

# Development of New Carbon-Based Sorbent Systems for an Effective Containment of Hydrogen

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This presentation does not contain any proprietary or confidential information

# Overview

## Timeline

- 2/04 – 2/07
- 40% complete

## Budget

- Total project \$6,121,279
  - DOE share \$4,346,108 (71%)
- FY04 funding \$771,000
- FY05 funding \$812,000

## Partners

- Current interactions: automobile OEM's, start-up companies
- Anticipated interactions: LANL chemical hydrides COE, catalyst companies

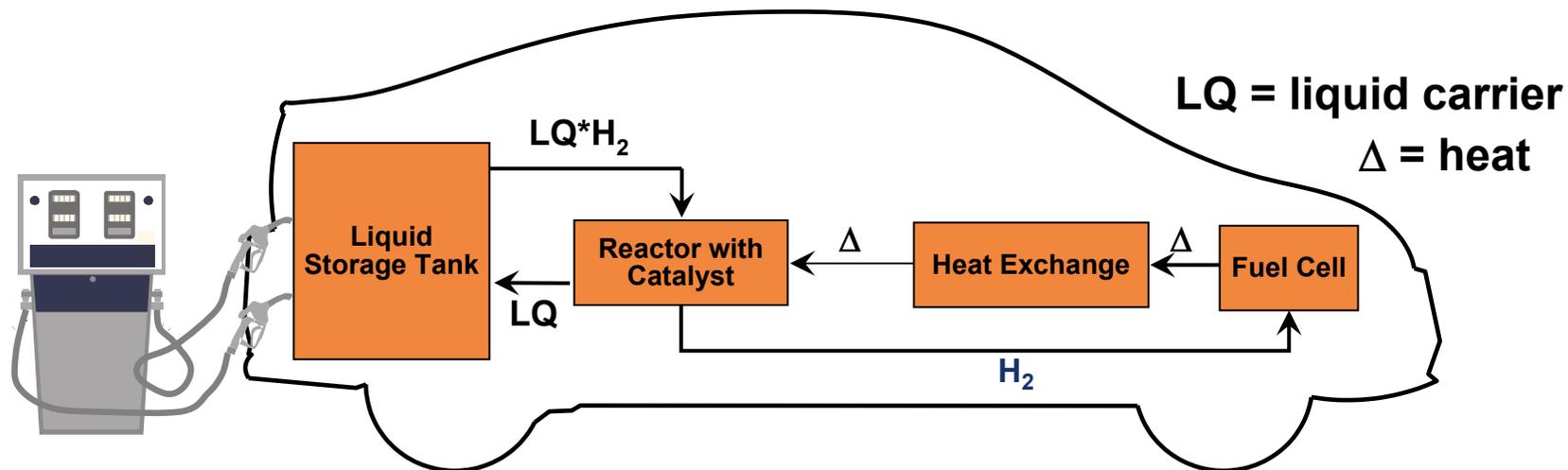
## Barriers

- Technical Barriers- Hydrogen Storage
  - A. Cost
  - B. Weight and Volume: 4.5 wt. % and 36 g H<sub>2</sub>/L (2005), 6.0 wt. % and 45 g H<sub>2</sub>/L (2010)
  - C. Efficiency
  - E. Refueling time
  - R. Regeneration Processes
  - S. Byproduct Removal
  - T. Heat Removal

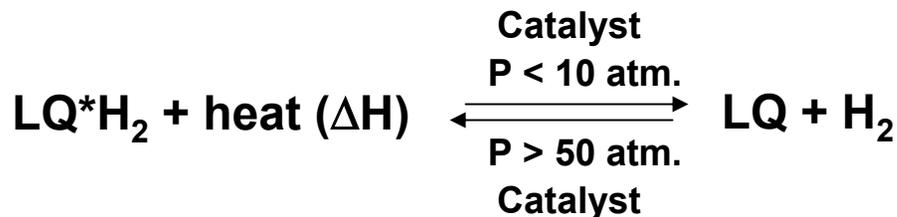
# Objectives

- Discovery of new, reversible liquid carriers for hydrogen storage and associated dehydrogenation / hydrogenation catalysts. Scale up of liquid carriers for further evaluation.
  - Selective, highly reversible catalytic hydrogenation and dehydrogenation, enabling multiple cycles of use with no significant degradation of the molecule - **barriers R, S**
  - Optimal heat of dehydrogenation (10-13 kcal/mole H<sub>2</sub>), enabling the catalytic dehydrogenation at unprecedented temperatures (<200 °C) – **barriers B, C, T**
  - Low volatility (b.p. > 300 °C), enabling the use of these liquids in simplified systems onboard vehicles and reducing exposure to vapors – **barriers E, S**
  - Low toxicity and environmental impact – **barrier R**
  - Acceptable cost for the liquid carrier and the hydrogenation process – **barrier A**
- “Ionic solids” for storage of hydrogen by physical adsorption
- Development of carbon-based solid and liquid hydrogen storage materials with capacities of >6 wt. % and >45 g H<sub>2</sub>/L

# Approach: An off-board regenerable liquid carrier for vehicles and stationary H<sub>2</sub> gas delivery



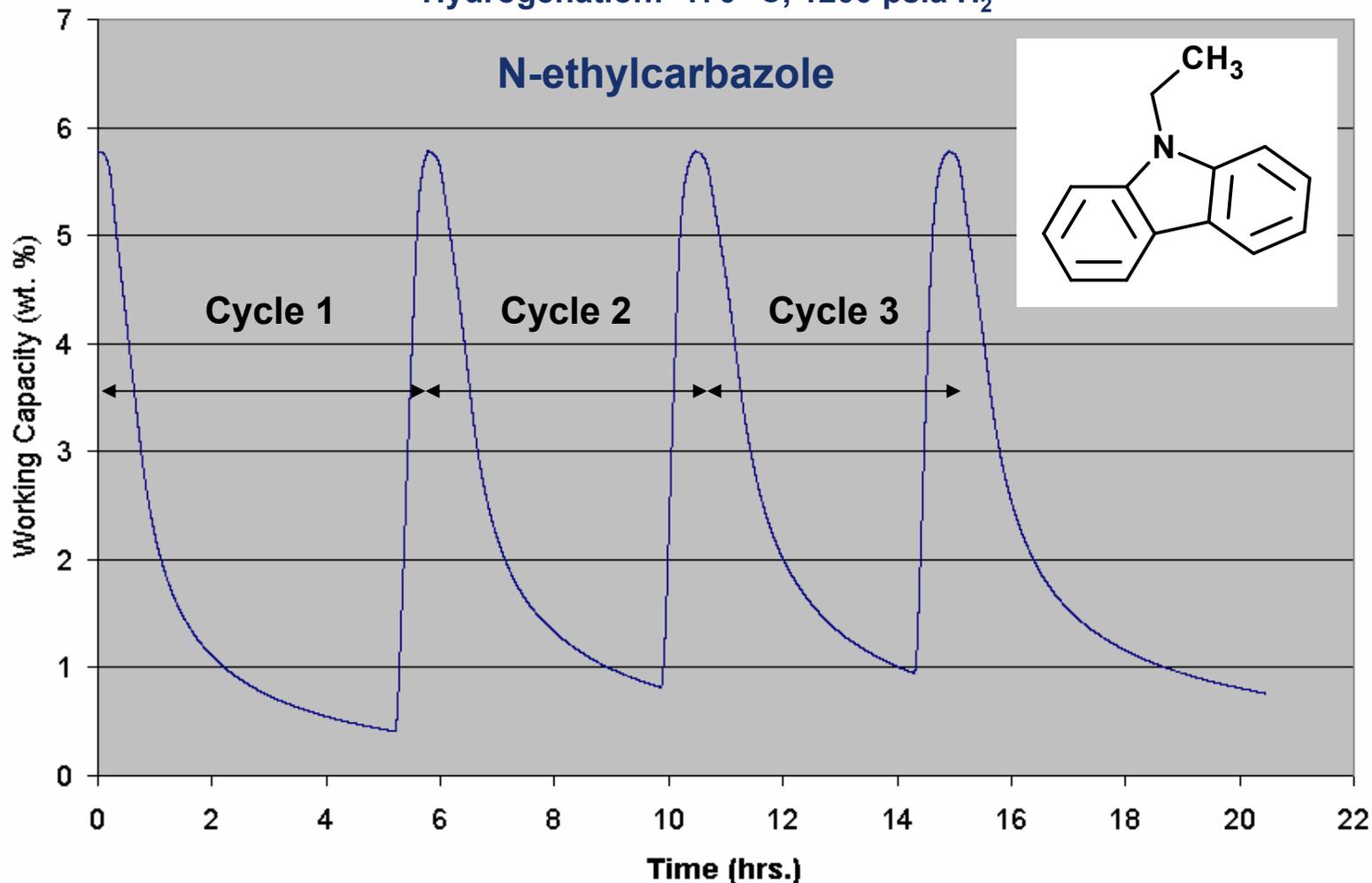
- Conformable shape liquid tank with design to separate liquids; 22.5 gallons for 5 kg hydrogen at 6 wt. % and unit density
- Heat exchange reduces the vehicles' radiator load by *ca.* 40% (for ΔH of 12 kcal/mol H<sub>2</sub> and 50% FC efficiency)



Maximum energy efficiency: by (a) recovering the exothermic (-ΔH) of hydrogenation and (b) utilizing the waste heat from the power source to supply the ΔH for the endothermic dehydrogenation.

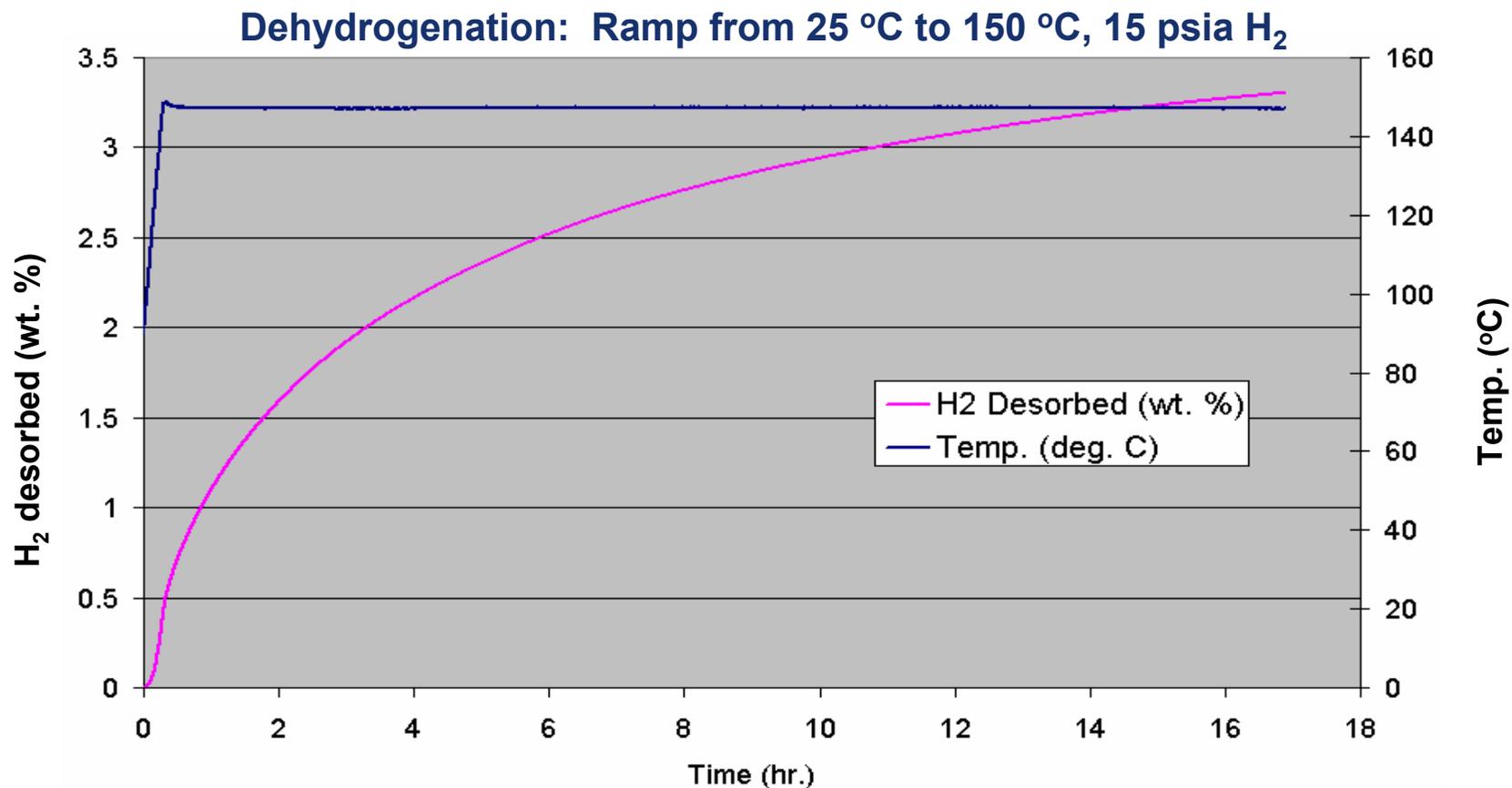
# Results: Cycling Studies

Dehydrogenation: Ramp from 25 °C to 200 °C, 15 psia H<sub>2</sub>  
Hydrogenation: 170 °C, 1200 psia H<sub>2</sub>



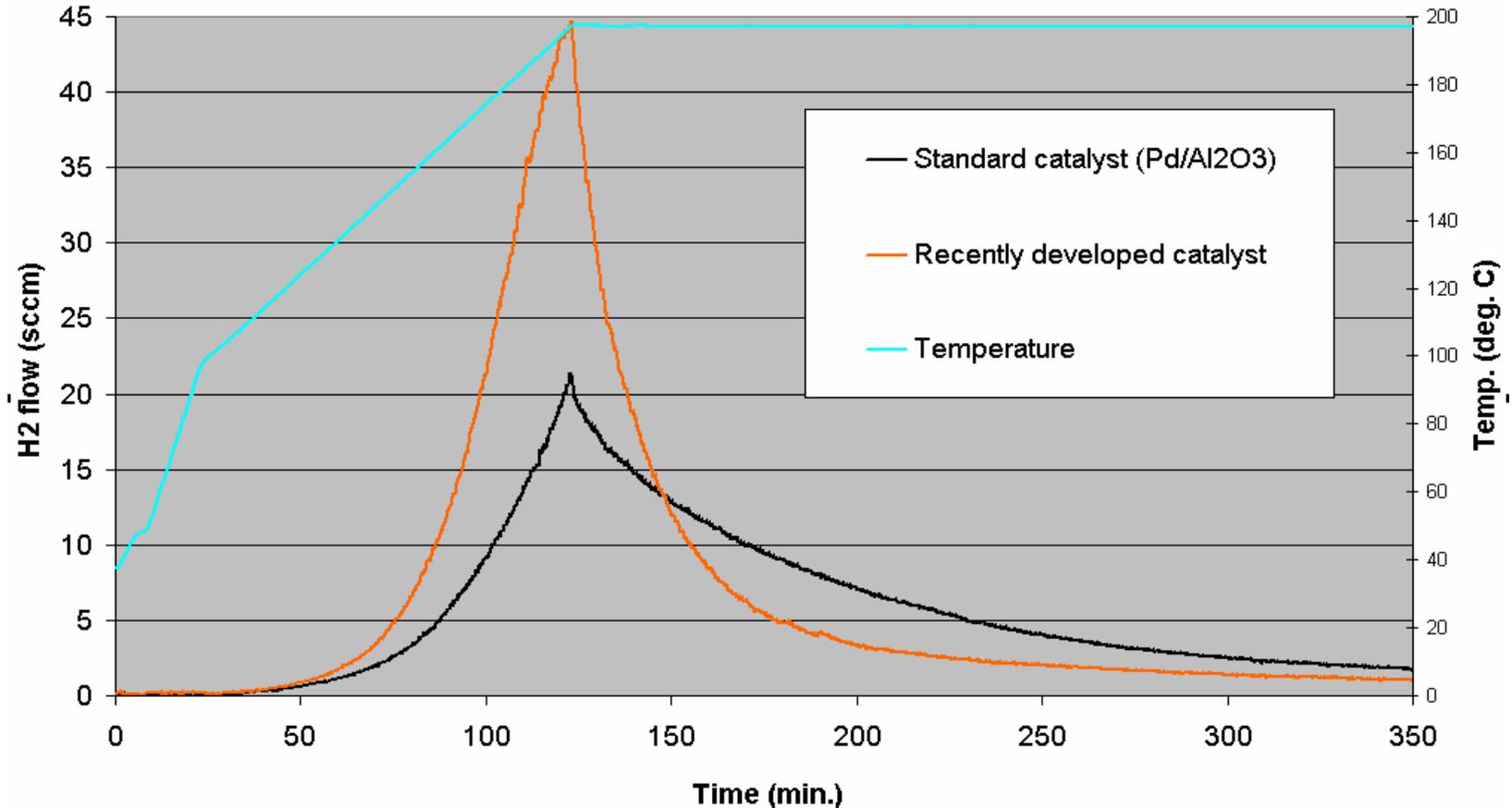
→ Rapid hydrogenation and cycling stability

# Results: Low Temperature Dehydrogenation



→ Met year 1 performance milestone (3 wt. % at 150 °C); but slow catalytic dehydrogenation rate at 150 °C

# Results: Higher Dehydrogenation Catalyst Activity



- Over 40 catalysts screened in last 3 months
- Base metal and precious metal catalysts

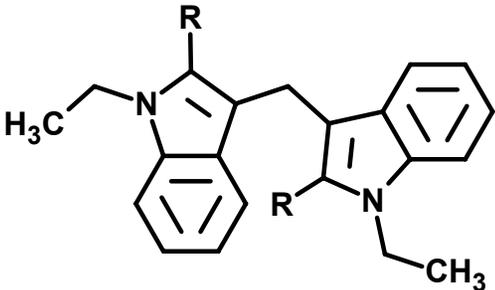
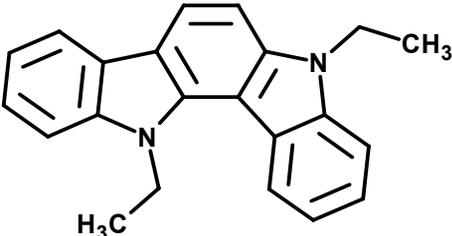
# Results: Typical H<sub>2</sub> Purity from Dehydrogenation Experiments

Component	Mole %
Hydrogen	99.9+
Methane	0.0013%
Ethane	0.0083%
Carbon Monoxide	ND
Amines	ND
C3's	ND
C4's	ND
C5's	ND
C6's	ND

ND – Not Detected

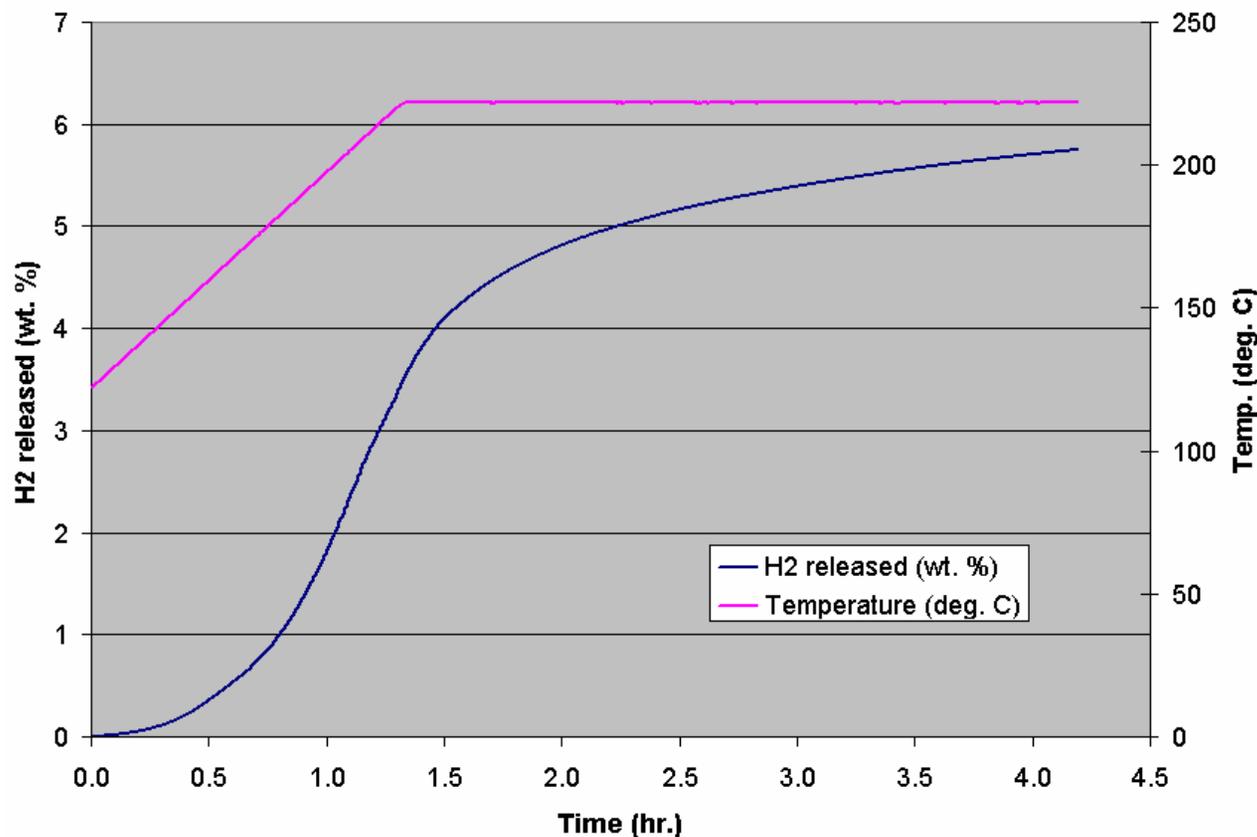
- Hydrogen purity from N-ethylcarbazole dehydrogenation runs determined by mass spectroscopy
- Detection limits <10 ppm for all species in table
- Recent results suggest that methane and ethane may arise from trace impurities in N-ethylcarbazole

# Results: New Liquid Carrier Development

Liquid Carrier	Positive Attributes	Performance Issues
 <p>R = H, CH<sub>3</sub></p> <p>Bis-indolylmethane</p>	<ol style="list-style-type: none"> <li>1) Liquid at all stages of hydrogenation</li> <li>2) Synthesis from low-cost raw materials</li> <li>3) Extremely low volatility (b.p. &gt;420°C)</li> <li>4) Heat of dehydrogenation (ca. 12.5 kcal/mol)</li> </ol>	<ol style="list-style-type: none"> <li>1) Cycling stability</li> <li>2) Maximum hydrogen capacity</li> </ol>
 <p>Indolocarbazole</p>	<ol style="list-style-type: none"> <li>1) Heat of dehydrogenation at favorable low end of appropriate range (10.5 kcal/mol)</li> <li>2) Extremely low volatility</li> </ol>	<ol style="list-style-type: none"> <li>1) Clean catalytic hydrogenation</li> <li>2) High melting point</li> </ol>

# Results: New carrier data

- Recent discovery of a new carrier with 6.9 wt. % H<sub>2</sub> capacity (potential)
- Initial testing confirms selective hydrogenation and dehydrogenation
- Heat of dehydrogenation in appropriate range (10-13 kcal/mol H<sub>2</sub>)



First dehydrogenation experiment

# Results: Adsorption of H<sub>2</sub> by novel porous ionic solids

- Computational modeling has identified a specific ionic solid composition with strong physisorption of H<sub>2</sub>
  - At a loading of 6.76 wt. % H<sub>2</sub>, the  $\Delta E$  (at 25°C) is -5.07 kcal/mole H<sub>2</sub>
- Computational work (*ab initio* DFT molecular dynamics) completed FY 04
- Satisfied technical criteria for go decision at end of FY04

# Summary: Technical Accomplishments/ Progress/Results

- Liquid carrier discovery effort
  - Several promising carriers
  - New carrier with capacity of 6.9 wt. % and >60 g H<sub>2</sub>/L (est. density of 0.9 g/cc)
- Increased dehydrogenation catalyst activity by 100% through screening and development effort
- Demonstrated high H<sub>2</sub> purity (99.9+%, no CO or amines)
- Demonstrated cycling stability for N-ethylcarbazole (7 cycles with no degradation observed by GC/MS analysis)
- FY04 milestones (>3 wt. % at 150°C) met on time
- Progress towards FY05 milestones on track

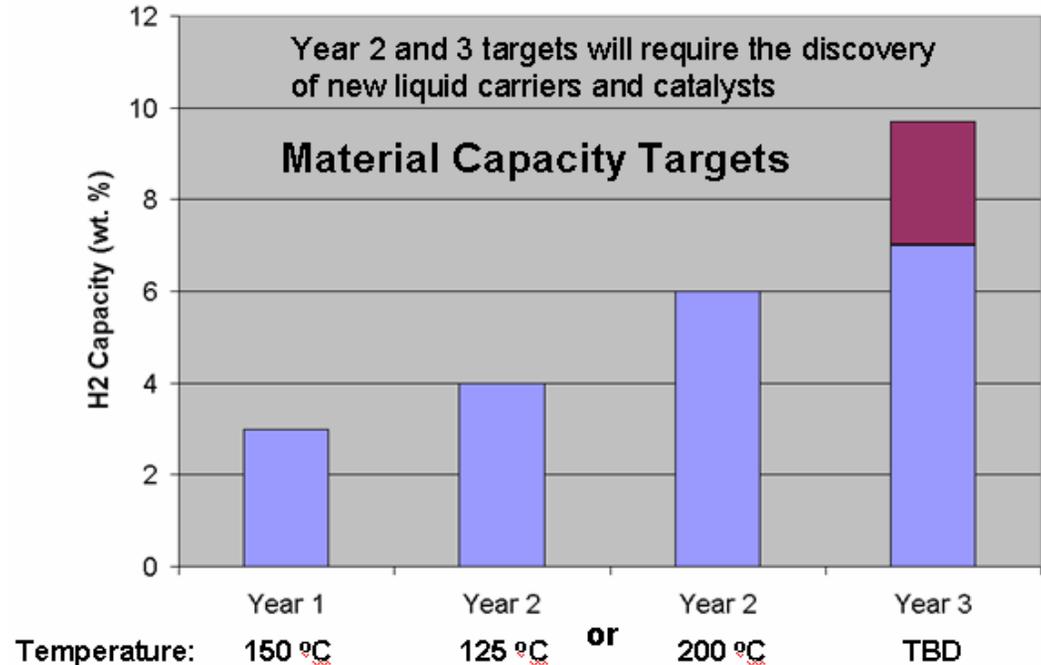
# Dehydrogenation Video Clip

# Responses to Previous Year Reviewers' Comments

- 1) No technical details for liquid carriers or catalysts disclosed
  - We have now disclosed technical details of liquid carrier compositions and catalysts
  - Two public presentations and papers (American Chemical Society national meeting 3/05; National Hydrogen Association 3/05)
  
- 2) Economic feasibility of liquid carriers?
  - We disclosed an preliminary economic evaluation at the FY04 DOE Hydrogen Program review (not funded by DOE)
  - A comprehensive economics study is planned as part of the new, complementary project: “Reversible Liquid Carriers for an Integrated Production, Storage & Delivery of Hydrogen” (G. Pez, PD-34, tomorrow afternoon in H<sub>2</sub> delivery session)

# Future Work

- **Development and testing of new liquid carriers:**
  - optimal heats of hydrogenation
  - increase hydrogen capacity
  - modify substrate melting points (eg. by the use of mixtures of multiple substrates)
- **Development of new dehydrogenation catalysts:**
  - increase rates at low temperatures
  - selective dehydrogenation



**Design and development of dehydrogenation reactors and FC/ICE heat integration are critical to understanding the system weight and volume**

# Publications and Presentations

- **Presentations:**

- **Presentation to FreedomCAR Hydrogen Storage Tech. Team (2/05)**
- **Hydrogen Storage and Delivery by Reversible Hydrogenation of Liquid-phase Hydrogen Carriers (invited presentation) – American Chemical Society national meeting (3/05)**
- **The “Non-Hydrogen” Approach to Hydrogen Storage – National Hydrogen Association annual conference (3/05)**

- **Publications:**

- **A.C. Cooper, L.D. Bagzis, K.M. Campbell, and G.P. Pez: Hydrogen Storage and Delivery by Reversible Hydrogenation of Liquid-phase Hydrogen Carriers. *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.* 50, 271 (2005).**
- **K. Campbell, A. Cooper, G. Pez: The “Non-Hydrogen” Approach to Hydrogen Storage. NHA Annual Hydrogen Conference Proceedings (2005).**

# Hydrogen Safety

- **The most significant hydrogen hazard associated with this project is: hydrogenation of liquid carriers**
  - **overpressure and over-temperature scenarios**
- **Liquid carriers are hydrogenated in our laboratories at scales ranging from 4 – 5000 cc/batch**
  - **Hydrogen pressure typically 700-1200 psia**
  - **Heat of hydrogenation (exothermic) must be removed from hydrogenation to prevent overheating – most relevant at large scale**

# Hydrogen Safety

## Our approaches to deal with this hazard are:

- Detailed Design Hazard Review (DHR) for all hydrogenation operations – with signoff from EH&S personnel
- Engineering controls
  - Overpressure relief devices (i.e. rupture discs)
  - Hydrogen monitors for leak detection
    - Linked to reactor control for automatic shutdown in the event of a hydrogen leak from the reactor
  - Over-temperature shutdown
    - Linked to reactor control for automatic shutdown in the event of a temperature excursion
    - Use a second, independent thermocouple from temperature controller