III.B.3 Chemical Hydride Slurry for Hydrogen Production and Storage

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Subcontractors:
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Boston University, Boston, MA
Metallurgical Viability, Inc., Newark, DE
HERA Hydrogen Storage Systems, Longueuil, Quebec, Canada

Objectives

- Demonstrate that magnesium hydride slurry can meet the cost, safety, and energy density targets for on-board hydrogen storage of hydrogen-fueled fuel cell vehicles.
  - Develop a stable and pumpable magnesium hydride (MgH_2) slurry with energy density of 3.9 kWh/kg and 4.8 kWh/L.
  - Develop a compact, robust mixing system to produce hydrogen from the slurry and to meet the energy-from-hydrogen targets of 2 kWh/kg and 1.5 kWh/L.
  - Define and assess the capital and operating costs of the recycling system required to make new magnesium hydride slurry from the materials remaining after the hydrolysis of magnesium hydride slurry and water.
    - Separate and recycle the organic compounds from the hydroxide byproduct.
    - Reduce the magnesium hydroxide [$Mg(OH)_2$] to magnesium.
    - Prepare magnesium hydride from magnesium and hydrogen.
    - Prepare magnesium hydride slurry from the magnesium hydride and recycled organics.

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
- G. Life Cycle and Efficiency Analyses
- Q. Regeneration Processes
- R. By-Product Removal

Approach

- Develop MgH_2 slurry.
- Develop slurry/water mixing system for production of hydrogen.
- Define organic recycle process.
- Define MgH_2 production process.
- Perform conceptual designs and economic analyses of four potential $Mg(OH)_2$ reduction processes: $MgCl_2$ electrolytic process, solid-oxide oxygen-ion-conducting membrane (SOM) process, improved Hansgirg carbothermic process, and one promising new Mg reduction process.
- Perform experimental investigation of the SOM process to provide additional data for the evaluation of a large-scale economic analysis of the SOM process.
- Perform experimental investigation of carbothermic process to provide additional data for a large-scale economic analysis of a carbothermic process.
- Reevaluate recycling process costs and recommend future cost reduction opportunities.

Accomplishments

- This is a new project begun in April 2004. Project subcontracts have been negotiated and signed. Subcontractors have begun work.
- Work on the first milestone, “Define Critical Issues of Feasibility”, is nearly complete.
- SOM process researchers at Boston University have reported success with further reductions of the process temperature. This will have the effect of increasing the lifetime of the furnace and thus reducing the operating costs. Energy costs for this process have previously been shown to be 60% of the competing $MgCl_2$ reduction process.
- Government-owned equipment utilized in the initial chemical hydride slurry project has been received, repaired where necessary, and set up.
- Preliminary experiment designs have been completed for the development of MgH_2 slurry.

Future Directions

- Define the composition and characteristics of a MgH_2 slurry and validate through experiments.
- Develop concepts and designs for the mixer system to meet DOE system-level targets.
- Perform system analyses of the carbothermic MgO reduction process, the electrolytic $MgCl_2$ process, and the SOM process to enable accurate estimates of the capital cost and operating costs of very large-scale versions of these processes.
- Evaluate current processes for production of MgH_2.

Introduction

Chemical hydride slurry provides a promising means for storing, transporting, and producing hydrogen. As a pumpable medium, it can be easily moved from tank to tank, can be easily metered and can be transported with the existing liquid fuel infrastructure. The chemical hydride slurry has a high energy density on a materials basis (twice the volumetric energy density of liquid hydrogen and 11.7% hydrogen by mass) and provides significant safety features. The slurry is slow to ignite and is protected from unwanted reaction with ambient moisture by the oil coating on the metal hydride particles. When hydrogen is needed, the chemical hydride slurry is metered into a chemical reaction vessel with water. The reaction between the water and the chemical hydride produces hydrogen. Heat and a hydroxide of the original hydride are byproducts.

$$MgH_2 + 2H_2O \rightarrow Mg(OH)_2 + 2H_2$$
$$\Delta H = -68{,}666 \text{ kJ/kg of } H_2$$

Figure 1. Lithium Hydride Slurry

After shedding hydrogen, the hydroxide slurry is returned to a large recycle plant in the vehicles that originally delivered the hydride slurry. Unlike the delivery of gasoline and diesel fuel, where tanker trucks return empty, the slurry tanker trucks are full in both directions. In the optimal approach, there should be little additional cost to return the hydroxide slurry. At the recycle plant, the hydroxide is separated from the slurry oils, it is reduced to metal, the metal is hydrided to the original chemical hydride, and the chemical hydride is incorporated into new slurry using the original oils. Full cycle efficiency has been estimated to be comparable to or better than that of liquid-hydrogen or compressed-hydrogen production, storage, and delivery systems. In addition to use for on-board vehicular storage, the proposed approach may be even more applicable to off-board storage systems, where there are fewer constraints for the additional weight and volume for the water reactant.

Figure 2. Laboratory Lithium Hydride Slurry Mixer System Mounting in a Hydrogen-Powered Pickup Truck

Previous work, performed by Thermo Power Corporation (Reference 1), demonstrated that LiH slurry is pumpable, easily metered, stable for months, and much easier to handle than dry powders. Figure 1 displays a LiH slurry used in the prior chemical hydride development projects. A simple mixing system was built to demonstrate the capability of producing hydrogen at a wide range of rates sufficient to supply a hydrogen-fueled vehicle. Figure 2 displays the mixing system mounted in the bed of a Ford Ranger pickup truck with its internal combustion engine modified to use hydrogen. Since the slurry is easily metered, the design of the mixing system is dependent only on the maximum rate required and the minimum amount metered. At the conclusion of the project, the assumptions and design criteria were reviewed to determine if they should have been changed. We concluded that the system could be safer if the reaction between the hydride and water proceeded slowly at room temperature; that the use of a cheaper metal would help the technology to be competitive at a smaller scale; and that the byproduct would be safer if it is less caustic (Reference 2). Some additional experiments indicated that MgH_2 could potentially meet these additional design criteria.

Approach

This project has been designed to define the characteristics and costs associated with a MgH_2 slurry system for producing, transporting, and storing hydrogen. The primary application defining the benchmarks is on-board storage and hydrogen generation for fuel cell vehicles. Figure 3 displays the anticipated energy densities and costs of a MgH_2 slurry system and the competing hydrogen storage systems defined by DOE. Slurry technology may

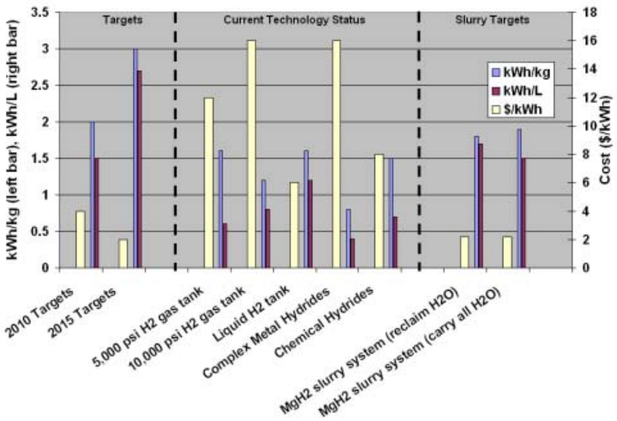

Figure 3. Slurry Anticipated Performance Compared to DOE Technical Targets and DOE Status

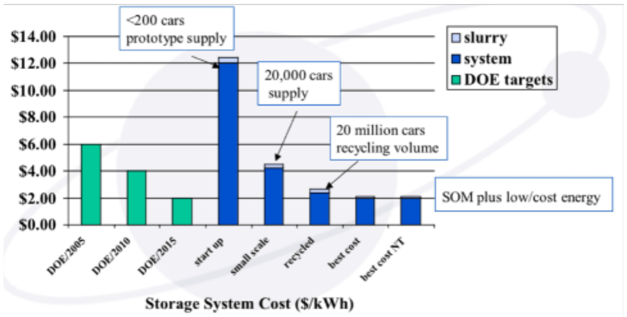

Figure 4. Estimated System Cost vs. Production Scale for MgH_2 Slurry System

also be applied to move hydrogen to the local filling station.

The project is focused on three areas: the development of a stable, pumpable MgH_2 slurry and the design of the process required to make the slurry; the development of a simple, compact, and light mixer system to produce hydrogen from the reaction between MgH_2 and water; and the development and definition of the processes required to recycle the byproducts of the reaction back to MgH_2 slurry. The recycle process involves several steps: the hydroxide must be separated from the slurry oils and reduced to metal; the metal must be hydrided; and the metal hydride must be incorporated into new slurry. Tasks have been defined to address each of the subsystem designs. Each process will be analyzed to estimate the capital and operating costs that are likely to be required for large-scale application of the process.

In the first year, we will perform an analytical comparison of four MgO reduction processes (two commercially demonstrated processes and two promising processes): the $MgCl_2$ electrolysis process; the Hansgirg carbothermic process (Reference 3) with improvements; the SOM process under development by Boston University (References 4 and 5); and an additional process to be determined. Experimental programs are planned to further the development of two promising MgO reduction processes so that the large-scale process can be better modeled. One of these processes, the SOM process, has been demonstrated in the laboratory with energy consumption about 60% that of competing electrolytic processes. The second experimental process is likely to be a carbothermic process, such as the Hansgirg process. Due to the fact that Mg may be an important component of other hydrogen storage approaches (e.g. metal hydrides and Mg-based alloys), the scope of work to reduce magnesium hydride cost may be of relevance to other approaches within the DOE Hydrogen Storage Program. Mg is the sixth most abundant element and widely used for the lightest available structural materials. However, cost is still an issue. Current manufacturing processes will be assessed in relation to the proposed approaches for cost reduction while maintaining required purity levels.

From the results of this project, we expect to be able to compare the cost of hydrogen – as measured at the filling process of a vehicle – using the MgH_2 slurry cycle with other competing cycles. We will also evaluate the use of MgH_2 slurry for infrastructure storage. Preliminary analyses indicate that the MgH_2 slurry cycle should be able to provide hydrogen at a cost competitive with liquid and compressed hydrogen cycles, and with rechargeable metal hydride cycles (see Figures 4 and 5). We also aim to demonstrate the safety and density characteristics of the MgH_2 slurry cycle.

Results

This is a new project. Our agreement with DOE was signed in late March, 2004. Progress has been made in the negotiations with our subcontractors and the design of some of our initial experiments. Subcontracts are in place with three of our four

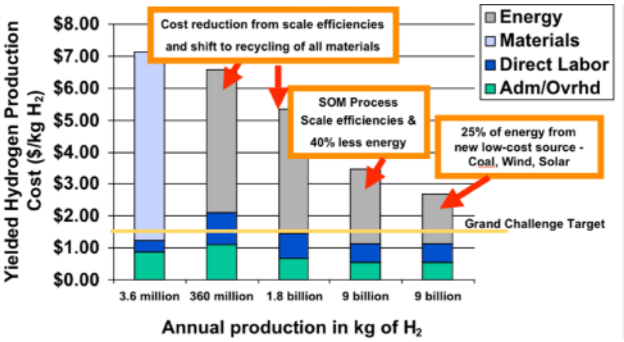

Figure 5. Estimated Cost of Hydrogen vs. Production Scale Using MgH_2 Slurry

subcontractors. DOE-owned equipment used in the prior chemical hydride slurry development program has been installed in the locations where it will be used and repaired as required.

The definition of the critical issues facing MgH_2 slurry is nearly complete. Decisions have been made on the design of experiments for the slurry development and mixer development tasks. A preliminary analysis of the water availability on a fuel cell vehicle, with detailed input from Daimler Chrysler, was completed. The fuel cell requires a large fraction of the water that can be recovered from a 50°C condenser. Much of this water is currently used to hydrate the hydrogen stream entering the fuel cell. Further analysis is planned to determine the advantages of supplying hydrated hydrogen from the storage system. Boston University (BU) has begun experiments toward a 100 gm/day scale system. BU has reported that the process can be operated at temperatures lower than earlier anticipated. This has the effect of increasing the process equipment life and thus reducing operating costs associated with maintenance. Process flow diagrams for the Hansgirg process, the $MgCl_2$ electrolysis process, and the SOM process are in progress.

Conclusions

No conclusions have yet been reached (this project has just started).

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3. Andrew W. McClaine, “Chemical Hydride Slurry for Hydrogen Production and Storage”, 2004 DOE Hydrogen, Fuel Cells & Infrastructure Technologies Program Review, Philadelphia, PA, 25 May 2004