

VI.B.3 Design and Development of New Carbon-Based Sorbent Systems for an Effective Containment of Hydrogen

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Objectives

- Liquid carrier discovery and development
 - Develop liquid-phase hydrogen storage materials with capacities of >6 wt. % and >50 g H₂/L
 - Discovery of novel organic liquid carriers as hydrogenation/dehydrogenation substrates using experimental and computational methods
 - Production of liquid carrier(s) in quantities sufficient for dehydrogenation testing
- Dehydrogenation catalyst discovery and development
 - Rapid testing of new catalysts
 - Verification of selectivity
- Hydrogen adsorption with novel ionic solids
 - Predictive quantum mechanics calculations
 - Synthesis and hydrogen adsorption testing

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- A. Cost
- B. Weight and Volume
- C. Efficiency
- D. Durability
- E. Refueling Time
- R. Regeneration Processes
- S. By-Product/Spent Material Removal
- T. Heat Removal

Technical Targets

This project is directed towards the discovery of new liquid-phase hydrogen carriers and dehydrogenation catalysts that will enable an integrated delivery and storage of hydrogen while meeting the DOE 2010 targets for hydrogen storage density and refueling time. This approach allows for a high energy efficiency compared to other materials-based hydrogen storage approaches and can potentially utilize the existing liquid fuels infrastructure for hydrogen distribution.

Approach

- Develop liquid-phase hydrogen storage materials (liquid carriers) that can be reversibly hydrogenated, allowing the storage of hydrogen in a safe, easily transportable form. The liquid carriers can be hydrogenated at large central or regional sites, in locations where inexpensive hydrogen is available, allowing for high overall energy efficiency through recovery and use of the heat generated by the exothermic hydrogenation. The hydrogenated liquid carrier could be distributed, potentially using the existing liquid fuels infrastructure, to distribution sites where the liquid would be dispensed to hydrogen-powered vehicles. With a reasonable gravimetric hydrogen capacity (6 wt. %) and density (1 g/cc), 5 kilograms of hydrogen would be contained in only 22.5 gallons of a liquid carrier.
- Develop liquid-phase hydrogen carriers that demonstrate characteristics including: dehydrogenation thermodynamics allowing for low-temperature operation, stability over many cycles of hydrogenation and dehydrogenation, and low volatility.
- Develop dehydrogenation catalysts that will display high activity at low temperatures, high selectivity towards dehydrogenation, and long lifetime.
- Investigate another potential hydrogen storage system consisting of a pressure/temperature, H₂-reversible, ionic solid sorbent material that is packaged in a lightweight container under a modest pressure of hydrogen.

Accomplishments

- Seven cycles of hydrogenation and dehydrogenation of a liquid carrier (Figure 1) with high selectivity (degradation of liquid carrier <1% after 7 cycles) have been demonstrated. High hydrogen quality (>99.9% purity) with detection of only hydrocarbon impurities (methane, ethane) has also been demonstrated (Table 1).
- FY 2004 milestone of demonstrating >3 wt. % hydrogen storage at temperatures <150°C using N-ethylcarbazole liquid carrier has been accomplished.
- The liquid carrier dehydrogenation rate has been improved by >250% by discovery of new dehydrogenation catalysts with higher activity.
- A new liquid carrier candidate with theoretical 6.9 wt. % and >60 g/L H₂ capacity has been developed and in preliminary testing has shown evolution of >6.25 wt.% hydrogen at temperatures <225°C.
- Computational modeling has identified a specific ionic solid composition with a strong physisorption of H₂. At a loading of 6.76 wt. % H₂, the ΔE (at 25°C) is -5.07 kcal/mole H₂

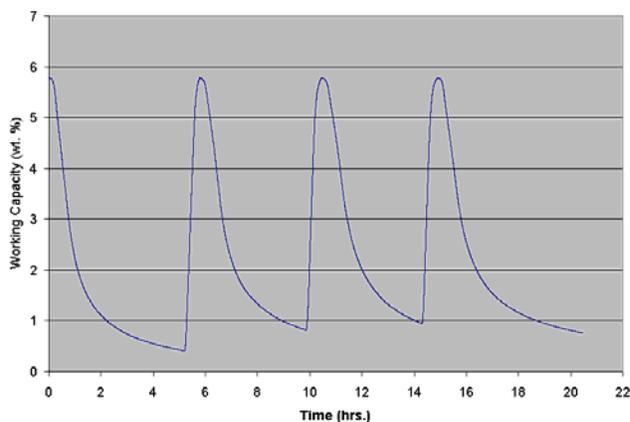


Figure 1. A plot of working hydrogen capacity vs. time for a cycling experiment with N-ethylcarbazole in a batch reactor with a slurry of hydrogenation catalyst and dehydrogenation catalyst. The hydrogenation conditions are 170°C and 1200 psia H₂, and the dehydrogenation is performed with a temperature ramp from 30 to 200°C over 1.75 hours, holding at 200°C, all under 15 psia H₂.

Table 1. Hydrogen quality from a N-ethylcarbazole dehydrogenation experiment as determined by mass spectroscopy (detection limits <10 ppm; ND = Not Detected)

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