

VI.B Chemical Hydrides

VI.B.1 Low Cost, Off-Board Regeneration of Sodium Borohydride

Ying Wu (Primary Contact), Michael T. Kelly and Jeffrey V. Ortega
Millennium Cell Inc.
1 Industrial Way West, Building E
Eatontown, NJ 07724
Phone: (732) 544-5718; Fax: (732) 542-2846; E-mail: wu@millenniumcell.com

DOE Technology Development Manager: Grace Ordaz
Phone: (202) 586-8350; Fax: (202) 586-9811; E-mail: Grace.Ordaz@ee.doe.gov

DOE Project Officer: Jim Alkire
Phone: (303) 275-4795; Fax: (303) 275-4753; E-mail: James.Alkire@go.doe.gov

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Subcontractor:
Air Products and Chemicals Incorporated, Allentown, PA

Start Date: November 1, 2003
Projected End Date: December 31, 2006

Objectives

- Develop an electrolysis-based process for the reduction of borates to borohydrides in order to meet cost targets
- Conduct experimental and economic analyses to select the most cost effective option and enable the demonstration of a prototype in year three

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:

- C. Efficiency
- G. System Life Cycle Assessments
- R. Regeneration Processes
- S. By-Product/Spent Material Removal

Technical Targets

The project objective is to study new syntheses of sodium borohydride or its precursors. Knowledge gained from these studies will be applied to updating, modifying, and replacing various steps of the current borohydride synthesis methodology, with an emphasis on process performance improvement, especially in the areas of fuel cost, energy efficiency, and minimizing greenhouse gas emissions.

Approach

The borohydride molecule can serve as either a hydrogen storage medium or as a precursor to other hydrogen storage species such as boron-nitrogen compounds, or boron-doped metal hydride reversible systems. Synthesis of boron-hydrogen bonded structures is thus taking on an increasingly central role in the chemical hydride and reversible hydride storage methods. At the present time, however, there are no cost effective techniques for making commodity-scale chemical hydrides. We believe that new or improved electrolytic methods of manufacturing chemical hydrides are the most likely to result in substantial cost savings over present methods. The approach employed in the first year of this contract was to survey a number of possible electrolytic pathways to show that:

- Borates can be reduced to boron hydrides in a single electrolytic step
- The raw material (sodium) for making borohydride could be produced much more efficiently than previously thought
- Sodium borate spent materials from borohydride hydrolysis could be conveniently reprocessed into starting materials for making borohydride

All three pathways showed excellent progress over the first year. Regarding the first pathway, borates were reduced to BH_4^- in a molten salt medium, and the presence of BH_4^- was demonstrated by nuclear magnetic resonance (NMR) spectroscopy. In our knowledge, this is the first example of a one-pot electrolysis process leading from borate to borohydride that has been verified by spectroscopic observation of the product. An NMR spectrum of BH_4^- ions generated from B_2O_3 in a molten halide melt is shown in Figure 1. More detailed reports on this reaction can be found in Millenium Cell, Inc. (MCEL) quarterly reports dated October 31, 2005 and January 31, 2005. Progress along the second pathway came from two results. The first is that sodium can be manufactured from molten NaOH using about only 20-30% of the electricity required to produce the same amount of the metal from NaCl. Secondly, sodium can also be manufactured from *aqueous* NaOH, lowering the cost of the sodium raw material and allowing the convenient recycle of sodium hydroxide generated as a byproduct of NaBH_4 manufacturing. The third pathway saw the efficient separation of sodium borate into boric acid and sodium hydroxide. The boric acid is a raw material for sodium borohydride production, so this separation represents a key step in regeneration of hydrolysis byproduct into new hydride material. Figure 2 shows how NMR was used to monitor the progress and efficiency of a separation.

The substantial amount of data collected on the reaction yield and reaction efficiency in the improved Na process allowed us to carry out an initial assessment of energy efficiency. The amount of initial energy input, both in the form of electricity and natural gas, was compared to the amount of stored hydrogen delivered on board. This energy efficiency obtained was in the range of 50-60%. Coupled with an assumed 50% fuel cell efficiency, we have a very encouraging estimate of the well-to-wheels efficiency of 25-30%. More details on this analysis can be found in MCEL quarterly reported dated October 31, 2004.

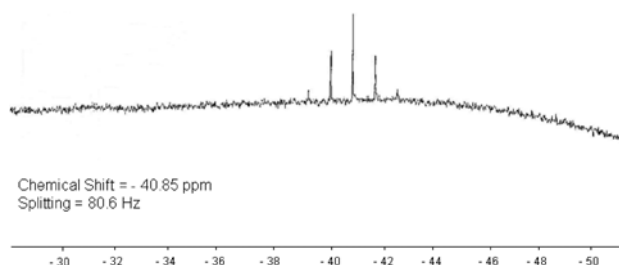


Figure 1. ^{11}B NMR of a Borohydride Ion Synthesized from B_2O_3 and H_2 in a One-Pot Electrolytic Reaction (The quintet with 1:4:6:4:1 intensity is characteristic of the boron nucleus split four times by equivalent protons.)

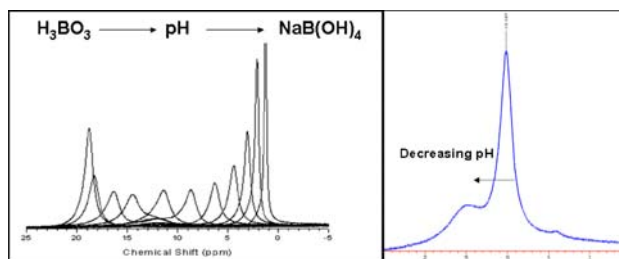


Figure 2. ^{11}B NMR Showing the Conversion of Sodium Metaborate to Boric Acid (The left hand traces are standard mixtures of boric acid and sodium metaborate, and the right hand trace is a sample of sodium metaborate that has been partially converted into boric acid and sodium hydroxide by electrolysis.)

Furthermore, research on systems incorporating electrocatalytic hydrides in organic media were also investigated in detail. However, our attempts failed to conclusively demonstrate the production of borohydride in significant quantities despite some observed activity. More details on this analysis can be found in MCEL quarterly reports dated October 31, 2004 and January 31, 2005.

A down selection process from among the three pathways was scheduled for the end of year one. The down selection was made difficult by the strong progress made in all three areas. The sodium production project was chosen for continuation in year two and three of the contract. The contract calls for a small-scale demonstration unit in year three, and as important a breakthrough as the one pot synthesis is, this brand new reaction will not be ready for a demonstration unit in less than two years. The sodium project has the advantage of being readily incorporated into the current borohydride synthesis methodology. This allows for a reasonable projection of the economic impact of the new method, and thus the initial forecast that a factor of three reduction in the price of sodium borohydride is possible. The recycling of sodium metaborate material into starting material is to be incorporated into the sodium synthesis effort, as it appears that the method of generating sodium metal from aqueous sodium hydroxide will be applicable to aqueous borate solutions as well.

Following the down select, year two progress will be toward a better economic understanding of the improved sodium process, as well as preparing to build a demonstration scale production unit. In the laboratory, the sodium metal from aqueous sodium hydroxide method will be modified to affect a separation of sodium metaborate into boric acid and sodium metal.

Accomplishments

- Demonstrated a highly efficient Na production process that will lower NaBH₄ production cost by a factor of ~ 3, from an estimated \$18/kg to less than \$7/kg
- Achieved a one-pot synthesis of NaBH₄ from borate starting materials. Product was positively identified by a number of analytical techniques including NMR and titrametric determination
- Demonstrated feasibility of Na metal synthesis from inexpensive, recycled, aqueous NaOH
- Showed the efficient recycling of borohydride hydrolysis byproduct (sodium metaborate) into boric acid, the preferred borate for borohydride synthesis
- Developed a number of NMR, infrared methods for the characterization and quantitative determination of NaBH₄ and other boron-containing compounds

Patents

Several patent applications were filed, and reported to DOE as a result of last year's work:

- "Synthesis of Borohydride in Halide Melt"
- "Process for the Production of Alkali Metals in Stacked Electrolytic Cells"
- "Electrolytic Process for the Separation of Boron and Sodium"
- "Synthesis of Boron Hydrides in Ionic Liquids"