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

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ST-14

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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_2/L (2005), 6.0 wt. % and 45 g H_2/L (2010)
  - C. Efficiency
  - E. Refueling time
  - R. Regeneration Processes
  - S. Byproduct Removal
  - T. Heat Removal

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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_2), enabling the catalytic dehydrogenation at unprecedented temperatures (<200 ^oC) – barriers B, C, T
  - Low volatility (b.p. > 300 ^oC), 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_2/L

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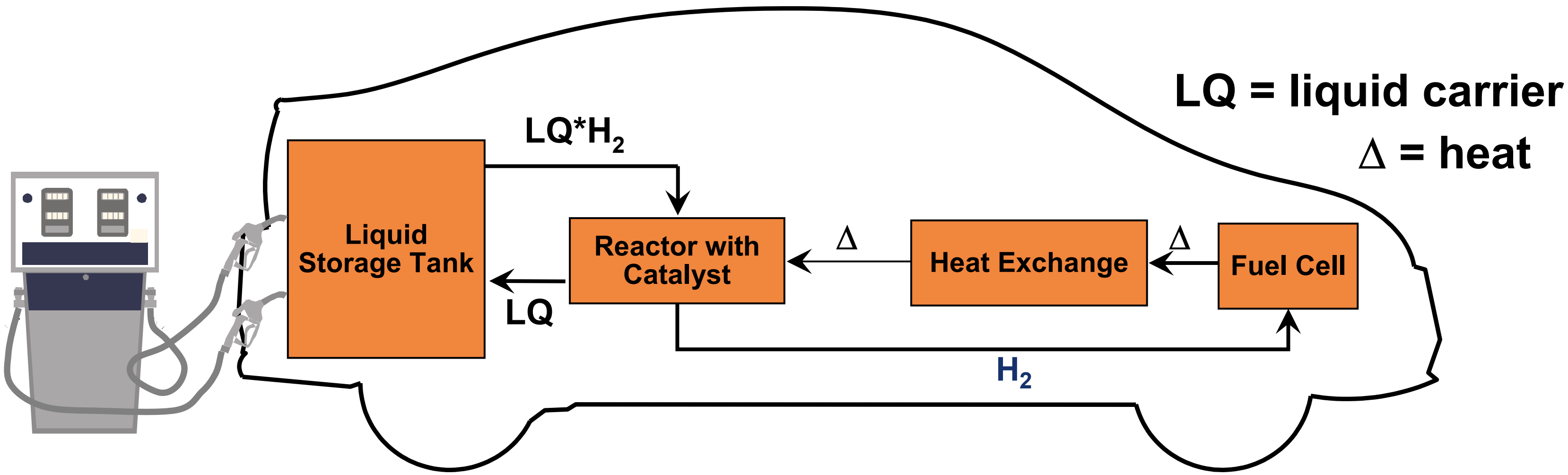
Approach: An off-board regenerable liquid carrier for vehicles and stationary H_2 gas delivery



- 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_2 and 50% FC efficiency)

$$LQ^*H_2 + \text{heat } (\Delta H) \underset{\text{P > 50 atm., Catalyst}}{\overset{\text{Catalyst, P < 10 atm.}}{\rightleftharpoons}} LQ + H_2$$

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.

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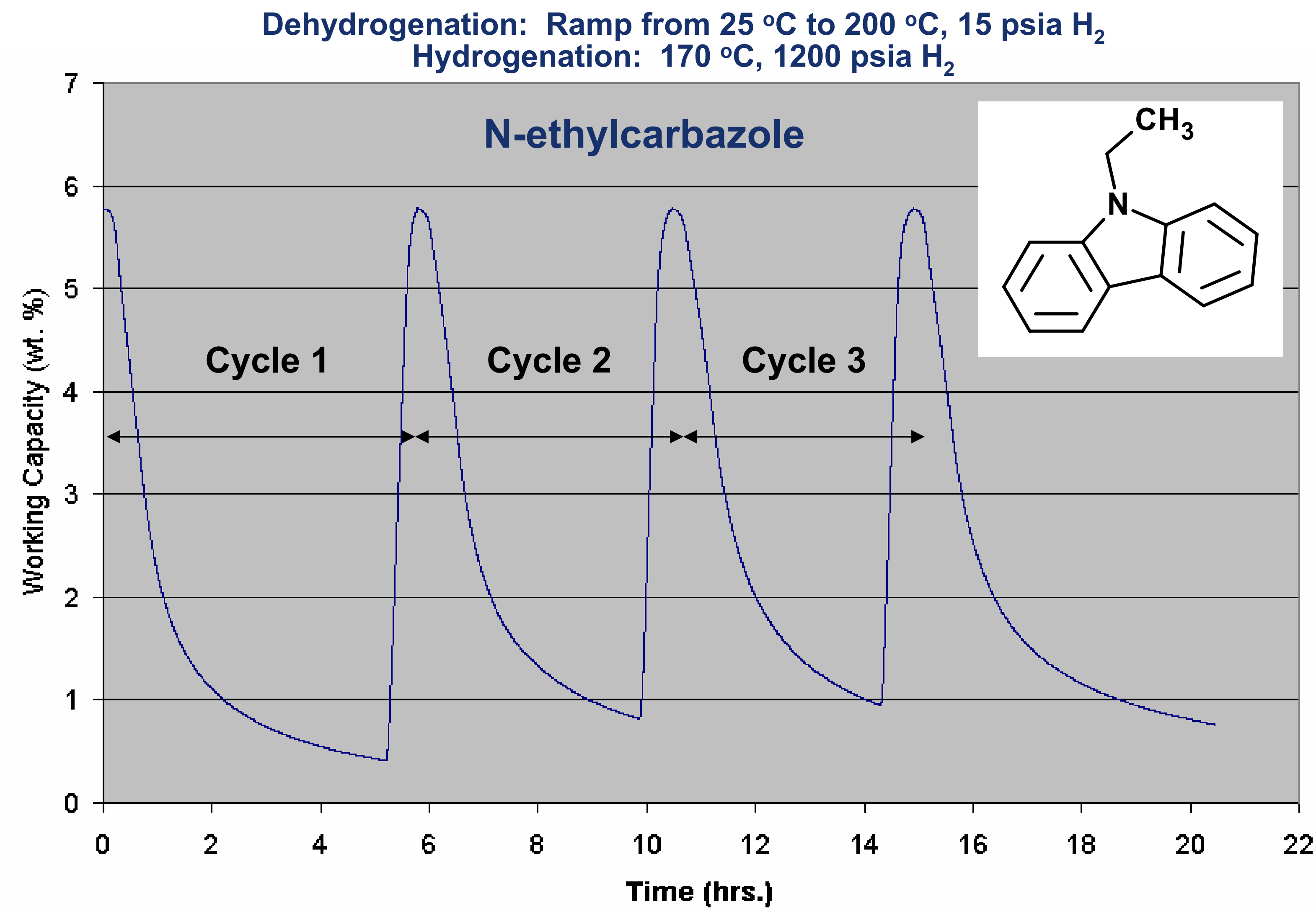
Results: Cycling Studies



➔ Rapid hydrogenation and cycling stability

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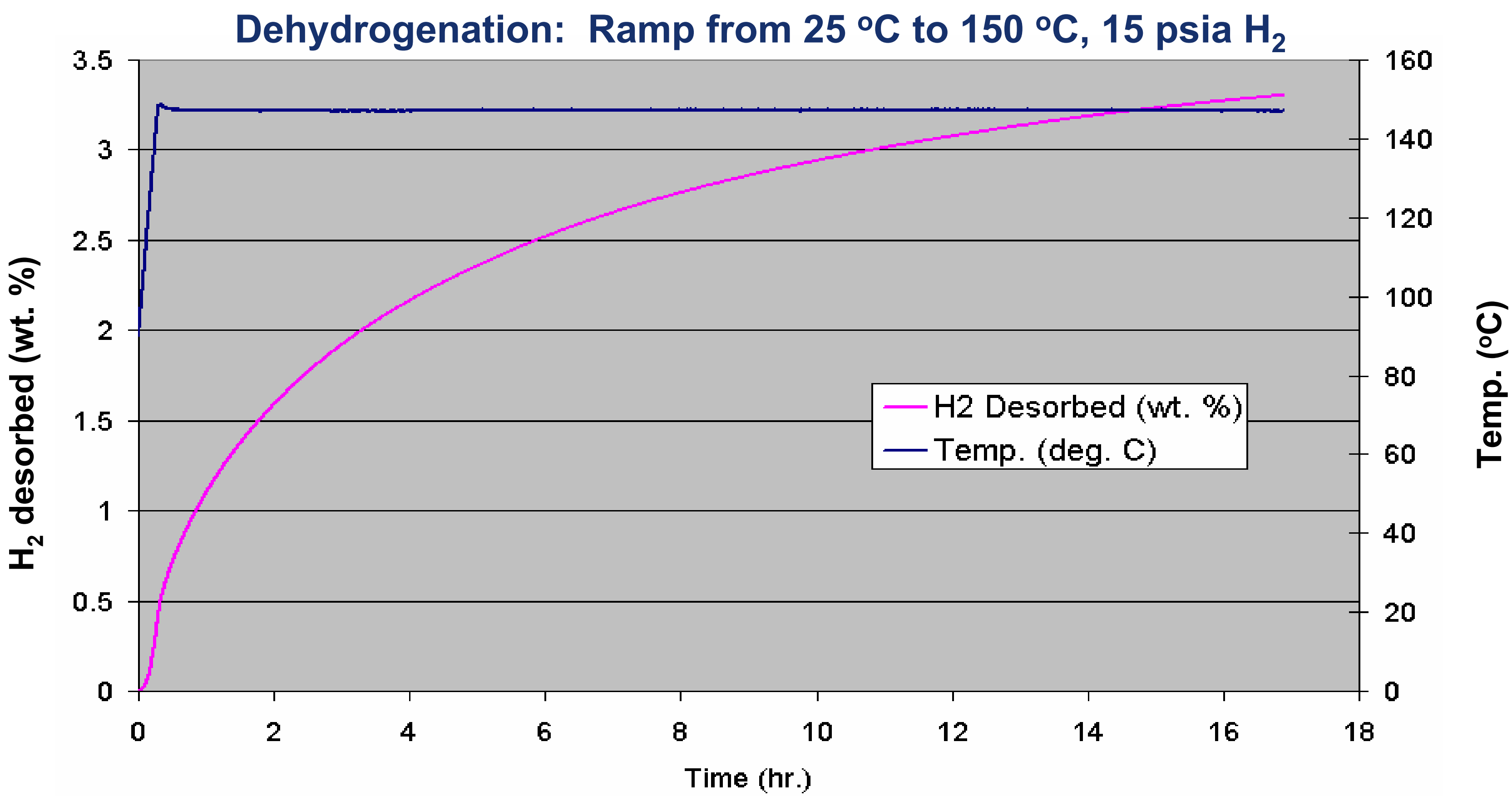
Results: Low Temperature Dehydrogenation



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

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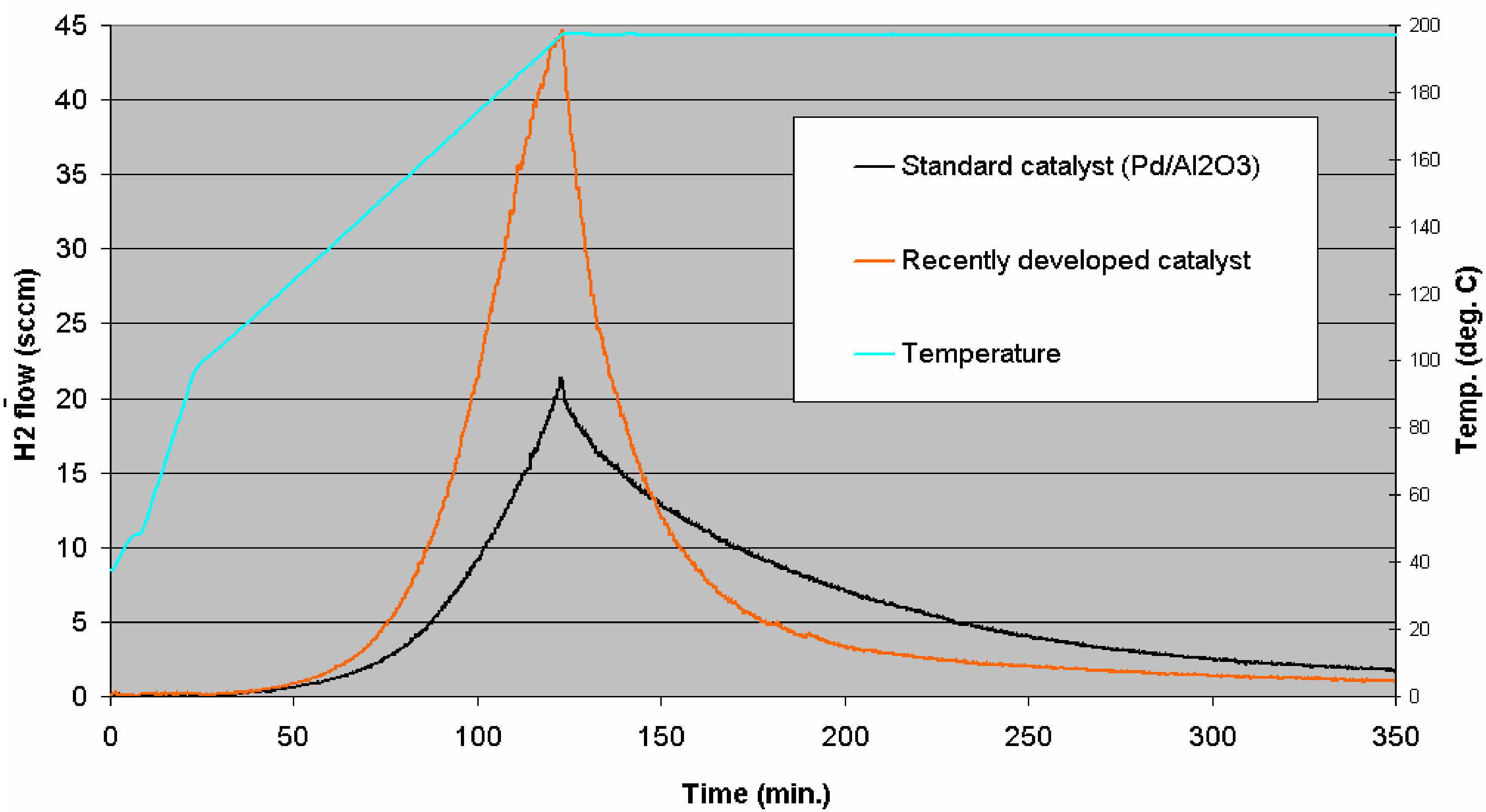
Results: Higher Dehydrogenation Catalyst Activity



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

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Results: Typical H_2 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

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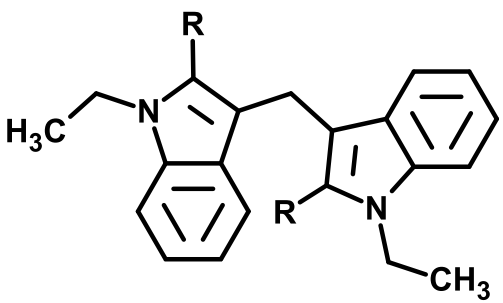
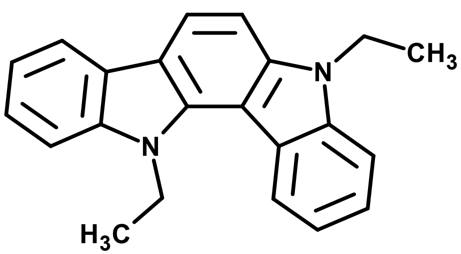
Results: New Liquid Carrier Development

Liquid Carrier	Positive Attributes	Performance Issues
 R = H, CH_3 Bis-indolylmethane	1) Liquid at all stages of hydrogenation 2) Synthesis from low-cost raw materials 3) Extremely low volatility (b.p. >420°C) 4) Heat of dehydrogenation (*ca.* 12.5 kcal/mol)	1) Cycling stability 2) Maximum hydrogen capacity
 Indolocarbazole	1) Heat of dehydrogenation at favorable low end of appropriate range (10.5 kcal/mol) 2) Extremely low volatility	1) Clean catalytic hydrogenation 2) High melting point

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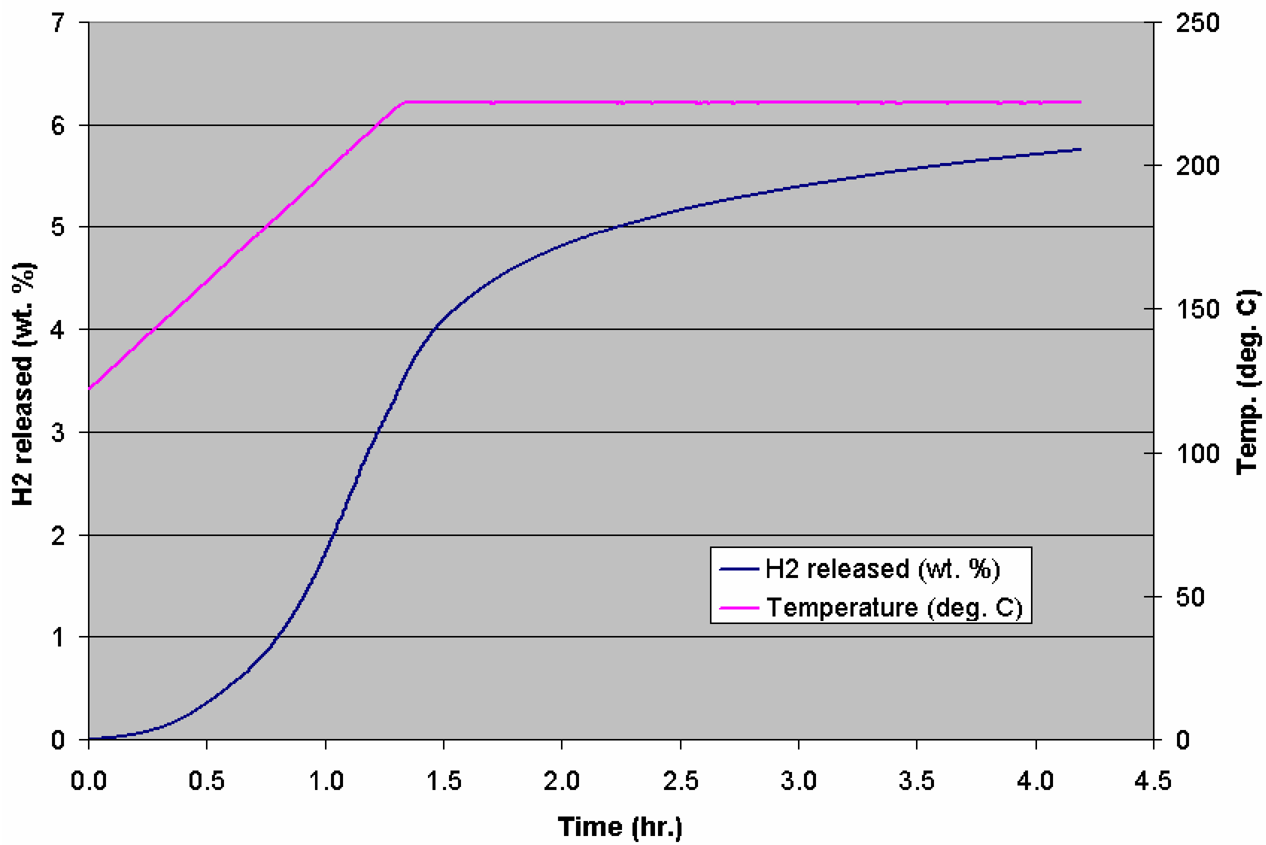
Results: New carrier data

- Recent discovery of a new carrier with 6.9 wt. % H_2 capacity (potential)
- Initial testing confirms selective hydrogenation and dehydrogenation
- Heat of dehydrogenation in appropriate range (10-13 kcal/mol H_2)



First dehydrogenation experiment

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Results: Adsorption of H_2 by novel porous ionic solids

- Computational modeling has identified a specific ionic solid composition with strong physisorption of H_2
  - At a loading of 6.76 wt. % H_2, the ΔE (at 25°C) is -5.07 kcal/mole H_2
- Computational work (*ab initio* DFT molecular dynamics) completed FY 04
- Satisfied technical criteria for go decision at end of FY04

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Summary: Technical Accomplishments/ Progress/Results

- Liquid carrier discovery effort
  - Several promising carriers
  - New carrier with capacity of 6.9 wt. % and >60 g H_2/L (est. density of 0.9 g/cc)
- Increased dehydrogenation catalyst activity by 100% through screening and development effort
- Demonstrated high H_2 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^{o}C) met on time
- Progress towards FY05 milestones on track

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Dehydrogenation Video Clip

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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_2 delivery session)

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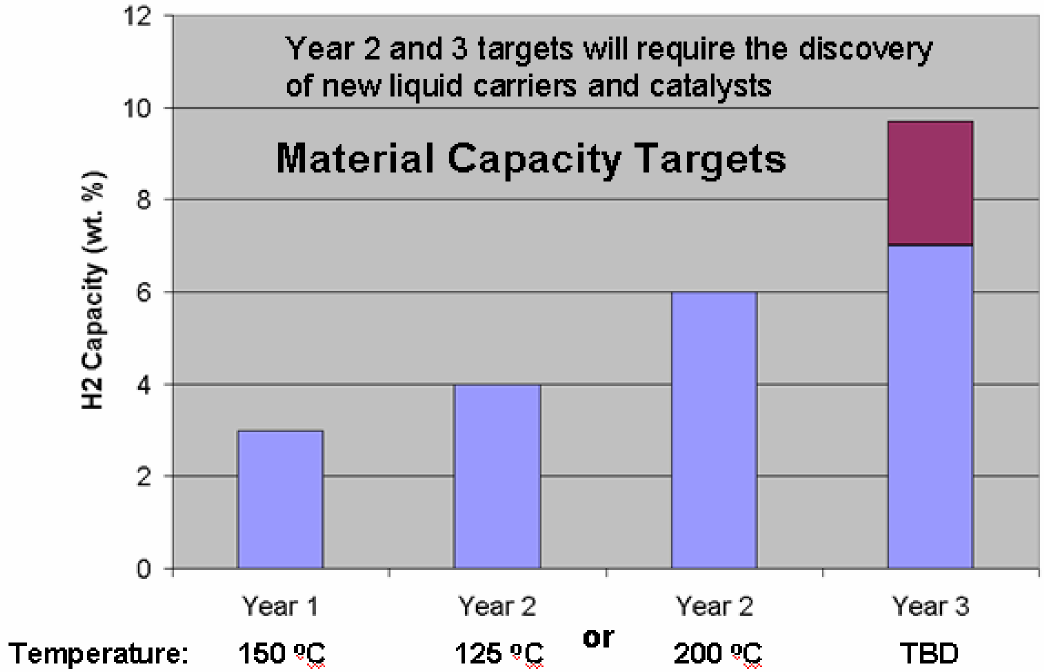
Future Work

- 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

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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).

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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**

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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

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