Hydrogen Storage by the Reversible Hydrogenation of Liquid and Solid Substrates

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Objectives

- **New Project (3 years) – Agreement signed 2/04**
  - Overall project objectives:
    - Develop carbon-based solid and liquid hydrogen storage materials with capacities of >6 wt. % and >45 g H_2/L
    - Develop hydrogen storage system prototype with 6 wt. % and 45 g H_2/L capacity in the range of –40 to 90-120 ^oC and less than 1000 psia H_2 pressure
- **Our current primary technical objectives:**
  - Discovery of novel substrates using experimental and computational methods
  - Demonstration of reversible hydrogen storage with liquid substrates
    - new liquid development
    - catalyst development
    - 1st year milestone: 3 wt. % hydrogen storage at temperatures at or below 150 ^oC
    - preliminary regeneration cost analysis

Budget

- Total funding for the project (3 yrs.)
  - $6,121,279
  - DOE share $4,346,108 (71%)
  - Air Products share $1,775,171 (29%)
- Funding FY04:
  - DOE funding estimated at $780,000

Technical Barriers and Targets

- Technical Barriers- Hydrogen Storage
  - A. Cost: \$3.00 per gallon gasoline equiv. (2005), \$1.50 per gallon gasoline equiv. (2010)
  - 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
  - G. Life Cycle & Efficiency Analyses
  - Q. Regeneration Processes
  - R. Byproduct Removal

- A. Cost: Facile regeneration of liquid substrates by hydrogenation at large central facilities
- B. Weight and Volume: Ongoing discovery effort for liquid and solid substrates with high useable capacity
- C. Efficiency: Total cycle – use and regeneration
- G. Life Cycle & Efficiency Analyses: Modeling of regeneration economics

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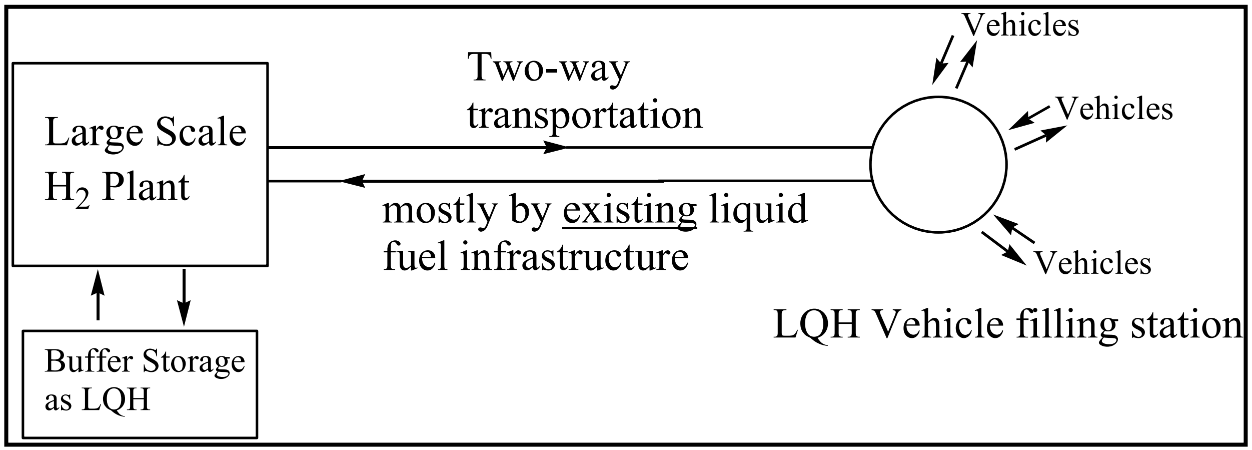
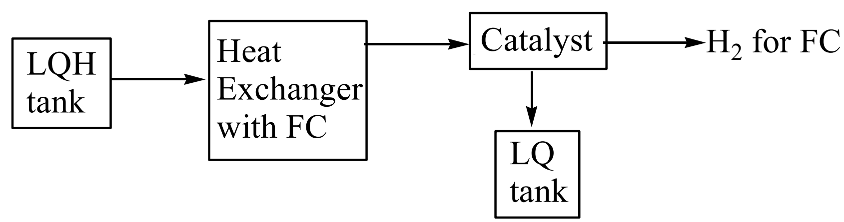
Approach

Utilizing Temperature/Pressure-Reversible "Liquid Hydride" ($LQ*H_2$) Carriers



Prior art $LQ*H_2$ compositions include cyclohexane and decalin.

In fuel cell (FC) vehicle
or stationary power source:



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.

Assuming an $LQ*H_2$ (d=1g/cc) carrying 6 wt. % H_2, 4 Kg H_2 (sufficient for compact FC vehicle 300-400 mile range) is equivalent to <u>18 gallons of the "liquid hydride" fuel</u>.

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Performance Limits and Comparison of "Chemical Hydride" Liquid Carriers

	Inorganic Hydride Hydrolysis	LQ*H_2
Max. Capacity (wt. % H_2)	6.5-11 (for current chemical hydrides)	6-7 No reagents – H_2O, etc.
ΔH (kcal/mol H_2) for H_2 release	-13 to -33 (exothermic) Spontaneous generation of H_2. Reaction heat has to be dissipated to environment.	10 to 15 (endothermic) Allows utilization of waste heat from the power source.
ΔG (kcal/mol H_2) for H_2 release	-19 to -38 Spontaneous at ambient temperature, cannot be reversed with H_2 alone.	~0 (at reaction temp.) Spontaneous upon heating, but only in the presence of appropriate catalysts.
Regeneration	Requires multi-step chemical processing or a direct electrochemical synthesis.	LQ* is easily regenerated with H_2 alone, using known, inexpensive catalytic hydrogenation technology.

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Project Safety

- Air Products: A world leader in hydrogen safety. Safety is an integral part of our corporate culture
- We utilize detailed hazard reviews for all lab operations and lab equipment
  - Use of written, peer-reviewed hazard reviews
  - Corporate EH&S oversight
- Specific engineering controls:
  - Hydrogen monitors that automatically shut down equipment in the event of a hydrogen leak
  - Overpressure and over-temperature controls
- We have strict chemical hygiene rules for synthesis work on solid and liquid substrates

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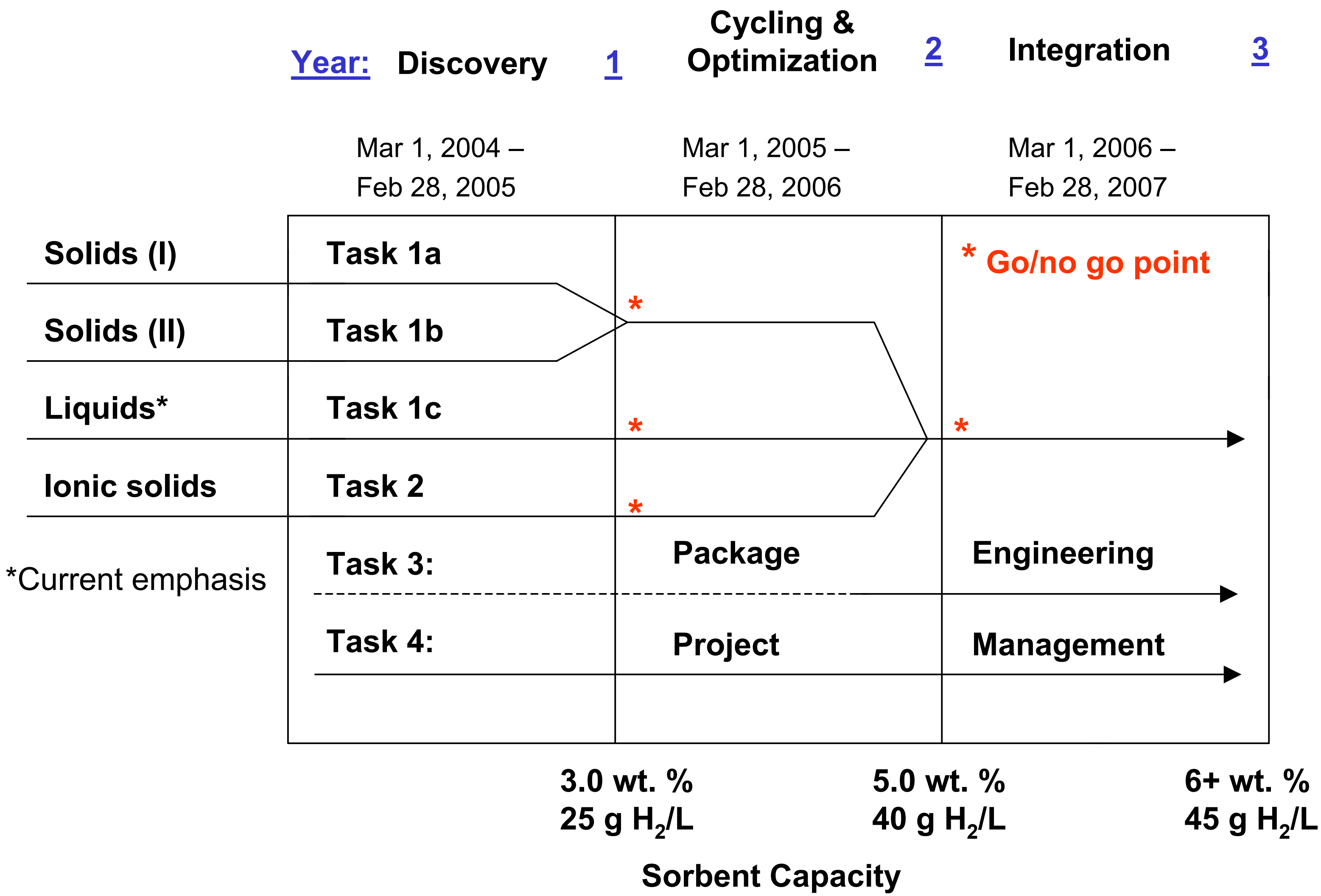
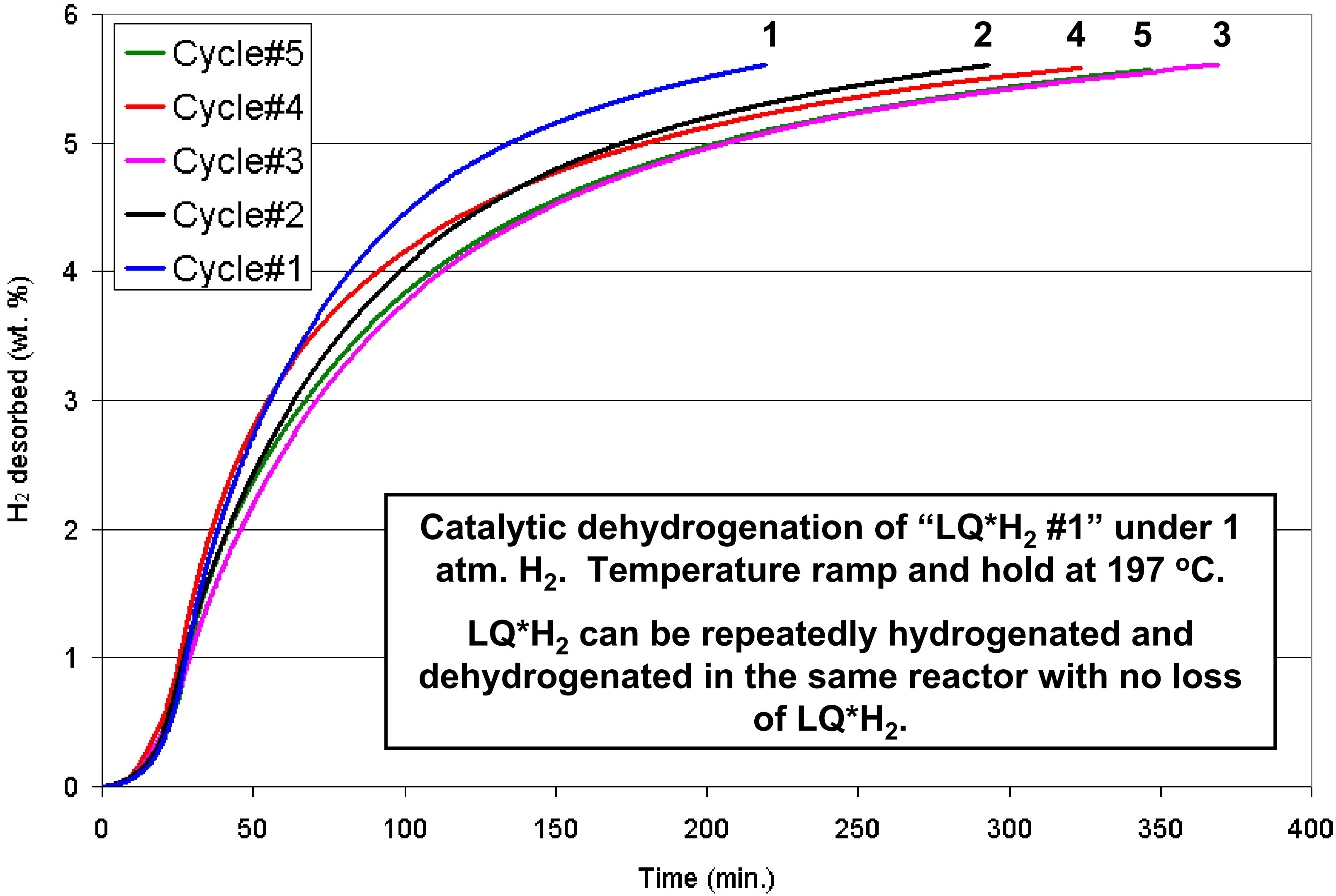
Project Timeline



Technical Accomplishments

- We have developed a number of novel liquid-phase hydrogen carriers. One example is "LQ*H_2 composition #1":
  - 5-7 wt. % H_2 gravimetric capacity
  - >50 g H_2/l volumetric capacity
  - Experimental heat of hydrogenation, ΔH, is -12.1 kcal/mol H_2 (cf. decalin ΔH = -15.8 kcal/mol H_2)
  - Low volatility
    - vapor pressure is approximately 10 torr at 200 °C
    - LQ*H_2 can be dehydrogenated to provide hydrogen free of liquid carrier contamination with no need for condensers or membranes

Reversible LQ^*H_2 Dehydrogenation to LQ*



5 cycles with no capacity loss or systematic changes in hydrogenation/dehydrogenation rate

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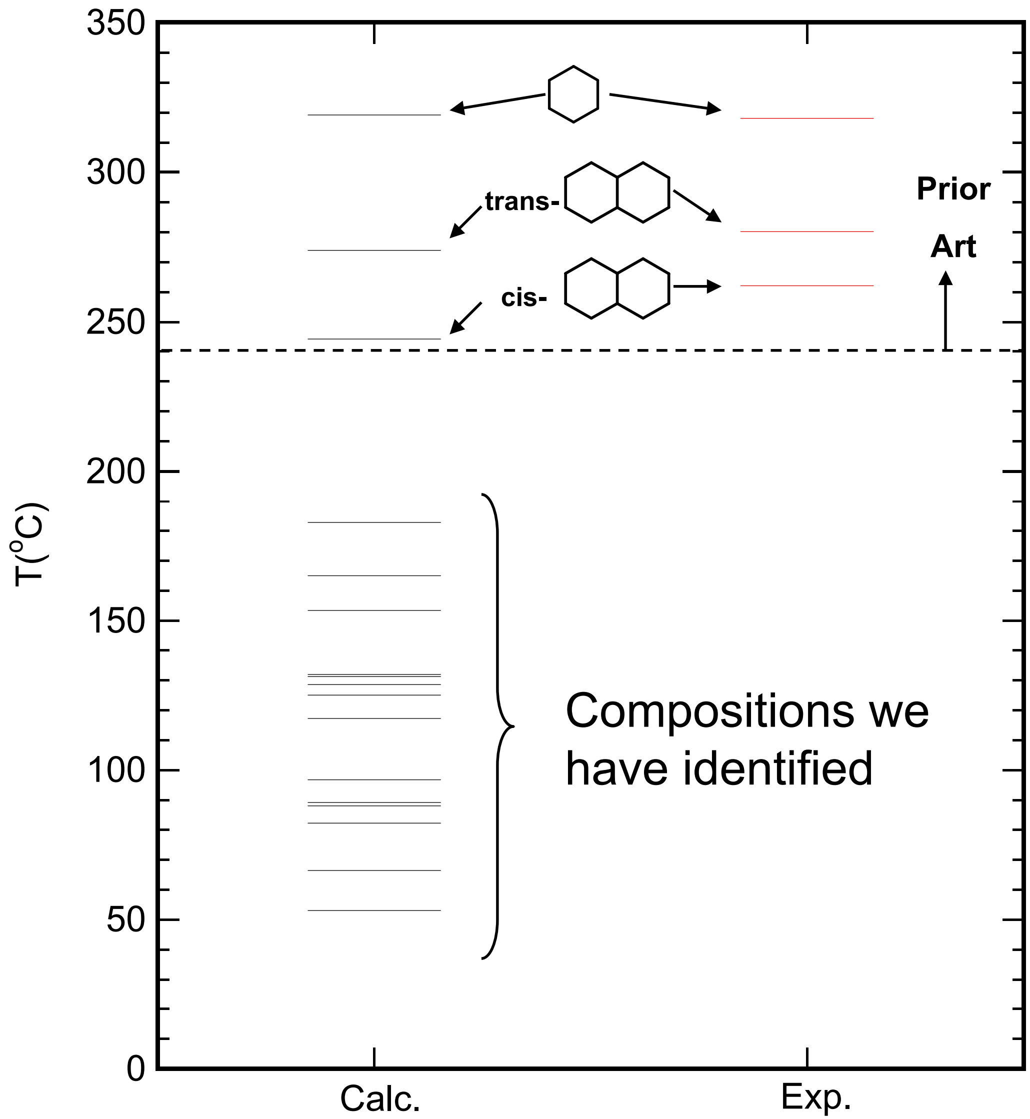
Dehydrogenation Temperatures for LQ^*H_2 Liquid Substrates



Temperatures for a 95% dehydrogenation of LQ^*H_2 in equilibrium with LQ* and 1 atm. H_2: (a) As calculated by high level predictive models and (b) As derived from published thermodynamic experimental data.

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Preliminary Projection of LQ* to LQ*H_2 Regeneration Cost

- Primary cost drivers include:
  - Capital for plant and LQ*H_2
  - Catalyst and LQ*H_2 operating lifetime
  - Energy recovery from LQ*H_2 regeneration
- Scale used in projections:
  - 15MM - 90MM kg H_2/year
- Regeneration cost range:
  - \$0.19 - \$0.73/kg H_2

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Interactions and Collaborations

- Fuel cell manufacturers: discussions of heat integration of dehydrogenation reactor with fuel cells
- Military fuel-cell developers: discussions of potential uses for liquid hydrogen storage substrates with existing fuel cell applications
- Penn State University: discussions of possible collaborative research with faculty
- Southwest Research Institute hydrogen storage measurement laboratory: assistance provided for instrument selection and high pressure H_2 handling issues
- Carbon H_2 Storage Materials Working Group: Standard sample testing and discussions of measurement standardization
- Publications (3) and presentations (2) in last year

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Response to FreedomCAR Tech Team Reviewers Comments (2/19/04)

- Scope of project is too ambitious-
  - We will downselect at the end of year 1 and year 2 to focus work on the most promising hydrogen storage substrates
- Technical Feasibility: Do liquid compositions exist than can provide a distinct improvement over the simple aromatics (benzene, naphthalene) previously described for hydrogen storage/delivery? What about catalyst and liquid lifetimes?
  - We have shown experimental and computational data that proves that significant advances are possible
  - Extended liquid cycling and catalyst lifetime studies slated for year 2
- Regeneration Cost / Energy Efficiency:
  - We have preliminary economic evaluations that suggest that the “liquid carrier” concept could meet the DOE cost targets for onboard delivered hydrogen.
  - Off-board H_2 storage and H_2 delivery possibilities are being addressed with DOE.

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Future Work

- Remainder of Year 1: Continue discovery effort towards "ideal" liquid and solid hydrogen carriers
  - predictive computational modeling
  - experimental efforts on selected substrates
  - catalyst screening
- Year 2:
  - More emphasis on cycling/lifetime studies
  - Preliminary engineering of hydrogen storage system (dehydrogenation reactor)
  - Catalyst development and hydrogenation/dehydrogenation rate optimization