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ADVANCED CHEMICAL HYDRIDE-BASED HYDROGEN GENERATION/STORAGE SYSTEM FOR FUEL CELL VEHICLES

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Abstract

Because of the inherent advantages of high efficiency, environmental acceptability, and high modularity, fuel cells are potentially attractive power supplies. Worldwide concerns over clean environments have revitalized research efforts on developing fuel cell vehicles (FCV). As a result of intensive research efforts, most of the subsystem technology for FCV's are currently well established. These include: high power density PEM fuel cells, control systems, thermal management technology, and secondary power sources for hybrid operation. For mobile applications, however, supply of hydrogen or fuel for fuel cell operation poses a significant logistic problem.

Currently, various technologies have been considered to provide hydrogen for FCV's. These technologies can be conveniently classified into two categories: (1) onboard fuel processing wherein liquid fuel stored on the vehicle undergoes reformation and subsequent processing to produce hydrogen; and (2) onboard storage of pure hydrogen provided by stationary fuel processing facilities. Onboard liquid hydrocarbon reforming provides an attractive way to supply hydrogen at a high system power density. In high temperature fuel cells, such as solid oxide fuel cells, low molecular weight hydrocarbons may be used directly via direct internal reforming. However, these types of fuel cells are not suitable for fuel cell vehicles, since they may require frequent on/off cycling. Although there has been limited success in direct methanol powered PEM fuel cell technology, the fuel crossover and CO poisoning still pose significant problems, and long term performance is yet to be demonstrated.

Over the last ten years, there have been extensive efforts to develop a reforming process to produce hydrogen from liquid fuels. As a result, numerous hydrocarbon reforming processes have been established. However, the product gas streams usually contain high levels of contaminants, such as CO. The presence of CO in the fuel gas stream is harmful to many fuel cells, especially PEM fuel cells, since the performance of the PEM fuel cell is substantially degraded over a short period of time via the catalyst poisoning. Despite costly efforts, limited success has been achieved to control the CO content in the fuel gas stream. We believe that the conventional approach to reform liquid hydrocarbons to produce hydrogen cannot meet the stringent requirements in fuel quality for the PEM fuel cells.

A great many technologies have also been investigated as candidates for the onboard storage of pure hydrogen for FCV's. These technologies include: (1) compressed hydrogen; (2) liquefied hydrogen; (3) rechargeable metal hydride; (4) carbon adsorption and hybrid systems; and (5) liquid hydrides and other chemical hydrides. However, the volume and/or weight energy densities of these onboard hydrogen storage technologies are significantly lower than those of internal combustion engines or the DOE hydrogen plan. Therefore, development of a high energy density subsystem to supply hydrogen for a fuel cell operation is an urgently needed technology for the successful development of FCV's.

To supply high purity hydrogen for FCV operation, Thermo Power's Advanced Technology Group is developing an advanced hydrogen storage technology. In this approach, a metal hydride/organic slurry is used as the hydrogen carrier and storage media, as shown in Figure 1. At the point of use, high purity hydrogen will be produced by reacting the metal hydride/organic slurry with water. In addition, Thermo Power has conceived the paths for recovery and regeneration of the spent hydride (practically metal hydroxide). The fluid-like nature of the spent hydride/organic slurry will provide us a unique opportunity for pumping, transporting, and storing these materials. The final product of the program will be a user-friendly and relatively high energy storage density hydrogen supply system for fuel cell operation. In addition, the spent hydride can relatively easily be collected at the pumping station and regenerated utilizing renewable sources, such as biomass, natural, or coal, at the central processing plants. Therefore, the entire process will be economically favorable and environmentally friendly.

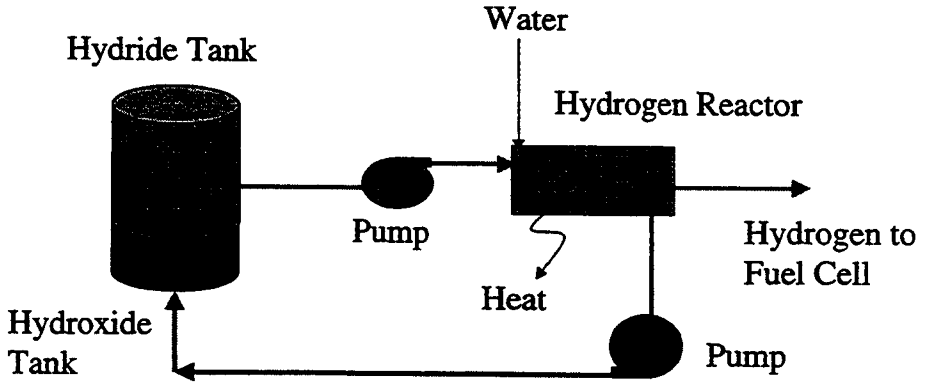

Figure 1. Vehicle Concept

Technology Development Areas

Overall Background and Technical Approach

Hydrogen (H_2) has been suggested as the energy carrier of the future. It is not a primary energy form, but rather serves as an energy carrier through which a primary energy source can be transmitted and utilized. Hydrogen has a number of advantages as an energy carrier, but several problems restricting widespread use of H_2. These include: (1) poor energy storage characteristics; and (2) relatively high production cost compared to fossil fuels. For example, specific weight and specific volume of the most hydrogen storage technologies, currently available and advanced future technologies, are not suitable for transportation applications. Some advanced technologies may satisfy the requirements of the DOE hydrogen plan. However, operational energy loss and infrastructure requirements may not be appropriate for transportation applications in the near future. Pros and cons of the currently available and advanced hydrogen storage technologies, along with expected performance of the proposed technology, are summarized in Table 1. A plot showing how chemically reacting hydrides compare with other fuels is shown in Figure 2.

Table 1. Hydrogen Storage Technology Status

Storage Technology	Specific Weight (HHV)		Specific Volume (HHV)		Remarks
	Wh/kg	%H_2	Wh/L	kg H_2/m^3	
DOE Goal: • Liquid/Gas	3963/5323	9.9/13.4	1100/828	28/21	DE-RA02-97EE50443
Liquid H_2: • Cryogenic	6350	16.1	1250	32	Not including boil-off loss
Gaseous H_2: • 5000 psia	2630	6.7	780	20	Could be better with new high-pressure tanks
Carbon Adsorption: • 794 psi at 78°K	2858	7.2	1535	39	New materials with better capacities
Liquid Hydride: • Methylcyclohexane	2070	5.9	1618	46	Need more fundamental research
Proposed Chemical Hydride Slurry:					Includes weight and volume of the container, and ancillary components. Does not include reactant water which is assumed to be provided partially from exhaust gas
• CaH_2	2670	6.8	2430	62	
• LiH	5050	12.8	2430	62	
• $LiBH_4$	4760	12.1	2570	65	

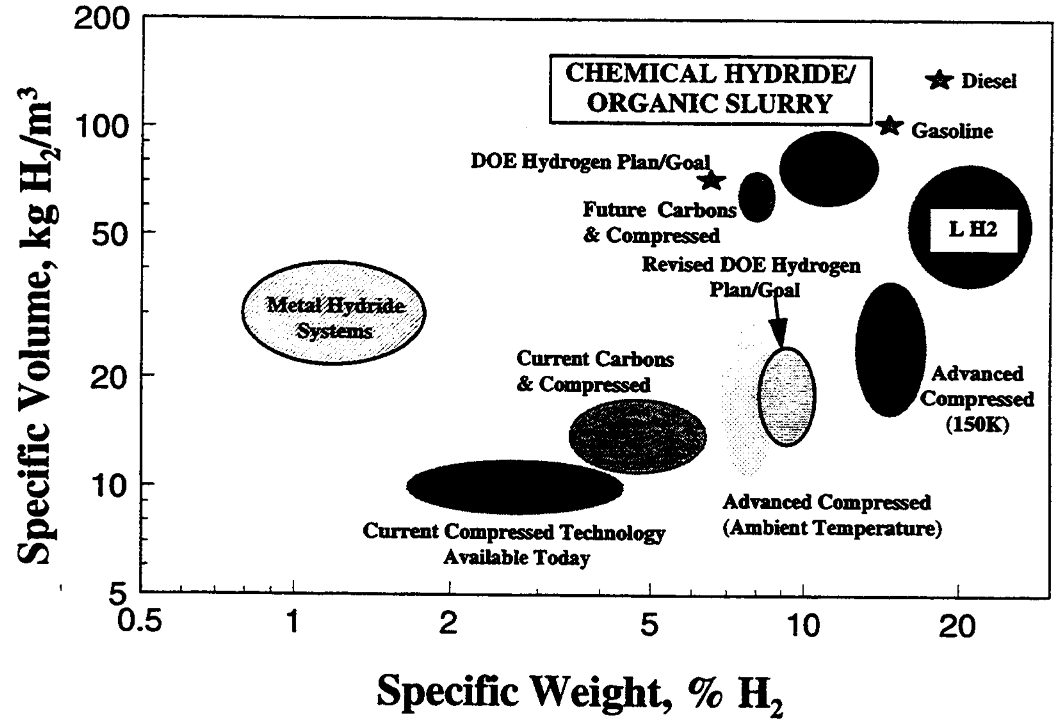

Figure 2. Summary of Current and Future Hydrogen Storage Systems

This new approach greatly improves the energy transmission and storage characteristics of H_2 as a fuel for transportation and industrial applications. An essential feature of the approach is to develop a relatively high energy storage density hydrogen supply system based on exothermic chemical reactions between metal hydrides and water. Hydrogen production via metal hydride and water reactions is a well-established industrial process. In fact, several groups of researchers have investigated the metal hydride/water reaction process to supply hydrogen for fuel cells for mobile power generations. In this research, it has been identified that reaction rate control, frequent on/off operation, and safety of the operation could be significant problems for high energy density operations.

One of the key technical challenges in the program is, therefore, to precisely control the metal hydride and water reaction. In the program, the continuous organic slurry media will act as a path for dissipating heat that is generated from hydride/water reaction. Furthermore, by controlling surface chemistry with the organic media, the water-metal hydride reaction rate can easily be controlled. In addition, Thermo Power has conceived the paths for recovery and regeneration of the spent hydride. Feasibility of the spent hydride regeneration, economical analysis, and engineering design of these processes will be conducted by Thermo Power under different DOE funding.

There are several factors needing consideration in hydride selection and storage system design. As an example, CaH_2 has been selected to illustrate some of the technical aspects and advantages of the concept, even though it does not have the highest volumetric or gravimetric energy density of the hydrides (Table 1). These advantages include low raw stock (calcium hydroxide) material cost, and ready availability of technical information on properties of materials and process reactions. Regarding safety, CaH_2 is highly ionic and insoluble in all common inert solvents. It can be handled in dry air at room temperature without difficulty. Only when heated to about 900°F will it react with air to form both calcium oxide and calcium nitride. CaH_2 is substantially inert to organic compounds that do not contain acidic hydrogen. CaH_2 reacts vigorously with water to form calcium hydroxide and hydrogen gas. Calcium hydroxide is slaked lime and non-hazardous. It is a component of mortar, plaster, cement, and other building materials, and widely used without difficulty.

One method of using hydride/water reactions as a source of pure hydrogen for vehicular applications is to pump a slurry into the vehicle as shown previously in Figure 1. Use of the slurry would permit refueling similar to current gasoline filling stations. The used reactant slurry containing the LiOH for a lithium hydride-based system is pumped out and returned to the fueling station. By providing a flexible bladder in the tank, the original and the spent hydride will never contact each other. In this way, the tank can easily be topped-off at any time.

Once in place, hydrogen will be generated on demand by water flow rate regulation to the reaction chamber. The pure hydrogen will be used in the fuel cell, producing water. This water will be collected and recycled as produced to use for additional hydrogen generation. Only a small water reservoir is thus required to even out surge demands and provide makeup for water lost and not recycled. The required water does not significantly affect the volumetric and gravimetric energy storage densities.

The used reactant slurry containing LiOH is returned to a central processing plant where the LiOH is recycled to LiH in a large scale chemical process. The LiH is remixed with the slurry fluid and transported back to refueling stations scattered over a large area as needed. The basic energy input to the system is provided at the central plant and can be from a variety of energy sources, including fuels like coal, biomass, natural gas, and petroleum oil. All environmental emissions occur at the central processing plant. The vehicle is zero emission, with no hydrocarbon, CO, or CO_2 emissions. The central plant can include more sophisticated emission cleanup processes than would be possible for an on-board processing system.

An important concept feature that needs to be pointed out, which is not part of this proposal effort, is the recovery and recycle of the spent hydride at centralized processing plants using a low cost fuel, such as coal or biomass. This regeneration effort is reported elsewhere and summarized here. The regeneration process analysis has indicated that recycling can be performed utilizing a carbothermal process with minimum energy input and at a low cost. Compared to current hydrogen costs of about $9.00 to $25.00 per million Btu, this concept should enable hydrogen costs of $4.00 per million Btu to be realized (Breault et al, 1998). Also, because the hydride reaction will liberate only pure hydrogen, fuel cell catalyst life should be maximized, resulting in high system performance and reliability.

Anticipated Results and Commercial Potential

At the completion of the proposed program (30 months), DOE will have a prototype system which can supply 3.0 kg/hr of pure hydrogen for fuel cell operation (50 kW electric power equivalent, assuming 50% fuel cell efficiency). This system will include: (1) ports and pump for hydride/organic slurry charge/discharge, a water addition device, a water/hydride reactor, a pressure/temperature measurements and control unit, and a connecting port to fuel cell stack. A race for the development of zero emission vehicles has already begun across the globe. Developing a reliable hydrogen source for fuel cell operation is the most serious technical challenge in developing fuel cell vehicle technology. Thermo Power's advanced metal hydride-based hydrogen supply system will fully satisfy all the requirements for FCV development.

In addition, Thermo Power has conceived the paths for regeneration of the spent hydride utilizing coal, biomass, or by-product hydrogen from other chemical processing. It will practically expand the range of fuel, which can be used efficiently and economically in fuel cells. Considering the abandoned coal reservoirs in the U.S. and the ever-increasing strategic importance of oil from foreign sources, the development of a reliable and adequate domestic energy supply system is vitally important. Thermo Power's proposed system will provide vital technology to efficiently produce and supply high purity hydrogen from non-petroleum based fuels for fuel cell power generation.

Technical Objectives

Thermo Power is developing a prototype, 50 kW electric power equivalent hydrogen supply system utilizing an innovative chemical hydride/organic slurry technology. The program covers a 30-month period which is comprised of two phases. During the first 15-month phase, we will optimize the hydrogen generation efficiency of the proposed process utilizing a laboratory-scale reactor unit (1 kW-equivalent). In the second phase, we will fabricate and evaluate the performance of a prototype hydrogen supply system for 50 kW fuel cell systems. The specific technical objectives are:

- Investigate and select metal hydride and organic slurry materials to achieve maximum specific energy;
- Develop the means for water and hydride in the minimum weight;
- Establish thermal management design for a prototype system including heat dissipation and use;
- Design and fabricate a 50 kW-equivalent prototype system;
- Evaluate and optimize performance of the prototype system; and
- Complete hydrogen supply system integration into simulated power sources and performance evaluation.

Description of Current Activities

The major objectives of this hydrogen storage system development program are twofold. First, we will use a laboratory-scale system to determine optimum materials and hydrogen generation process conditions to achieve high specific energy for hydrogen supply. The second objective will be the design and fabrication of a prototype hydrogen storage capable of supplying 3.0 Kg of high purity hydrogen for fuel cells.

Although there are numerous metal hydrides and organic carrier candidate materials, only a limited number of metal hydrides and organic carrier materials can be used to satisfy DOE's goals of specific weight and volume. One of the essential considerations for the metal hydride will be its hydrogen generation efficiency which include reaction chemistry between metal hydride and water to complete hydrolysis reactions in a safe and controlled manner. The organic carriers should be chemically inert toward metal hydrides and spent hydrides for storing, transporting, and during hydrolysis reaction. These materials also should be easily separated from spent hydrides, either thermally or mechanically, and be recycled for reuse.

In this task, we will thoroughly analyze, both theoretically and experimentally, the reaction chemistry of a variety of metal hydrides and water, and the chemical stability of the organic carriers in contact with metal hydrides and spent hydrides. Since detailed hydrolysis reaction kinetics of the metal hydride/organic carrier slurry is not known, we will conduct these experiments using a high pressure (2000 psi) and high temperature (232°C) vessel with temperature, pressure, and magnetic stirrer control capabilities (500 cm^3 internal volume).

The first requirement for the organic carrier materials is chemical stability of the materials in contact to metal hydrides and spent hydrides. Most hydrides are chemically reactive with aldehydes, ketones, lower aliphatic alcohols, olefins, etc. But they are relatively stable in saturated hydrocarbons and mineral oils. The selected organic carrier materials should have low molecular weight (to achieve high specific weight density), reasonably low melting point (to prevent freezing) and relatively high boiling point (to prevent vaporizing during hydrolysis reaction). Candidate organic carrier materials and their properties are listed in Table 2.

Table 2. Candidate Organic Carrier Materials and Their Properties

Materials	Molecular Weight (g)	Density	Melting Point (°C)	Boiling Point (°C)
Hexane	86.18	0.659	-95	69
Octane	114.23	0.703	-57	126
Nonane	128.26	0.718	-53	151
Decane	142.29	0.73	-30	174
Dodecane	170.34	0.75	-12	216
Mineral oil	-	0.84-0.88	-	>200

Investigate and Select Metal Hydride and Organic Slurry Materials

Organic Carriers

Initially it was thought that the aliphatic hydrocarbons from C6 to C12 (Hexane, Octane, Nonane, Decane, and Dodecane) were desirable candidates for the organic phase of the slurry. Evaporative losses of the organic media during slurry handling or transfer was considered in their suggestion. Compared to current gasoline fuels, even hexane, the lowest boiling candidate, was not dismissed on this basis. (See Figures 3 and 4.)

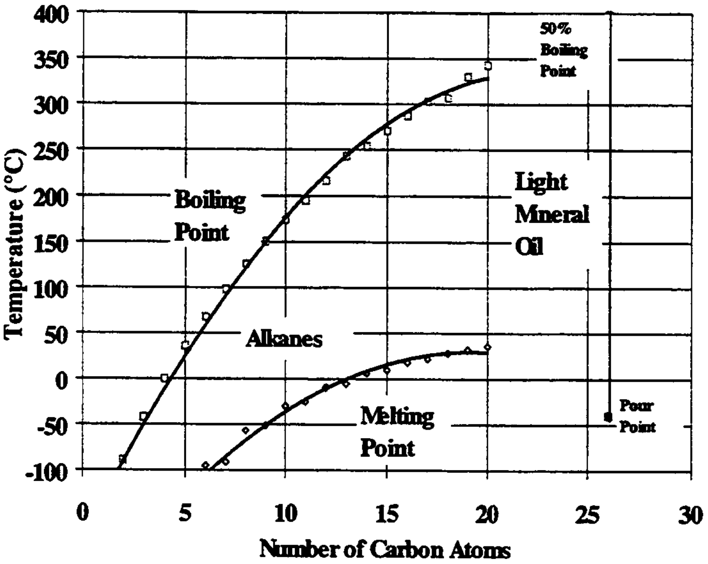

Figure 3. Freezing Point and Boiling Point of Alkanes

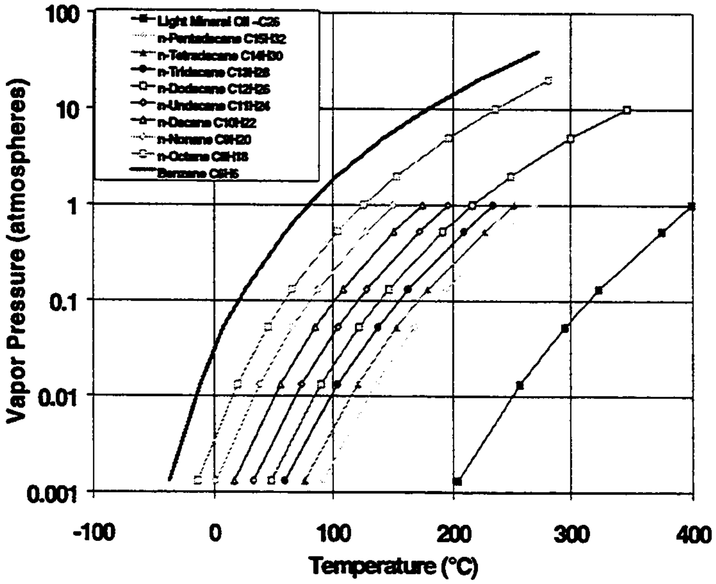

Figure 4. Vapor Pressures of the Alkanes

Experience gained during the testing of many candidate slurry formulations showed that local temperatures within the reaction mass often approach or exceed the boiling points of many of these compounds. More often, it was not the actual boiling, but the increase of vapor pressure of the compounds which presented a risk of hydrocarbon contamination of the hydrogen and subsequent harm to the fuel cell. Early reactions with n-Hexane did boil small amounts of the hydrocarbon.

Therefore, early in the investigation, several mineral oils were used, and the results with these materials were encouraging enough that these materials were pursued for the majority of the slurry tests. At first, some slurries were prepared from heavy mineral oil. Rapid sedimentation of the hydride particles as supplied made the use of the heavier oil necessary. After several appropriate polymeric dispersants were found, it was possible to use the lower viscosity mineral oil as a base for stable slurry formulations. Then, when methods of milling the metal hydrides to obtain finer particle sizes (5-10μ) were applied, experiments to obtain the maximum hydride content for a manageable viscosity were performed.

The mineral oils are generally mixtures of a variety of straight and branched-chain hydrocarbons of a range of molecular weights. Some mineral oils are of napthenic species as well. They are made from the hydrocarbon fractions boiling between 330°C and 390°C . The absence of reactive sites, such as hydroxyls, and stability to high temperatures of short duration are reasons for using these materials. In addition, they have low vapor pressures, so that evaporative losses of the organic carrier or concerns of contamination of the generated hydrogen are nearly nonexistent. In anticipation of future use of the slurry, the nontoxic nature of mineral oils as opposed to some of the lighter paraffins is desirable.

Slurry Physical Stability

The metal hydrides are supplied as a coarse powder, typically 80 Mesh and smaller, with a wide and variable distribution of sizes. Because of differences in polarities and densities, a slurry cannot be successfully prepared by simply mixing the hydride with the oil.

The hydride must be milled to yield smaller particles with higher surface area-to-volume ratios and more predictable size distribution. These particles, ranging from 5-10 microns, may then be sterically stabilized with a polymeric dispersant.

Initially, when slurries were prepared by simply mixing the hydride with the oil, they would sediment in a day or two, into a "Soft Pack". With proper milling in the oil media, slurries are routinely prepared which withstand centrifugation for five minutes at 5,125 G. It requires twenty minutes at this RCF to completely separate the hydride.

Because of the transportation end-use planned, concern had been raised regarding the possibility of continued milling by particle-to-particle attrition caused by sloshing. This effect could result in unmanageably high viscosities after a time. Long-term tests were initiated using a laboratory shaker table, whose sample platform was agitated orbitally in a horizontal plane. The tests have been ongoing since December 1997, and the table has been operated at 120 cycles per minute at a magnitude of 9 mm.

Slurry Chemical Stability

The organic carrier must be stable, and not contaminate the hydrogen generated by the hydrolysis reaction with organic compounds. Ideally, the organic phase will protect the hydride from degradation from atmospheric moisture.

Metal Hydrides:

Sodium Borohydride:

Despite its high hydrogen content to weight and stability, the borohydrides are not suited to slurry systems for vehicular applications. Sodium borohydride does not spontaneously release its hydrogen upon contact with water, and in fact, has been sold in basic water solutions. The addition of a mineral acid, or the use of a catalyst such as cobalt, is needed to release its hydrogen. Acetic acid cannot be used, as it has been reported to generate boranes in these systems. It is imperative for handling and storage safety that the post-reaction products of hydrolysis have been entirely reacted, and will not continue to release hydrogen after being discharged from the automobile or other system.

Lithium Hydride:

Lithium hydride mills easily to produce physically stable slurries. While not having the energy density of the borohydrides, at 15,500 Btu/Lb (HHV/Mass) as lithium borohydride at 22,5600 Btu/Lb, its hydrolysis is a simple reaction which proceeds to completion.

Sodium Hydride:

While having a better energy density than calcium hydride, sodium hydride presents some difficulties with its pH limited reaction. At the high pH values generated by the production of sodium hydroxide, and the formation of saturated sodium hydroxide solutions as the hydrolysis product, an additional reactant such as aluminum is needed to force the reaction to completion. If aluminum is used, the resulting sodium aluminate is not as dangerous or as corrosive to materials and human tissue as the concentrated sodium hydroxide solutions. Calcium and lithium hydroxides are not as soluble as sodium hydroxide, and these hydroxides precipitate when saturation is reached, thereby allowing the hydrolysis reaction to proceed to completion.

Calcium Hydride:

Less desirable from an energy density at 5,850 Btu/Lb, calcium hydride has some benefits. The end product, calcium hydroxide, is a relatively nontoxic and harmless compound. Further, the hydrolysis of calcium hydride appears to be pressure-limited, stalling at approximately 300 psi at some molar ratios with water. Future safety considerations could make calcium hydride attractive in this sense. Calcium hydride requires three times as long to mill into a 5-10 micron slurry as does lithium hydride in an alumina ball mill, but the apparently greater hardness of the particles could address concerns with agitation stability.

Selection and Definition of Formulation To Be Used in Subsequent Tasks

It is anticipated that remaining work will be performed with lithium hydride slurries for several reasons:

1) It has a superior energy density per weight.
2) It reacts to completion, producing a fully depleted and relatively safe end product.
3) The end product, lithium hydride, can be regenerated.
4) It mills readily to produce stable slurry suspensions.

Performance Schedule

The tasks are briefly defined in this section.

Task 1: Investigation and selection of metal hydride and organic carrier materials to achieve high specific energy. Reaction chemistry between metal hydride and water to achieve high hydrogen generation efficiency will be the key technical consideration, completed five months after start of work.

Task 2: Optimization of the hydride/organic slurry configuration, completed nine months after start of work.

Task 3: Development of the hydride/water activation process, completed twelve months after start of work.

Task 4: Establishment of the thermal management design for prototype system, completed fifteen months after start of work.

Task 5: Design and fabrication of the prototype system, completed nineteen months after start of work.

Task 6: Evaluation of the prototype performance, completed twenty four months after start of work.

Task 7: Integration of the hydrogen supply system into operating conditions of simulated fuel cell power source, completed twenty six months after start of work.

Task 8: Testing and performance evaluation of the final system, completed twenty nine months after start of work.

Task 9: Final Report preparation, completed thirty months after start of work.

Summary and Future Activities

From the work conducted thus far, the following results and conclusions can drawn, respectively.

Results:

- Best Organic - Light Mineral Oil
- Best Hydrides -LiH & CaH_2
- +95% Hydrogen Release/Recovery
- Stable slurry produced.
- Polymeric dispersants sterically stabilize the suspension.

Conclusions:

- A chemical hydride slurry can be used to generate hydrogen for transportation vehicle applications.
- The system has the potential to be safe and easy to use.
- Chemical hydride based systems can achieve DOE's energy density goals.

During the next year, the following activities will be conducted:

- Continue the optimization of the hydride/organic slurry composition.
- Development of the hydride/water activation process (hydrogen generation reactor).
- Establishment of the thermal management design for prototype system.

References

"Hydrogen Transmission/Storage With A Metal Hydride/Organic Slurry," Breault, R.W., A.W. McClaine, and J. Rolfe, 1998 DOE Hydrogen Program Technical Review, Washington, D.C., April 28-30, 1998.