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HYDROGEN TRANSMISSION/STORAGE WITH METAL HYDRIDE-ORGANIC SLURRY AND ADVANCED CHEMICAL HYDRIDE/HYDROGEN FOR PEMFC VEHICLES

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Abstract

This paper describes the work performed on two programs supported in part by the U.S. Department of Energy. These programs are aimed at evaluating the potential of using slurries of chemical hydrides and organic liquids to store hydrogen. The projects have been very successful in meeting all project objectives. After a detailed analysis of chemical hydrides, lithium hydride was selected for use in these programs. Lithium hydride has been prepared as a slurry with light mineral oil and a dispersant and has been found to be stable for long periods of time at atmospheric temperatures and pressures. We have demonstrated that the lithium hydride slurry can be mixed with water to produce hydrogen on demand. Reactions between the lithium hydride slurry and water take place rapidly and completely. The resulting lithium hydroxide can be recycled either by electrolytic methods or by a carbo-thermal process. Experiments with the carbo-thermal process indicate that the regeneration of lithium hydride can be accomplished at temperatures of 1500°K or less enabling the use of economically acceptable furnace materials. A cost analysis of the regeneration process indicates that the process should be cost competitive with hydrogen produced from natural gas and stored as a liquid or a highly compressed gas.

NOTICE

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INTRODUCTION

Objective

We refer to these two programs as the Transportation/Storage Program and the Vehicle Program. The objective of the Transportation/Storage Program is to demonstrate the technical viability and economic attractiveness of chemical hydride slurry based hydrogen generation/storage systems. This program is intended to take a broad view of the entire chemical-hydride hydrogen-storage cycle. Technical validations and economic analyses are the primary focus of the program.

The objective of the Vehicle Program is to demonstrate a prototype storage and delivery system for vehicular applications. In this program, we are taking a more detailed look into the ability of the chemical hydride slurries to store hydrogen for PEM fuel cell applications in vehicles.

The programs are intended to answer the following questions:

- Can the reaction rate of a chemical hydride with water be controlled to provide a safe and stable storage and hydrogen production process utilizing a slurry based approach?
- Are the physical properties of the reactants and products acceptable for transportation and bulk storage systems?
- Can a cost effective design of a storage and hydrogen production system be made to meet the energy density criteria for transportation applications?
- Can a hydroxide-to-hydride regeneration system design be identified that is able to produce hydrogen at a cost competitive with present fuels?

Technical Concept

The concept behind the use of chemical hydrides is that when the chemical hydrides are mixed with water they will produce hydrogen. Table 1 displays several of the chemical hydrides evaluated for use as part of these investigations. Lithium hydride produces hydrogen with a relatively high gravimetric density. In considering a recyclable process, one of the important issues is the ability to regenerate the chemical hydride. We selected lithium hydride because it was a mono-metal hydride rather than a bi-metal hydride. We felt that it would be easier to reduce a mono-metal hydroxide than to separate and reduce a multi-metal hydroxide. An additional consideration is that many of the hydroxides form hydrates. Lithium hydroxide forms a mono-hydrate. Many of the bi-metal hydrides for multi-hydrates when reacted with water. The lithium hydroxide hydrate decomposes when it is heated above the temperature of boiling water. Many of the bi-metal hydroxide hydrates do not decompose until they are heated to quite high temperatures.

Table 1 - Chemical Hydrides and Their Gravimetric Densities

Chemical Reaction			Gravimetric Density, %H2 (Hydride Only)
$CaH_2 + 2\ H_2O$	→	$Ca(OH)_2 + 2\ H_2$	9.6%
$MgH_2 + 2\ H_2O$	→	$Mg(OH)_2 + 2\ H_2$	15.3%
★ $LiH + H_2O$	→	$LiOH + H_2$	25.2%
$LiBH_4 + 4\ H_2O$	→	$LiOH + H_3BO_3 + 4\ H_2$	37.0%
$NaBH_4 + 4\ H_2O$	→	$NaOH + H_3BO_3 + 4\ H_2$	21.3%

The process envisioned is that lithium hydride will be prepared as a slurry at centralized plants. The slurry will be pumped into tanker trucks or pumped through pipes to distribution centers where it will be loaded into vehicles or carried to storage vessels in homes, business, or industry. When hydrogen is required, the chemical hydride slurry will be mixed with water to produce a high quality hydrogen that can be used in fuel cells. The resulting hydroxide waste product will be picked up when the next delivery is made and transported back to the regeneration plant where it will be separated from the mineral oil and where the lithium hydroxide will be regenerated to lithium hydride.

Slurry Concept

A slurry is a mixture of a solid and a liquid to make a pumpable mixture. The main issue in preparing a slurry of a solid is to distribute the solid in the liquid in such a way that the solid does not settle out. We have selected light mineral oil in which to suspend finely ground lithium hydride. A dispersant is used to prevent the particles from settling out of the suspension. Figure 1 displays a conceptual view of the dispersant action. The dispersant is made with an anchor group and a lyophile. The anchor group attaches to the particle and the lyophile streams outward forming a set of tendrils that fend off other particles and slow the movement of the particles within the mineral oil. Particles are typically about 20 microns in diameter.

A major feature of the use of mineral oil to form the slurry is that it forms a protective coating around the particle that slows the movement of water toward the particle. Figure 2 diagrams this effect. This protective coating allows the lithium hydride to be safely handled and stored in the air without absorbing moisture from the air. It also slows the kinetics of the reaction allowing the development of reaction vessels to mix the hydride with water for releasing hydrogen.

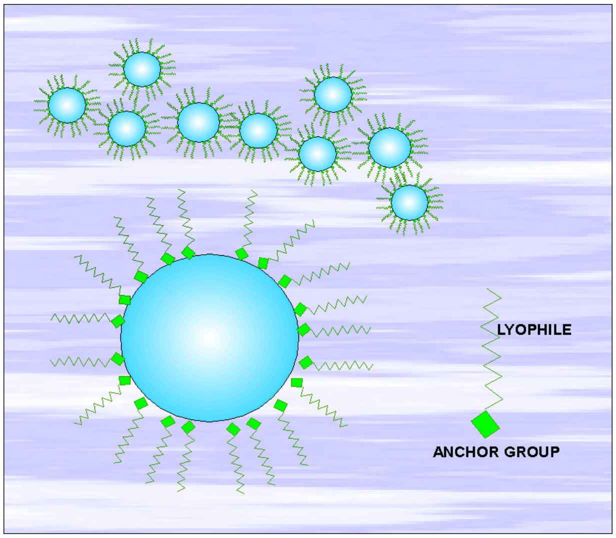


Figure 1 - Chemical Hydride Slurry

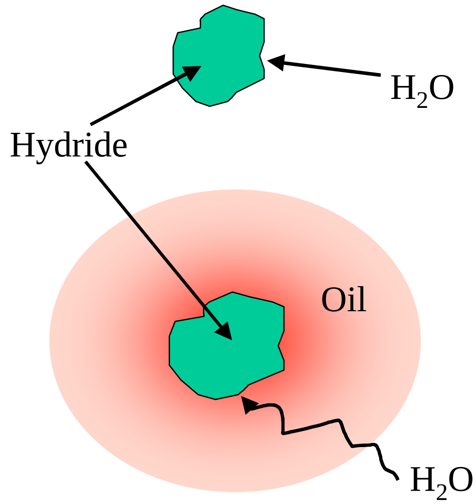


Figure 2 - Rate Limiting Reaction Kinetics

Over the past couple of years, we have developed the ability to produce lithium hydride slurries in a nearly continuous operation. Figure 3 is a picture of a 3 gallon batch of lithium hydride slurry being poured into a storage vessel that we were using in the vehicle program. This is 60% lithium hydride in mineral oil with a dispersant to maintain the slurry properties. The viscosity of the slurry is about 2000 cp. This slurry is stable for several weeks or more.

Figure 3 - Lithium Hydride Slurry

An important feature of the slurry is its ability to protect the lithium hydride from inadvertent exposure to water or water vapor. If allowed to, powdered lithium hydride will absorb water vapor from the air. The reaction of the water vapor and the hydride produces hydrogen and heat. If the day is sufficiently humid, the heat will build up until it ignites the hydrogen. When mixed with mineral oil, the hydride cannot absorb moisture rapidly enough to be a hazard. In addition, because mineral oil has such a high vapor pressure, the mineral oil actually prevents the ignition of the lithium hydride from open flames. Figure 4 is a sequence of photographs of a test performed with a propane torch. A spoon full of lithium hydride slurry was placed in our fume hood. The flame from the torch did not light the slurry when passed near. Gasoline would have ignited. When the flame was held on the slurry for sufficient time, some of the mineral oil evaporated and burned. But the flame went out when the torch was removed.

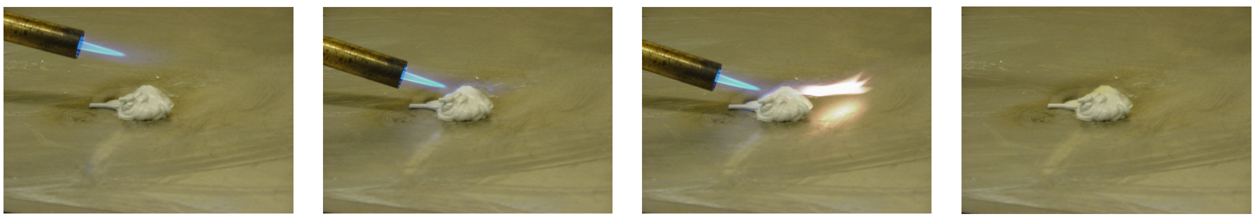


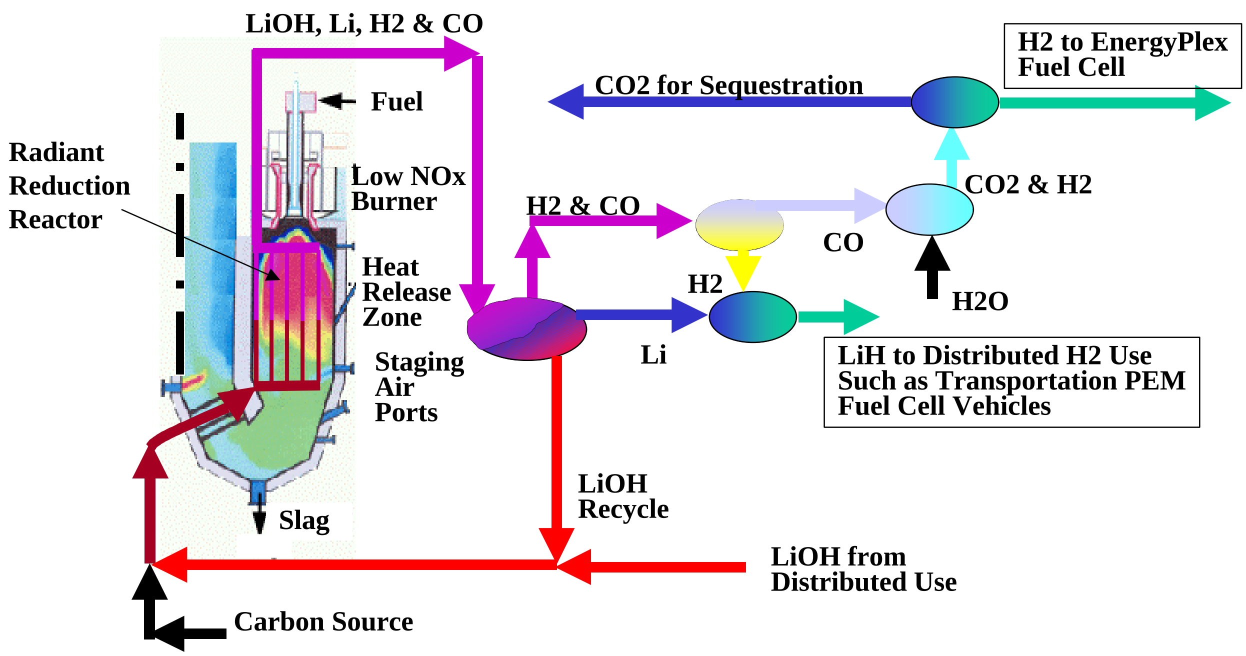
Figure 4 - Flame Test with LiH Slurry

TRANSPORTATION/STORAGE PROGRAM

The focus of our attention in the Transportation /Storage Program during the past year has been to better understand the regeneration process. We have performed a large number of tests with a controlled atmosphere high-temperature furnace that we built for this application. We have also performed a preliminary system design and economic analysis of the regeneration process to identify the relative cost of hydrogen that can be expected from a chemical-hydride hydrogen-storage system.

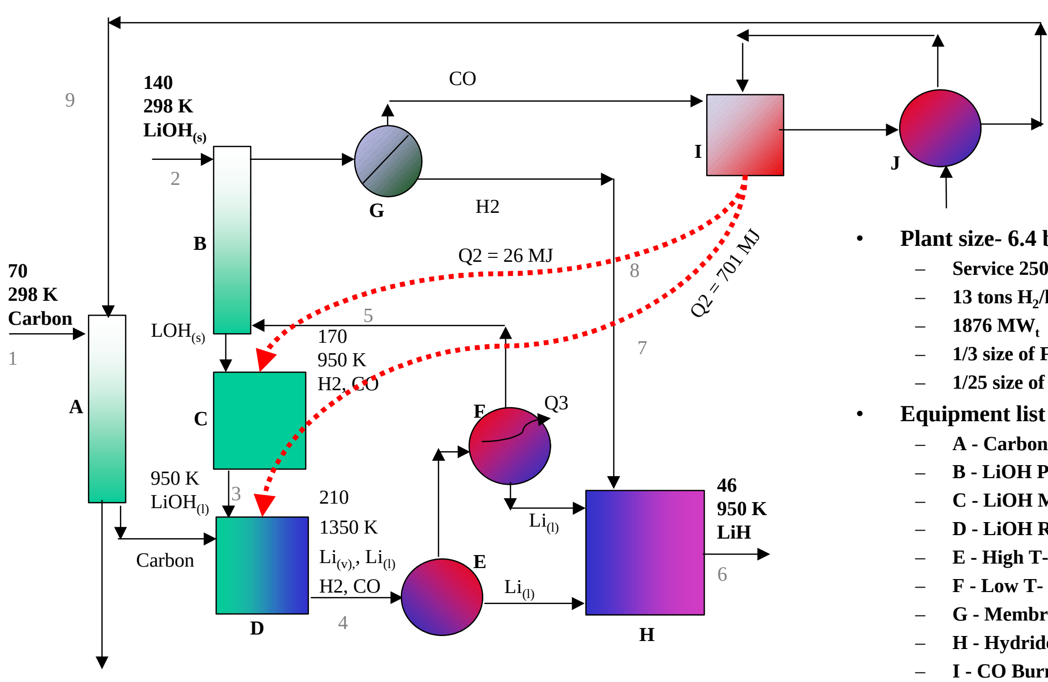
Regeneration Process

The proposed regeneration process is a carbo-thermic reduction process based on the use of low cost carbon from coal or biomass. The objective is to have zero net carbon dioxide emissions from the regeneration plant by capturing the highly concentrated carbon dioxide stream leaving the plant for sequestration. Regeneration will be performed in centralized plants much like refineries using technologies synergistic with blast, aluminum reduction, and glass furnaces. Figure 5 is a diagram showing the regeneration process that was evaluated. Figure 6 shows a simplified ASPEN Plus process flow diagram. Lithium hydroxide and carbon are fed to a radiant reduction reactor where they are heated to 1350°K. During this reaction, hydrogen and carbon monoxide are released and lithium is melted. We have assumed that this reduction process is about 50% effective so the lithium oxide that is not reduced is returned to the reactor. Hydrogen and carbon monoxide are separated from the lithium and from each other. Carbon monoxide is put through a shift reaction to form carbon dioxide and hydrogen. The hydrogen is used to produce electric power and lithium hydride.



$$LiOH\ (l) + C\ (s) \rightarrow Li\ (l,g) + CO\ (g) + H_2\ (g)$$

Figure 5 - Lithium Hydride Regeneration Process



- Plant size- 6.4 billion Btu/hr
  - Service 250,000 cars
  - 13 tons H_2/hr
  - 1876 MW_t
  - 1/3 size of First FCC unit
  - 1/25 size of Today's FCC units
- Equipment list
  - A - Carbon Preheater
  - B - LiOH Preheater
  - C - LiOH Melter
  - D - LiOH Reduction Reactor
  - E - High T- Condenser
  - F - Low T- Condenser
  - G - Membrane Separator
  - H - Hydride Reactor
  - I - CO Burner
  - J - Air Preheater
- Flow rates - metric tons/hr

Figure 6 - Simplified ASPEN Plus Process Flow Sheet

A series of experiments were performed to verify that regeneration takes place at the temperatures desired. Equilibrium thermochemical calculations showed that the reduction of lithium hydroxide with carbon typically takes place at temperatures above 1800°K except when the carbon monoxide formed is swept away from the reaction. Figure 7 shows pictorially the effect of removing CO from the reaction zone. By removing the CO, the reaction is allowed to proceed toward completion at lower temperatures. Figure 8 shows the high temperature controlled atmosphere furnace used for the experiments.

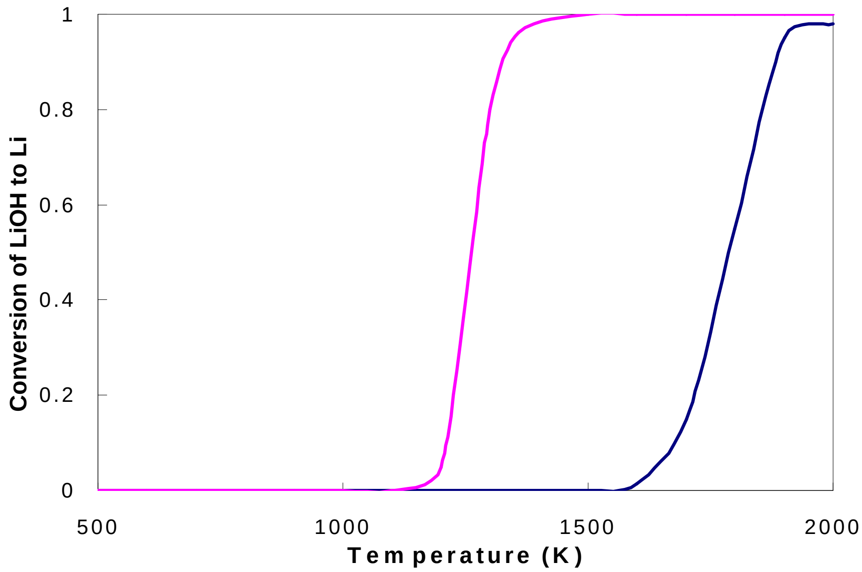


Figure 7 - Effect of Removing CO from LiOH/C Reaction

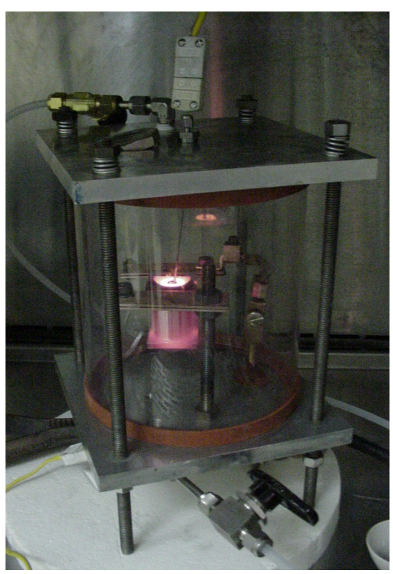


Figure 8 - High Temperature Controlled Atmosphere Furnace

Figure 9 displays some of the data collected during the test program and confirms the hypothesis of the regeneration process. It can be seen that the analytical result appears to be supported by the data collected.

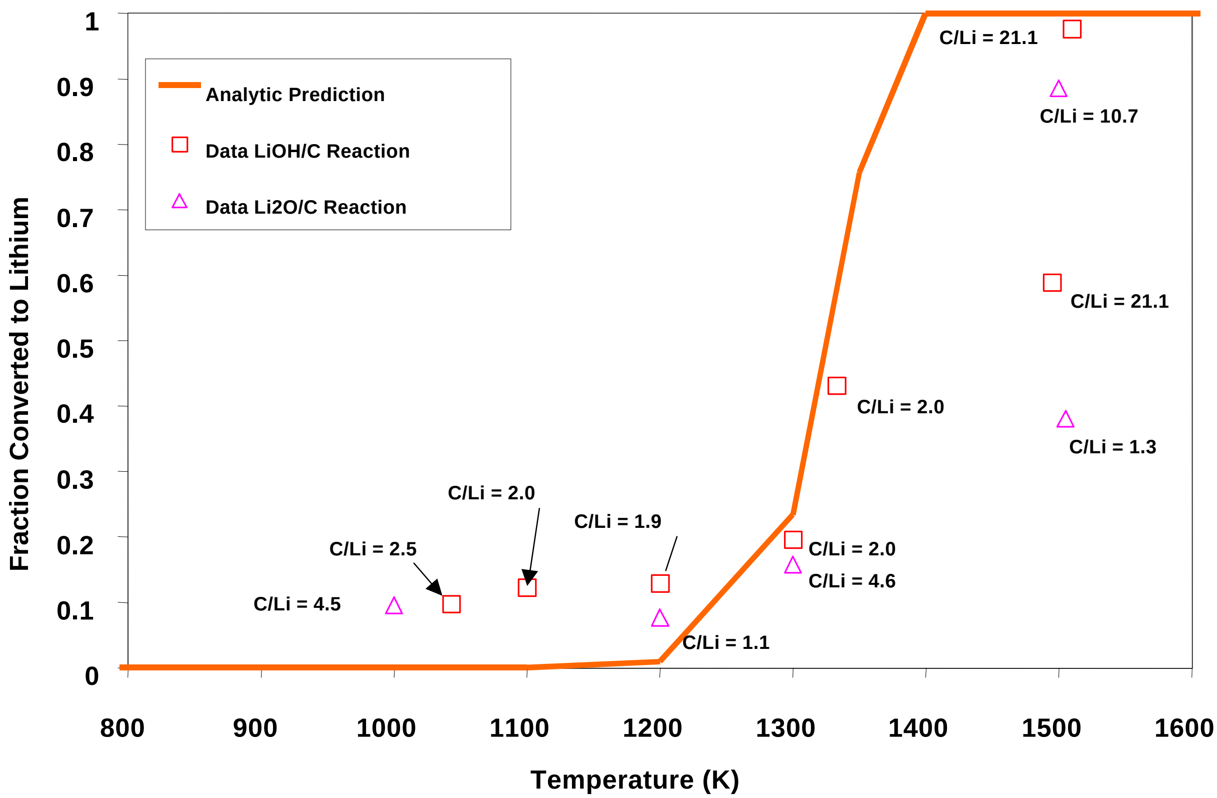


Figure 9 - Data Collected from High Temperature Furnace Experiments

Economic Analysis

An economic analysis was performed for the regeneration process described above to determine the cost of hydrogen to be expected. Table 2 displays the assumptions used in the economic analysis. The analysis began with a preliminary design of the various components required in the process.

Table 2 - Assumptions Used in Economic Evaluation

Capital	$ 58.8 Million
Carbon	Variable
Labor	
Operators	25 at $35,000/yr
Super. & Cleric.	15% of Operators
Mainten. & Repairs	5% of Capital
Overhead	50% of Tot. Lab. + Mtnc.
Local Tax	2% of Capital
Insurance	1% of Capital
G&A	25% of Overhead
Fed. and State Tax	38% of Net Profit

We found this process to be sensitive to the cost of carbon. However, carbon sources appear to be available at costs that will make this process economical. Figure 10 displays the results of our analyses for two size plants. The first plant would serve about 250,000 cars per day. The larger plant would serve about 2,000,000 cars per day.

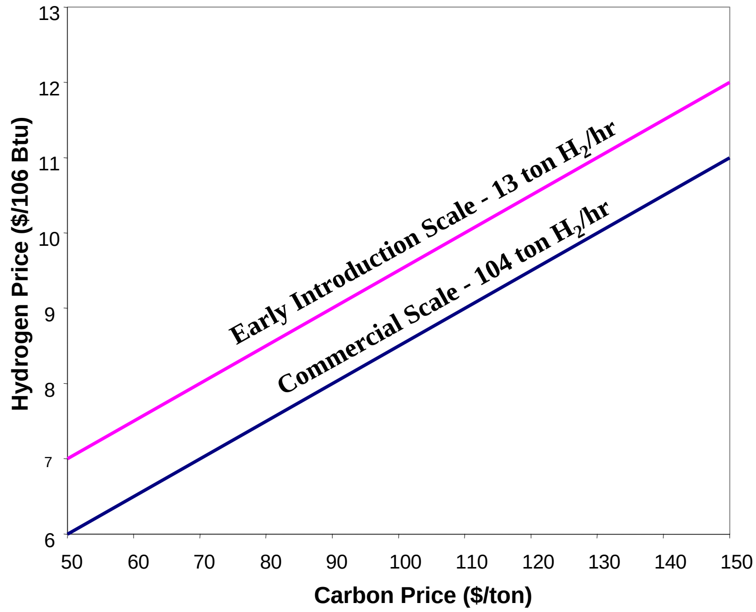


Figure 10 - Results of Economic Analysis

Figure 11 displays the cost of hydrogen from the lithium hydride slurry system and other systems. When compared to the cost of stored hydrogen form other production methods, the chemical hydride slurry approach appears to be very competitive. It is even competitive to the cost of tax free gasoline.

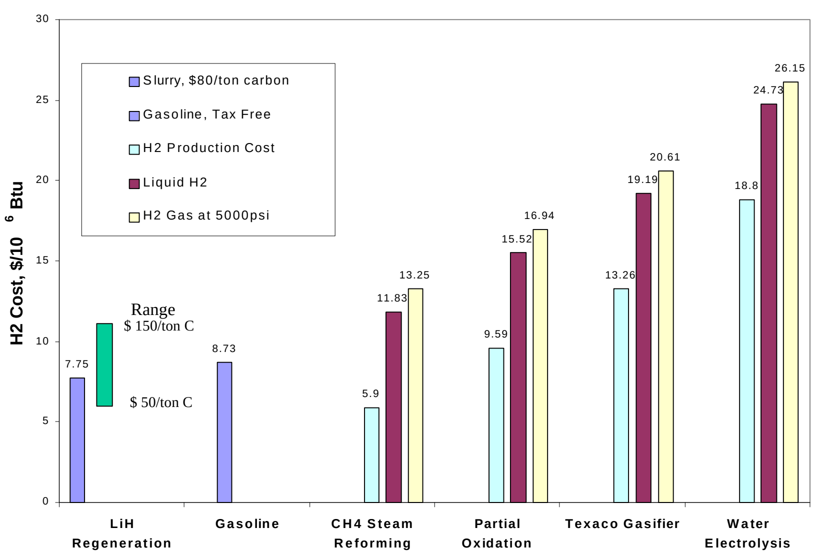


Figure 11 – Cost of Stored Hydrogen as a Chemical Hydride and by Conventional Methods

VEHICLE PROGRAM

The focus of our attention in the Vehicle Program during the past year has been the completion of the demonstration of the mobile chemical-hydride hydrogen generator. To satisfy the goals of the program, the hydrogen generator must demonstrate that it can produce 3 kg/hr of hydrogen, and that it can meet or exceed the gravimetric density goal of 3355 Wh/kg and the volumetric density goal of 929 Wh/l.

The chemical-hydride hydrogen-storage system developed during this program has achieved all its goals. An advanced system design based on the developed system and recycling water from the fuel cell would have a gravimetric energy density of 3364 Wh/kg and a volumetric energy density of 1954 Wh/l. The system has been demonstrated to follow the hydrogen demand rapidly and to produce in excess of the 3 kg/hr hydrogen flow rate target.

Hydrogen Generator Design

The hydrogen generator design is made up of storage vessels for the lithium hydride slurry and a small amount of water, pumps for both the slurry and the water, a mixing reactor, a heat exchanger, and a hydroxide storage tank. Figure 12 is a diagram of the design. Figure 13 is a picture of the prototype hydrogen generator after one of its final test sequences. The reactor is a tube with an auger/mixer running through it. Hydride slurry and water are pumped into the reactor at one end. The auger/mixer moves this mixture through the reactor and mixes it as it is being moved. Excess water is evaporated, absorbing and carrying the heat of reaction out of the reactor with the hydrogen. Hydrogen and water vapor are separated from the hydroxide product in the head of the hydroxide tank. The water vapor is condensed in the heat exchanger. Condensed water is returned to the water circuit and hydrogen is delivered to the fuel cell.

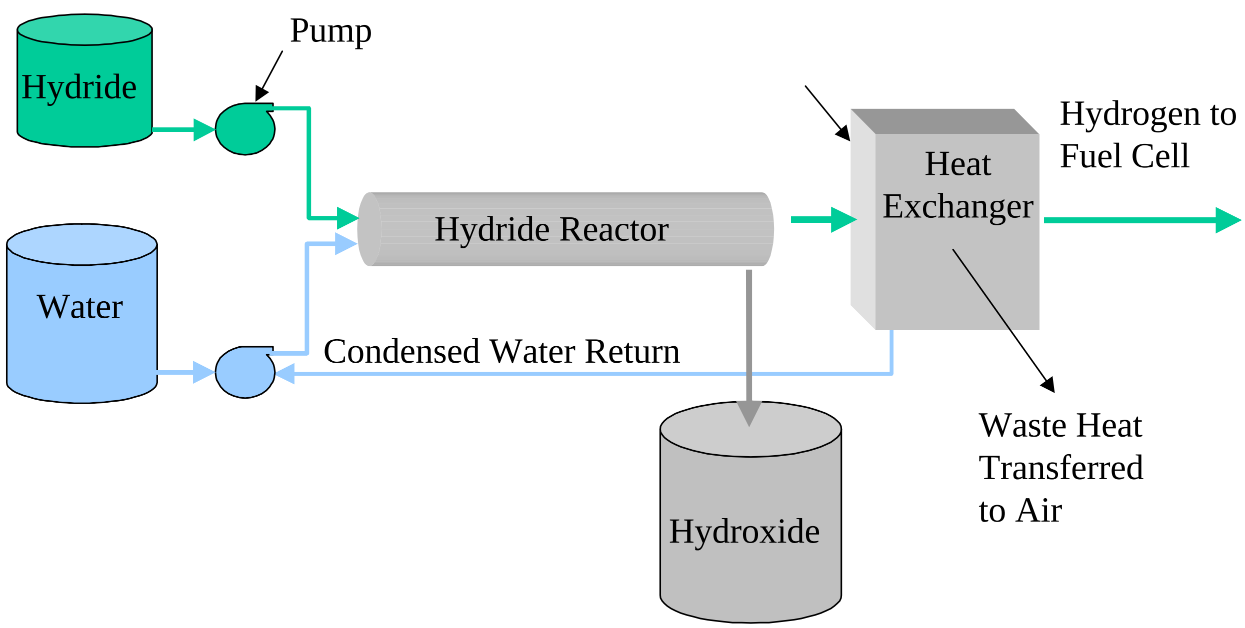


Figure 12 - Diagram of the Hydrogen Generation System

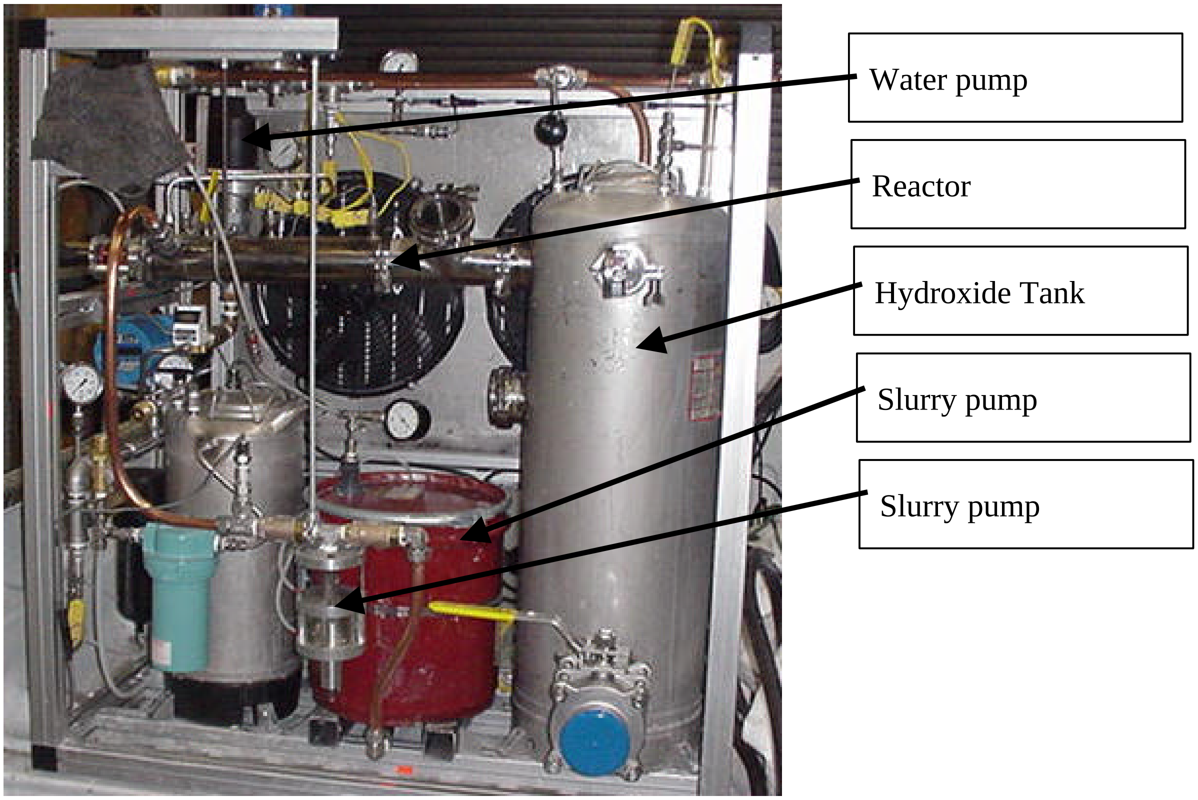


Figure 13 - Picture of the Prototype Hydrogen Generator

Hydrogen Generator Performance

Figure 14 shows the hydrogen and hydride slurry flow rates during a typical test of the system. During this test, the maximum flow rate was a little over 2 kg/hr of hydrogen. An important thing to note is the rapid rise in hydrogen flow rate with increases of the slurry and the rapid drop in the hydrogen flow rate with decreases of the slurry. By having the hydrogen flow stop when the hydride slurry flow stopped, we were assured that the mixing and reaction in the reactor were complete.

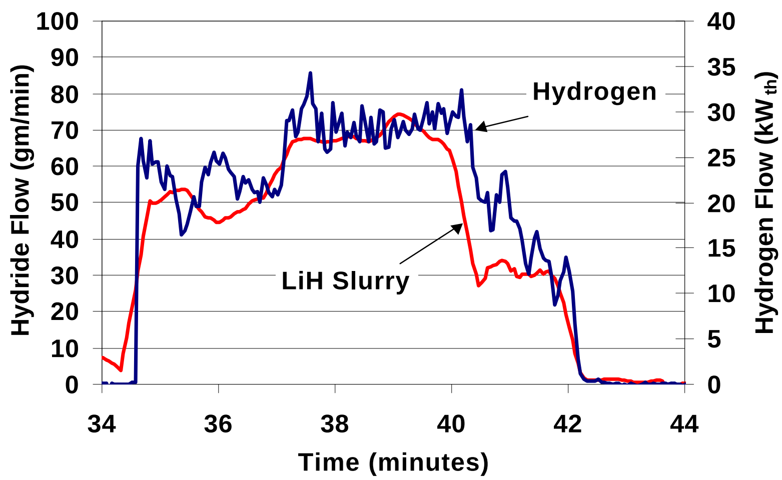


Figure 14 - Data Showing the Slurry and Hydrogen Flow Rates

Quality of the Hydrogen

In order to be acceptable in a fuel cell, the hydrogen produced from the lithium hydride slurry reactor must have very low concentrations of carbon monoxide. Fuel cell researchers have noted that the concentration of carbon monoxide must be less than 10 ppm.

Measurements were made during one test of the hydrogen leaving the system at points before and after a carbon filter. Table 3 displays the results of these measurements. In both measurements, the carbon monoxide measurements showed that levels were well below the tolerable levels of a PEM fuel cell. Also measured were concentrations of oxygen, nitrogen, carbon dioxide, mineral oil, and hydrocarbons. The ratio of oxygen to nitrogen was the same as that of air and was different in each measurement indicating that air contamination may have occurred during the measurement process. Measurements of mineral oil and hydrocarbons were both low. Carbon dioxide was also low. One possible source of the carbon dioxide is from the water used in the system. Untreated tap water was used in all our experiments.

Table 3 - Measured Contaminants in Hydrogen

Before Carbon Trap -	CO2	=	2.4 ppm	CO	=	1.5 ppm
	O2	=	25 ppm	Oil	=	0.1 ppm
	N2	=	95 ppm	HC	=	1.2 ppm
After Carbon Trap -	CO2	=	0.7 ppm	CO	=	0.1 ppm
	O2	=	10 ppm	Oil	=	0.1 ppm
	N2	=	40 ppm	HC	=	0.8 ppm

As expected the carbon monoxide and hydrocarbons were lower after having passed through a carbon filter. The results of this test indicate that a carbon filter is probably not necessary for this system.

SUMMARY/CONCLUSIONS

In summary, the lithium hydride slurry approach for storing hydrogen provides a viable alternative to hydrogen storage as liquid hydrogen or highly compressed hydrogen. Storage densities are higher than those for metal hydrides. The gravimetric energy density of 60% lithium hydride slurry is 5110 Wh/kg or 15.3% hydrogen. The volumetric energy density is 3937 Wh/l or 118 kg H_2/m^3. This is more than twice the volumetric energy density of liquid hydrogen and it is at ambient pressure and temperature. The slurry is easily pumped and can be reacted with water with mixing to produce hydrogen on demand.

The mobile generator developed for the vehicle program has been shown to produce hydrogen on demand with complete reaction occurring in the reactor volume. Hydrogen production has been measured up to 3 kg/hr. Based on the prototype generator design, an advanced design is anticipated to provide a gravimetric energy density of 3361 Wh/kg and a volumetric energy density of 1954 Wh/l assuming that the water from the fuel cell is condensed and used to produce hydrogen in the hydride reactor.

The cost of hydrogen resulting from the carbo-thermal regeneration of the lithium hydroxide to lithium hydride is estimated to range from $6.04 for carbon costing $50/ton to $11.30 for carbon costing $150/ton. This is competitive with hydrogen produced by natural gas and stored as a liquid.

The chemical hydride slurry approach provides other desirable features. The slurry protects the hydride from accidental contact with moisture in the atmosphere or otherwise. Hydrogen produced by the reaction of the slurry with water can be performed at elevated pressures allowing additional power to be generated from the exhaust hydrogen/steam from the reactor and/or allowing the exhaust hydrogen/steam to be used to pressurize air for a more compact fuel cell. Production of hydrogen at elevated pressures also allows the components of the hydrogen generator to be reduced in size.

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