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

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Subcontractors:

- Hatch Technology LLC, Fall River, MA
- Boston University, Boston, MA
- Metallurgical Viability, Inc., Elkton, MD
- HERA Hydrogen Storage Systems, Longueuil, Quebec, Canada

Project Start Date: January 1, 2004
Project End Date: December 31, 2007

Objectives

Demonstrate that magnesium hydride slurry can meet the cost, safety, and energy density targets for on-board hydrogen storage of hydrogen fuel cell vehicles.

- Develop a stable and pumpable magnesium hydride 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 2 kWh/kg and 1.5 kWh/L system targets.
- 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 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) System Weight and Volume
(B) System Cost
(K) System Life-Cycle Assessments
(R) Regeneration Processes

Technical Targets

This project is investigating the capability of magnesium hydride slurry to meet the DOE 2010 hydrogen storage targets

H_2 Storage Target	Target Value	MgH_2 Slurry System Estimate
Gravimetric Energy Capacity	2.0 kWh/kg	1.8 kWh/kg
Volumetric Energy Capacity	1.5 kWh/L	1.7 kWh/L
Price of Hydrogen	$3/kg at the pump	$4.50/kg H_2 at the pump
System Cost	$4/kWh ($133/kg H_2)	No estimate yet

Accomplishments

- Efficiency: While laying the groundwork for achieving a 76% solids loading, we continued working on the rest of the process using MgH_2 slurry with 70% solids loading. This provides a fresh slurry storage capacity of 3.6 kWh/kg and 4.2 kWh/L (capacity based on spent slurry 2.2 kWh/kg and 4.3 kWh/L). Indications are that a 76% solids loading slurry is achievable and continues as our goal. Gains in storage efficiency would provide energy densities of 3.9 kWh/kg and 4.8 kWh/L (capacity based on spent slurry 2.3 kWh/kg and 4.8 kWh/L). Alternate MgH_2 particle size reductions techniques are in progress.
- Improved reaction management and control: Began development of the Model #4 mixer system. Completed preliminary testing of the concepts to be employed. Demonstrated enhanced mixing of slurry and water into the reaction vessel. Reaction rates between slurry and water remain high. Control of the reaction has been enhanced. Design of the mixer system has been completed. System is currently under construction.

- Verification of fluidity in cold temperature ranges: Viscosity measurements of the slurry versus temperature indicate that slurry pumping should perform well to temperatures below 0°C.
- Cost estimation improvements: Based on further analysis, the cost of MgH_2 slurry at the pump is estimated to be \$4.50/kg of hydrogen delivered. This includes a cost of \$3.88/kg H_2 for Mg reduction, \$0.16 for terminal cost, \$0.20 for transportation costs (200 km round trip), and \$0.24 for forecourt costs.
- Regeneration cost: Solid-oxide oxygen-ion-conducting membrane (SOM) process development has focused on the design of a multi-tube design to confirm the process design concept used in the scale-up cost studies. The experimental apparatus is currently being modified and testing is scheduled to begin later this summer.

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Introduction

Magnesium hydride slurry provides a means of transporting, storing, and producing hydrogen in a single system. The slurry will be produced in large-scale production facilities to take advantage of economies of scale and to minimize the cost of producing the slurry. The slurry will be transported using the existing liquid fuels infrastructure including tank trucks on the roads, tank cars on the rails, and barges on water to minimize the cost of transportation. The slurry is pumpable and stable for weeks to months. This minimizes the cost of hydrogen. When hydrogen is needed, the slurry is mixed with water. Two moles of hydrogen are produced for each mole of MgH_2 in the slurry. The chemical relationship is $MgH_2 + 2H_2O = Mg(OH)_2 + 2H_2$. The slurry can be used to produce hydrogen at a consumer station or on-board a vehicle. The oils of the slurry protect the MgH_2 from inadvertent contact with moisture in the air and the MgH_2 reacts very slowly at room temperatures, so it is relatively safe to handle and can be handled in the air. The byproduct is "Milk of Magnesia" and it also is relatively benign.

This project has been underway for about three years. At this time, we have produced stable MgH_2 slurry that remains in suspension for weeks to months. We are developing a mixing system to release the hydrogen and have demonstrated continuous operation for several hours with no external heat addition except at the beginning of the test. We have been evaluating the recycling of the byproduct. Using the SOM process under development by Boston University (BU), we have estimated that hydrogen could be supplied, in a mature large-scale system, for about \$4.50/kg of H_2 at the pump. We have also been evaluating the recycling of the oils from the byproducts and the production of MgH_2 from recycled magnesium. Our current estimates for system weight and volume compare quite favorably with all other hydrogen storage technologies (1.8 kWh/kg [5.3%H_2], and 1.7 kWh/L [52g/L]).

Approach

The approach used in the project has been to evaluate the showstopper issues first and then to develop the slurry, the mixer, and the recycle processes in successively greater detail. Significant attention is being paid to estimating the cost of hydrogen resulting from this process. The process involves the production of MgH_2 slurry, the transportation and distribution of that slurry, the production of hydrogen on-board or off-board, the return of the byproduct, and the recycling of the byproduct back to high energy capacity slurry. Recycling involves the separation of the oils from the byproduct for reuse, the calcination of $Mg(OH)_2$ to MgO, the reduction of MgO to Mg, the hydriding of Mg and H_2 to MgH_2, and the production of new slurry from the MgH_2. Tasks have been included in the project for slurry exploration and development, mixer system development, recycling oil byproduct, recycling magnesium hydroxide byproduct, hydriding the magnesium, and estimating the costs of the processes. An experimental task is directed at evaluating a promising technology under development at Boston University to electrolytically convert MgO to Mg.

Results

During the past year, we have focused on storage efficiency improvement, confirming functional slurry flow in low temperatures, regeneration cost reduction, and improved management of the hydrogen release from the slurry. Efficiency was addressed by increasing the solids loading of the slurry. Viscosity confirmation was established by precise measurement of the fluid characteristics of the slurry over the temperature range of interest. Improved reaction management was addressed by exploring several concepts for an improved mixer system. Based on results a new system has been designed and is now under construction.

To reduce regeneration costs, focus has been on the BU SOM system. Unfortunately, the the delays in funding delayed some of the work until April 2007. BU is currently preparing to experiment with a 3 tube SOM process this summer.

To improve volumetric and gravimetric values we have explored the use of bi-modal size distributions to increase the solids loading of the slurry. We observed increased settling rates when we mixed as-received MgH_2 powder with milled powder. The 70% solids loading material was prepared from MgH_2 powder that was milled dry in a roller mill. Recently, we have been exploring wet milling options. Wet milling may help to reduce production costs by simplifying the handling of the magnesium hydride powder. A 76% solids loading will provide an 8.5% improvement in gravimetric and a 12.5% improvement in volumetric energy density of the slurry. When the mass and volume of the water and system are included the improvement resulting from slurry solids loading is expected to be about 5%.

To verify fluidity at low temperatures we measured the slurry viscosity versus temperature over the range of interest. Figure 1 displays the viscosity measurements. We found that when we changed the turning speed on the Brookfield Model LVDVE115 viscometer, the measured viscosity changed at comparable temperatures. The data shown at the top of the chart was taken at a low turning speed. This indicates that the slurry is non-Newtonian and that it exhibits shear-thinning characteristics. The slurry has a viscosity at room temperature similar to thick paint as shown in Figure 2. Future work will demonstrate how the pump is able to move the slurry around as the temperature of the slurry is varied. The viscosity data indicates that the pumping system should be able to handle the slurry until its temperature is below 0°C.

The new designed Model #4 mixer system will enable improved reaction management and demonstrate all the characteristics of a full-scale system. Slurry and water will be pumped from storage tanks into a mixer system. The slurry and water mixture will be reacted in a reactor and the generated hydrogen will be collected in a buffer volume. The pressure in the buffer volume will be used to control the production of hydrogen in the reaction vessel. When the pressure drops below a low set point, hydrogen production will be started. When it increases above a high set point, the production will be stopped.

Figure 3 displays the experimental apparatus used to test the mixer and pumps that will be used in the new mixer system. Two piston pumps were used to pump slurry and water through a mixing system that produces an emulsion. The emulsion then enters the reaction vessel where hydrogen is produced. Figure 4 displays the mixer system under construction. The system is intentionally designed in a planar form to aid in the maintenance and modification of the experimental system. The system can be reconfigured to minimize volume. In addition, the valving system has been designed for flexibility of operation while we learn how best to operate this system. An advanced system is expected to use valve blocks to minimize the amount of mass and volume required for the valves.

Better regeneration cost estimates can only be based on larger scale testing of the SOM process. Consequently, BU work has focused on the design and evaluation of a three tube SOM system for reducing MgO to Mg. The system will employ three tubes all of the scale of the single tube system employed in the past experiments. Modeling has been performed of the electrical connections to aid in the selection of the positions of tubes and support equipment.

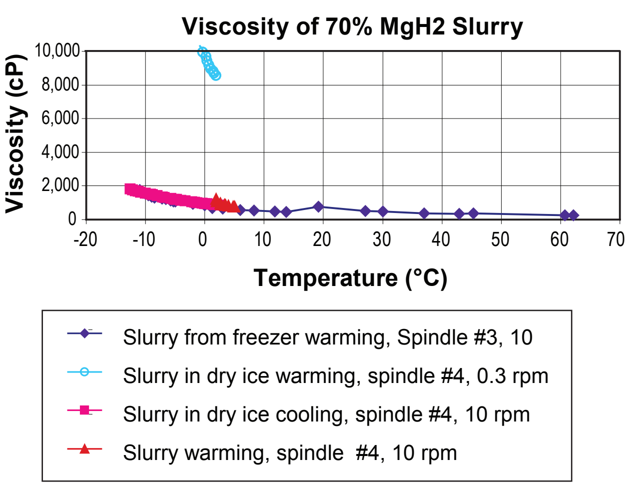

FIGURE 1. Slurry Viscosity vs. Temperature

FIGURE 2. 70% MgH_2 Slurry Made From Milled Particles

FIGURE 3. Experimental Apparatus Used to Test Concepts For Model #4 Mixer System

FIGURE 4. Model #4 MgH_2 Slurry Mixer Apparatus

Conclusions and Future Directions

During the past year, we have focused our attention on cost estimation improvement, cost reduction of yielded hydrogen, and laying the ground work for volumetric and gravimetric value improvements. Also, initial work was completed to insure functionality of the slurry at low temperatures.

These issues were addressed by further development of the slurry, the mixer, and the economics of the system. Our conclusions are that the magnesium hydride slurry system remains a viable option for the production, transportation, and storage of hydrogen. The anticipated values for gravimetric and volumetric energy density compare favorably with all the competing technologies. In addition, the use of magnesium hydride slurry offers considerable safety and handling advantages that will make it a very promising mass-market fuel. We anticipate that systems built using magnesium hydride slurry will be able to meet the 2010 DOE targets for volumetric energy density and almost meet the gravimetric energy density target. We have estimated that the cost of hydrogen from the system should be about \$4.50/kg H_2 for a mature large-scale implementation of the technology. We have demonstrated 70% solids loading in MgH_2 slurry, which is close to the 76% target we estimated at the beginning of the project. We have demonstrated the rapid reaction between MgH_2 slurry and water, and the continuous operation of a mixer system. We have demonstrated oil recovery from the byproducts and the production of magnesium hydride from magnesium powder and hydrogen using magnesium hydride powder as a catalyst.

During the next year, we will be completing the work planned for this project. We plan to:

- Complete the fabrication and testing of the Model #4 mixer system using lighter and lower cost pumps and demonstrating an approach to byproduct handling.
- Perform slurry/mixer testing to demonstrate the laboratory mixer and slurry robustness, and the hydrogen purity.
- Complete the cost estimates of the oil recycle process and the magnesium hydriding process to improve the system cost analysis.
- Perform experiments with a three-tube SOM process and to improve the cost analysis of the system.
- Evaluate process cost reduction options.

FY 2007 Publications/Presentations

1. Kenneth Brown, "Materials for the Hydrogen Economy", Presentation to the Summer School of University of Iceland, Reykjavik, June, 2006.

2. Tullmann, Sigmar, "Enabling Hydrogen Energy", Maine Hydrogen Center General Meeting, October 10, 2006, Brunswick, Maine.

3. Uday B. Pal, Rachel DeLucas and Andrew McClaine, "Cost-Effective Magnesium Oxide Recycling and Economic Viability of Magnesium Hydride Slurry Technology for Hydrogen Storage", SOHN International Symposium on

Advanced Processing of Metals and Materials: Principles, Technologies, and Industrial Practice, August 27–31, 2006, San Diego, CA.

4. Uday Bhanu Pal, Rachel De Lucas, Guoshen Ye, and Marko Suput, "Magnesium Extraction from Magnesium Oxide Using SOM Process", SOHN International Symposium on Advanced Processing of Metals and Materials: Principles, Technologies, and Industrial Practice, August 27-31, 2006, San Diego, CA.

5. Sigmar Tullmann, "Status of Hydrogen Fueled Vehicles", Massachusetts Hydrogen Coalition and TIE joint meeting, January 10, 2007, Waltham, MA.

6. Andrew W. McClaine, "Chemical Hydride Slurry for Hydrogen Production and Storage", 2007 DOE Hydrogen, Fuel Cells & Infrastructure Technologies Program Review, Arlington, VA, 16 May 2006.