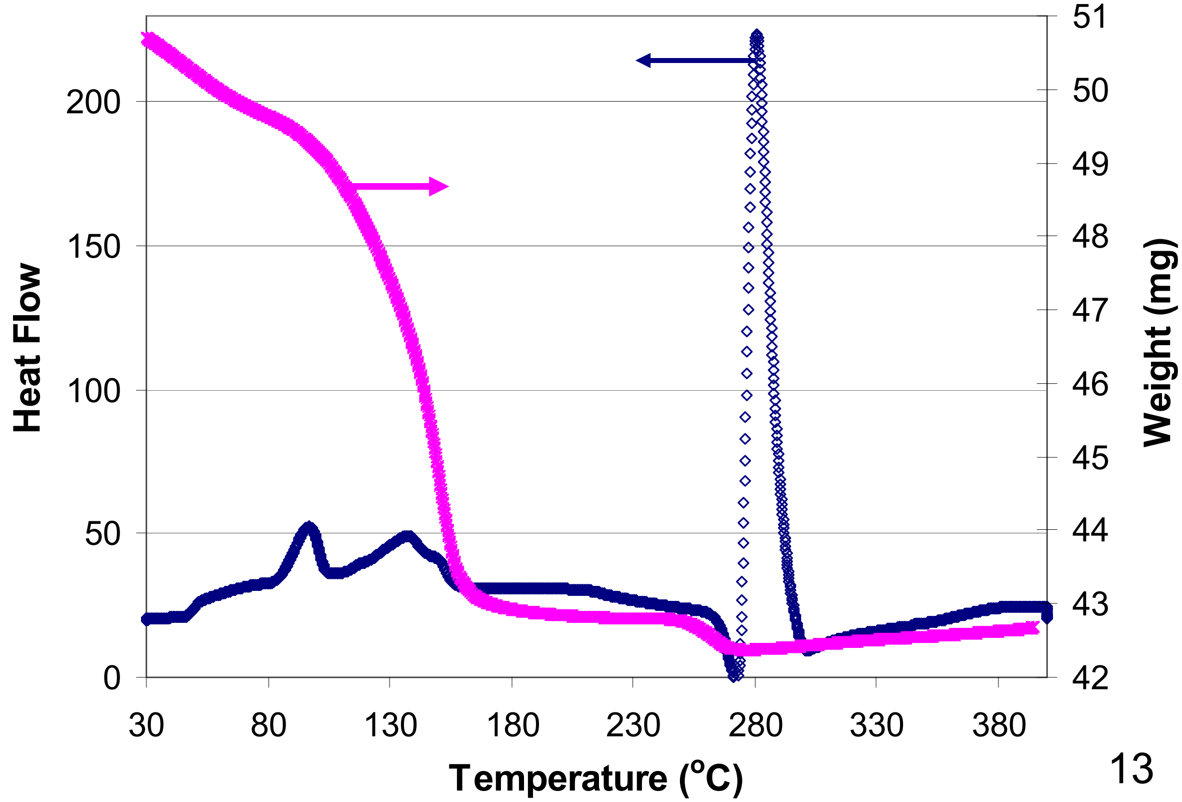
- Powder data
  - Rate at higher temp ~ 53% of rate for lower temp
  - Yield at high temp ~61% of yield for lower temp
- Thin film data
  - Rate for thin film ~5x rate for powder data
  - Yield for thin film ~25% of yield for powder data

Water Utilization and Product Characterization



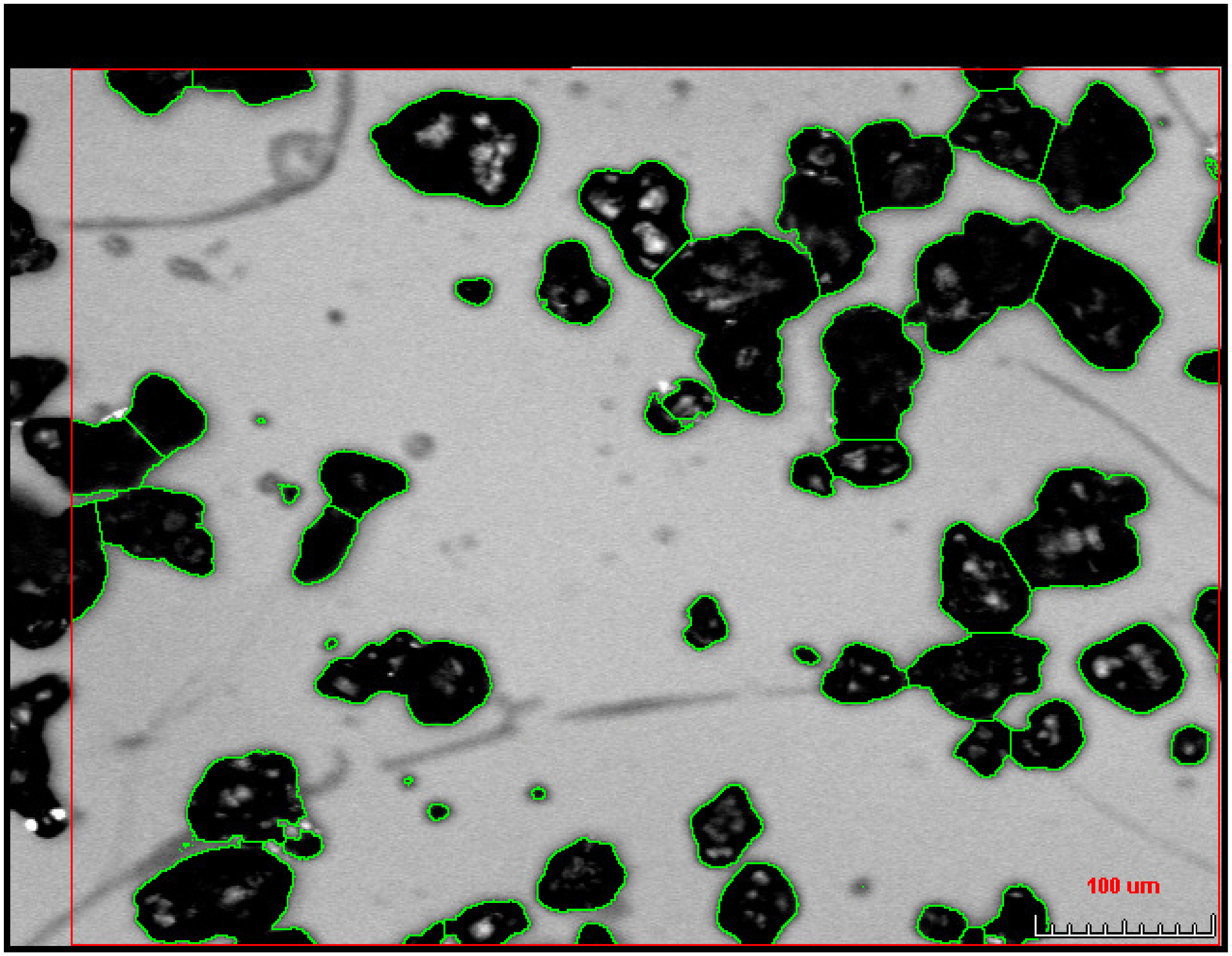
- $NaBO_2 \cdot xH_2O$ product is a dense solid
  - Dense by-product causes mass transfer limitation
  - Highly hydrated byproducts
- Waste water and decrease gravimetric efficiency

- Investigate hydration properties of products with Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC)
  - TGA: 17 wt% loss associated with H_2O loss by borate product
  - DSC: peak indicates phase transition in products



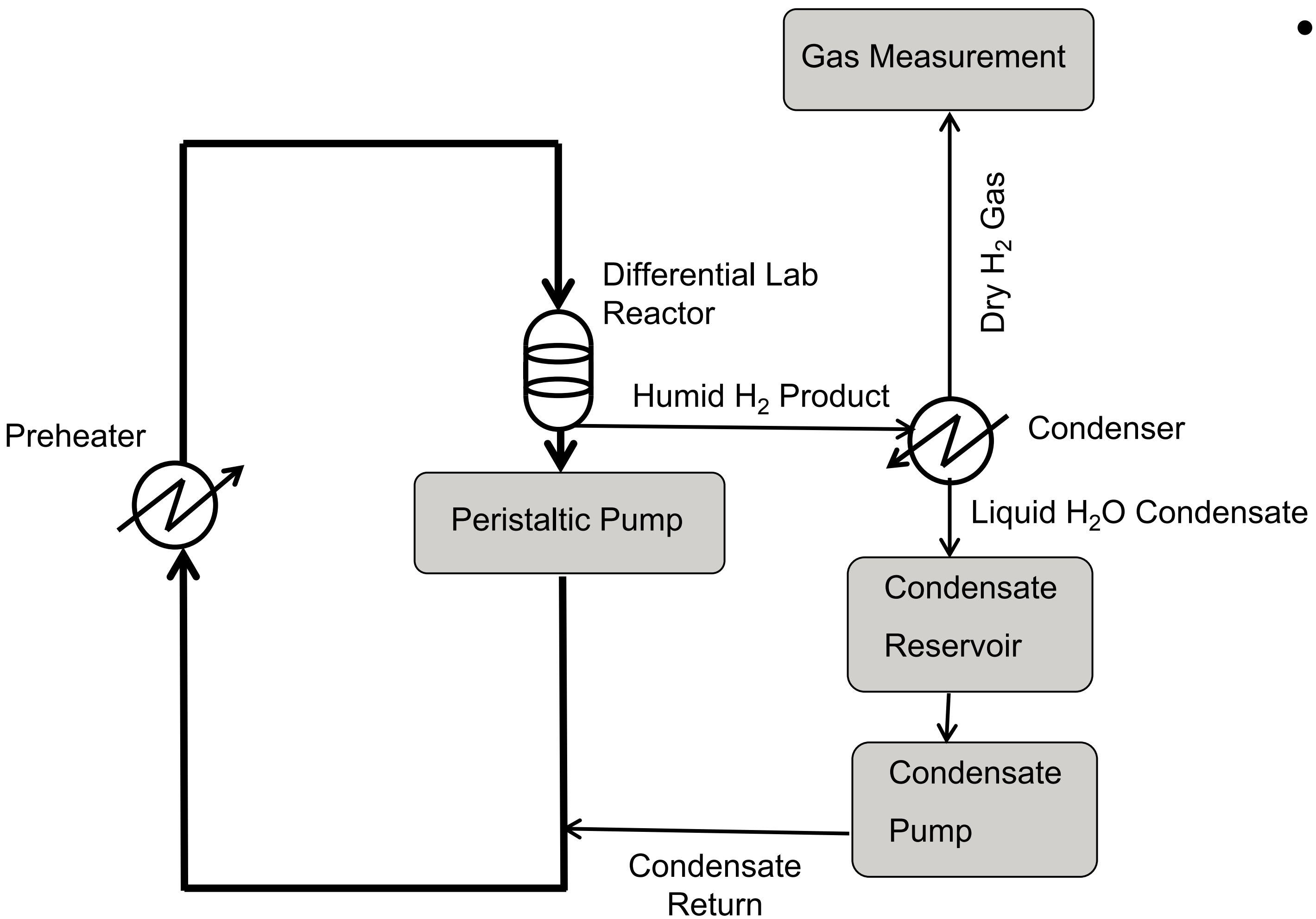
Particle Size Distribution

Microscope image of $NaBH_4$ powder



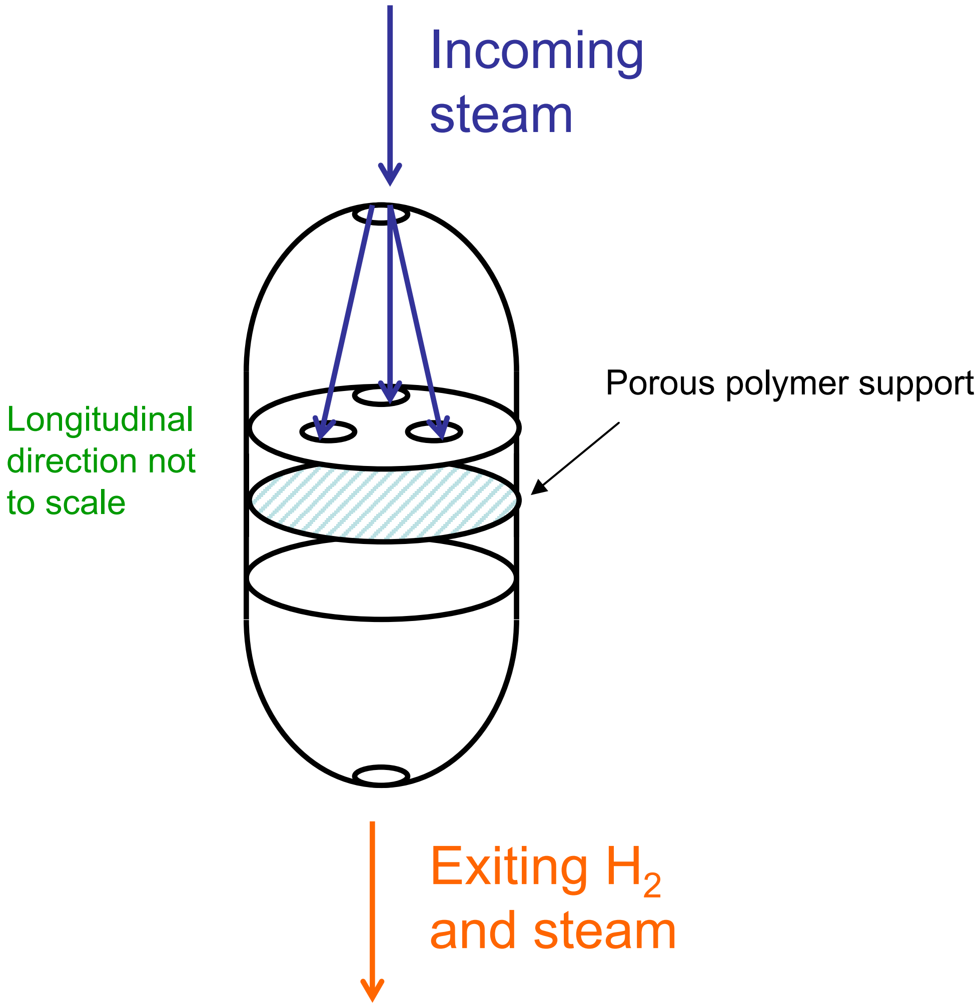
- Determine effect of particle size
  - Kinetic rates and H_2 production
  - Reduce shell inhibition
- Optical method with digital analysis to measure PSD

Construction of Differential Reactor with Water Recirculation



- Differential lab reactor
  - Uniform steam/solid contact
  - More compact
  - Controlled steam flow rates
  - Water utilization tracked by closed condensate loop

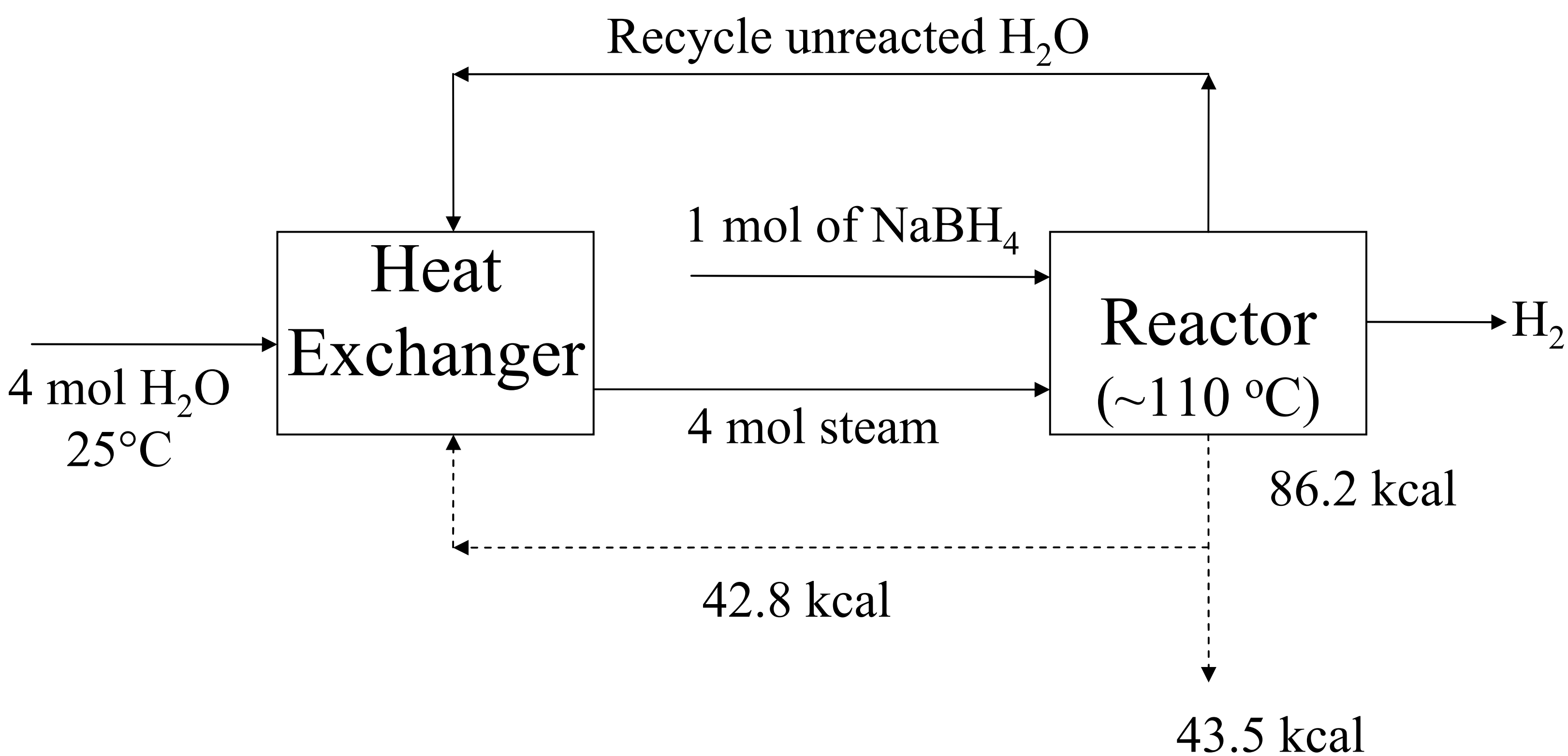
Differential Lab Reactor Details



- $NaBH_4$ powder dispersed on porous polymer support
  - Particles ≈ 150 μm
  - Pore size ≈ 0.50 μm
- Achieve uniform contact
  - Reduce agglomeration and shell formation
  - Reduce mass transport limitations
  - De-couple kinetics from transport

Thermally Neutral Hydrogen Generator

(Energy balances for *x*=2)



*R.Aiello, J.H.Sharp ,M.A.Matthews, International Journal of Hydrogen Energy, 24(1999)1123-1130

Increased Range of T_{rxn}

- Objective is to design thermally-integrated storage and delivery reactor

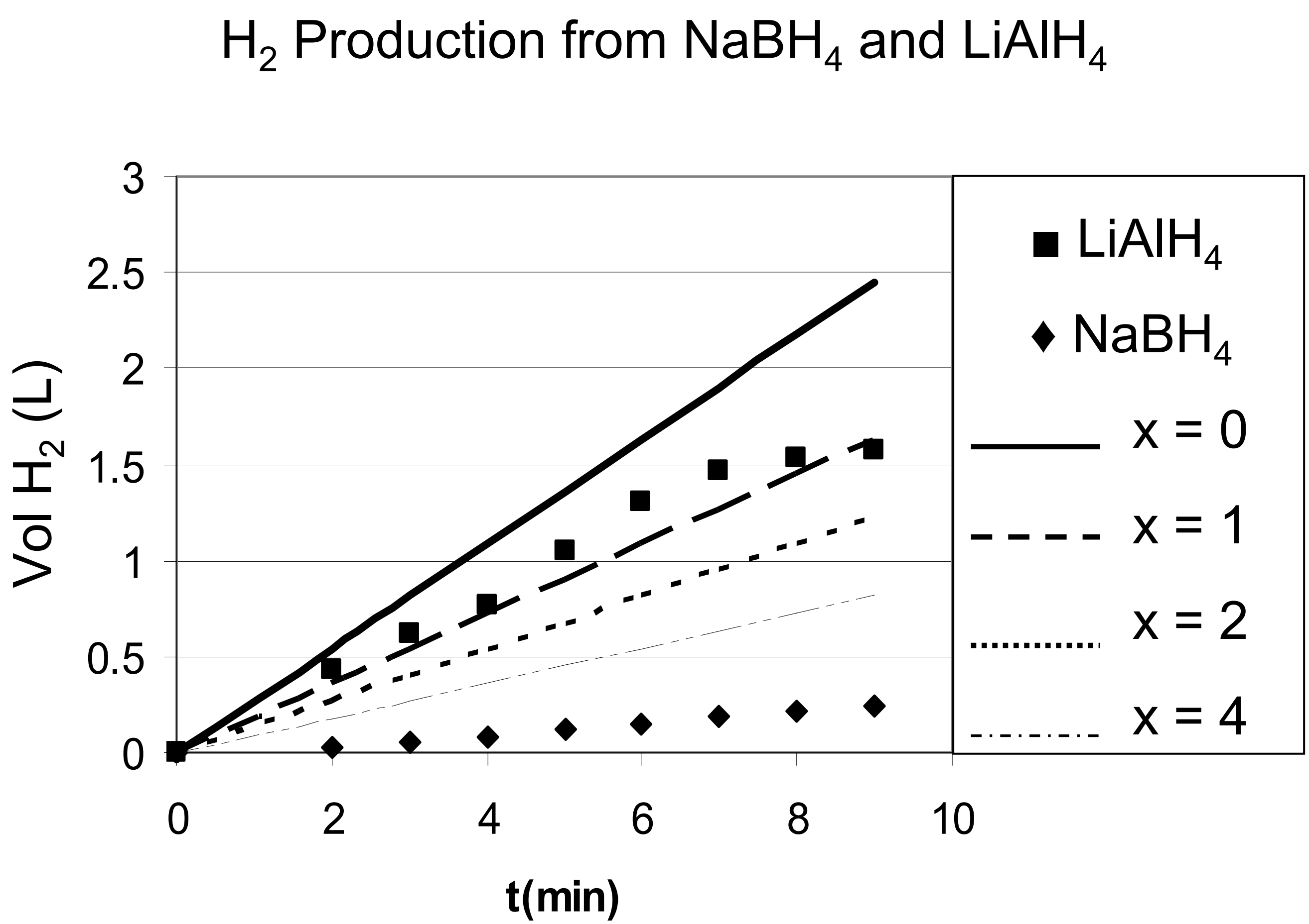
- Reaction is currently more efficient at lower T_{rxn}

- Need techniques to operate at higher temperature for efficient heat transfer
  - $Q = UA\Delta T_{lm}$

- Better understanding of reaction kinetics and product formation is crucial

Potential for Other Hydrides

$LiAlH_4$



- Other hydrides more reactive
  - May be difficult to control reaction
  - May be unstable for extended shelf-life
- $NaBH_4$ *could be* benchmark for prototype development

Responses to Previous Year Reviewers' Comments

- Not applicable – first year project.

(See Notes page for further information)

Future Research Directions

FY05

- Steam/solid $NaBH_4$ system
  - Obtain improved gravimetric efficiency of reaction
    - Liberate H_2 wt% > 4.5 by 4/30/2005
  - Measure intrinsic kinetic rate of reaction under different operating temperatures, pressures and reactant preparations
    - Full flow of H_2 in < 10 sec by 10/30/2005
  - Clarify the effect of particle size on reactant contact and mass transfer
  - Determine hydration characteristics of products in order to improve gravimetric efficiency and understand shell formation
- Investigate additional solid hydride systems
  - Evaluate additional hydrides based on FreedomCAR requirements

FY06

- Submit description of prototype system design
  - Design will be based on laboratory-scale experiments
  - Design will be evaluated according to FreedomCar targets such as mass and volumetric efficiency and startup dynamics

Publications and Presentations

1. Michael A. Matthews, Thomas A. Davis, and Eyma Y. Marrero-Alfonso, “Hydrogen storage in chemical hydrides”. ***ACS National Meeting***, Philadelphia. (Aug. 2004)
2. Michael A. Matthews, Thomas A. Davis, and Eyma Y. Marrero-Alfonso, “Production of hydrogen from chemical hydrides via hydrolysis with steam”. ***AIChE Annual Meeting***, Austin. (Nov 2004)

Hydrogen Safety

- The most significant hydrogen hazards associated with this project are:
  - High reactivity of solid chemical hydrides when exposed to humidified air
  - Toxicity: Avoid ingestion or contact with eyes and mucous membranes

- Our approach to deal with this hazard is:
  - Handle hydrides in an inert atmosphere within a glove box
  - Use small quantities for laboratory experiments
  - Blanket reactor with inert gas