

IV.B.1 Process for Regeneration of Sodium Borate to Sodium Borohydride for Use as a Hydrogen Storage Source

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Objectives

- The primary objective is to develop low-cost pathways to sodium borohydride (NaBH_4) in order to meet cost targets.
- Two general approaches are being undertaken: (a) lower the cost of sodium metal substantially, which contributes to over 60% of the NaBH_4 production cost, (b) develop a direct electrolytic reduction of borate to borohydride (B-O to B-H).
- It is also the objective of this project to conduct preliminary engineering and economic analyses to select the most cost effective option and enable the demonstration of a laboratory prototype in the final year of the project.

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:

- (B) System Cost
- (C) Efficiency

- (K) System Life-Cycle Assessments
- (R) Regeneration Processes
- (S) By-Product/Spent Material Removal

Technical Targets

Current manufacturing practice and the accepted market price of NaBH_4 give rise to an equivalent hydrogen cost in the range of \$188-259/kg H_2 . Regeneration and spent material management are key aspects of the electrochemical syntheses. Efficiency is being evaluated through reaction engineering assessment. Several interim cost targets have been set, leading to the final target of meeting DOE's \$2-3/kg H_2 goal.

- Interim Target 1: Improved Na Electrolysis Yields \$50/kg H_2 via \$10/kg NaBH_4
- Interim Target 2: Incorporation of Waste Material Recycling: \$2/kg NaBH_4 and \$10/kg H_2
- Interim Target 3: One-Pot Electrochemical Method: \$1/kg NaBH_4 and \$5/kg H_2

Accomplishments

- Demonstrated the feasibility of reducing NaBH_4 manufacturing cost and projected cost reduction by a factor of three through a more efficient and less costly Na production process. Future cost models were generated based on the 2004 and 2005 findings that map out the cost reduction pathway to DOE goals.
- Demonstrated that sodium metal can be manufactured from aqueous solutions of NaBO_2 , $\text{Na}_2\text{B}_4\text{O}_7$, "spent fuel" from the Hydrogen on Demand[®] process, and other sources of sodium ions in a fashion similar to the synthesis of sodium from NaOH. This demonstration indicates that all necessary sodium and boron for the Schlesinger process can be obtained from recycled products (NaBO_2 and spent fuel) and byproducts (NaOH) of the process itself.
- A current density of 100 mA/cm² at 4 V for Na generation from NaOH was obtained. This value is sufficient for manufacturing-scale production.
- Designed a reactor to carry out NaOH to Na metal synthesis on a scale of 1 kg/day. Included in the design is the set-up to hold the reactor, manage the reagents and products and provide for operator safety in the event of direct contact between reagents and products.

- The reaction of lithium hydride with borate species in various ionic liquids has been shown to yield borohydride product, at temperatures ranging from room temperature to 100°C. This result strengthens our expectation that borohydride will be synthesized directly from various borates and hydrogen via electrolysis in ionic liquid media.

Introduction

On the basis of weight, volume, and performance hydrogen storage systems based on NaBH_4 hydrolysis are among the most promising systems constructed to date. The high relative cost of NaBH_4 , however, makes its use prohibitively expensive for automotive applications. The purpose of this project has been to address this cost barrier, through energy, materials, and process improvements. The work completed to date shows that with sufficient continuing research, the cost of NaBH_4 may be lowered by as much as a factor of 40 (Figure 1). This cost reduction would render the purchase price of the NaBH_4 adequately low for the American consumer to employ the H_2 generated from it in general transportation applications.

Approach

Two parallel routes toward achieving a low-cost process for the synthesis of NaBH_4 have been pursued during this project: (1) use of the traditional Schlesinger route, except with the employment of a lower cost sodium source from a herein devised novel electrochemical process, and (2) an electrochemical reduction of a boron-oxygen (B-O) species with an electrochemically generated hydride or with hydrogen used directly as a co-reactant.

Sodium metal accounts for about two-thirds of the cost in the manufacturing of NaBH_4 , as well as most of the energy input. In the context of the Schlesinger process, sodium would be generated from the Schlesinger NaOH by-product, which provides about 75% of the sodium raw material. Current efforts also include extending the sodium recycling technology from sodium hydroxide to sodium borate. Sodium borate contains the remaining 25% of the needed sodium to make sodium borohydride. Between sodium hydroxide and sodium borate, 100% of the necessary sodium and boron needed to make sodium borohydride comes from recycled chemicals.

The second approach is an attempt to arrive at sodium borohydride by an electrochemical process that transforms B-O species to B-H species. We have attempted to do this by a cathodic reduction of neutral borate species in a melt. Demonstration has taken place

in halide melts, and additional work is being carried out in low-melting ionic liquids.

Results

Cost Reduction. The most significant result of the last year has been the refinement of NaBH_4 cost predictions, summarized in Figure 1. Building on last year's breakthrough of manufacturing Na metal from aqueous (aq.) NaOH , this year's laboratory results for NaOH electrolysis have shown near quantitative current efficiency, meaning that every mole of electrons converts one mole of sodium ions into one mole of Na metal. For example, a sodium generation run began with 1.0567 g of Na acting as the cathode. A constant potential was applied until 1173.7 mAh of current passed through the cell. In theory, 1173.7 mAh of current will generate an additional 1.0068 g of Na. After the run, the weight of the sodium increased to 2.0491 g, a net of 0.9924 g of Na, representing a current efficiency of 99%. In many runs, the sodium was also hydrolyzed to H_2 , which was collected and quantified. Hydrolysis data and weight data show excellent agreement, further verifying the results.

Through engineering assessments, economic analysis, and process modeling this breakthrough has been used to make a reliable estimate regarding the future cost of Na manufacturing, and by extension, the future cost of NaBH_4 . This year it was shown that various sodium borate minerals and/or the borate products of the hydrogen generation reaction could be recycled into new sodium metal with the simultaneous enrichment of the boron value in the remaining material. This process was submitted to analyses similar to

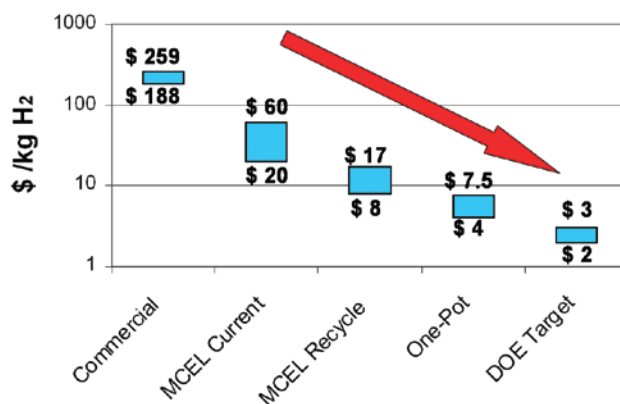


FIGURE 1. Cost reduction pathway for H_2 obtained from NaBH_4 . The left most price range is for today's commercially available product. The Millennium Cell, Inc. (MCEL) Current estimate employs the technology developed in this project. The MCEL Recycle employs the same technology, and recycled process products. One Pot is a best-case forecast of the single chamber electrochemical synthesis. The scale is logarithmic.

the ones outlined for Na metal from NaOH, further developing future price models for NaBH₄. Additional information on the NaBO₂ recycle is included in the following.

The knowledge gained regarding electrochemical plant engineering was also applied to a “best-case” scenario regarding the one-pot synthesis of borohydride ions in high temperature melts and room temperature ionic liquids. This led to an estimation of the possible price of NaBH₄ synthesized by this new method, should the method have the same mass and electrochemical efficiencies already demonstrated for the sodium synthesis. All of these models are compared to the DOE goal for hydrogen cost, and used to generate a roadmap (Figure 1) showing the steps from today’s NaBH₄ cost structure to the future use of NaBH₄ as a H₂ storage medium for transportation applications. Additional information on the one-pot synthesis is included in the following.

In addition to the cost models, the engineering analysis generated important results that continue to guide current research and resulted in the following observations. 1) Electricity is likely to be a less expensive utility than hydrogen gas from methane for the plant. 2) The operating cost of the plant is dominated by electricity usage and this cost appears to be more important than the capital cost of the membrane material. 3) The current density requirement is likely to be in the range of 100 mA/cm². The key assumption in this assertion is that the membrane does not need to be replaced too frequently. The actual current density that optimizes the balance between membrane lifetime and electrolyzer cost remains to be determined. Because of this, a major portion of the research this past year was directed towards determining membrane characteristics such as current density and stability.

Sodium Metaborate Recycle. To fully recycle NaBH₄ from its synthesis byproducts and hydrolysis products, borate must be converted to sodium and boric acid. This year it was shown that this conversion can be carried out in a cell similar to the one used to synthesize Na metal from NaOH. A schematic drawing of the NaBH₄ synthesis process employing both NaOH and NaBO₂ recycle is shown in Figure 2. Implementation of this recycling process advances the cost goal from the current status bar of Figure 1 to the recycle bar in Figure 1, and indicates a cost improvement from today’s price of NaBH₄ by more than a factor of 10.

Current Density and Membrane Performance. At the heart of the sodium synthesis cell for either NaOH or NaBO₂ recycle lies the sodium β⁺-alumina (Sβ⁺A) membrane. The Sβ⁺A membrane can be modified to obtain a solid state sodium ion conductor with different physical properties. The performance of a standard sodium β⁺-alumina (s-Sβ⁺A) was compared

against the performance of a modified sodium β⁺-alumina (m-Sβ⁺A). Current density measurements for molten NaBO₂·4H₂O (melting point ~60°C) at about 120°C show that the maximum current density is achieved with m-Sβ⁺A membranes rather than s-Sβ⁺A. The current density for NaBO₂ at 66 mA/cm², is lower than in the sodium hydroxide (100 mA/cm²) using the m-Sβ⁺A membranes. Figure 3 shows a comparison of three different concentrations of hydroxide with three similar concentrations of borate. There are a number of factors that can contribute to the lower current density. Important among these factors are the intrinsically lower ionic conductivity of NaBO₂·4H₂O compared to NaOH, and the fact that electrolyte is essentially lost when NaBO₂ converts into Na and B(OH)₃. However, while there was a difference in the current densities, there was no difference in the current efficiencies for all of the borate and hydroxide melts which were greater than 99% utilizing the alumina membranes.

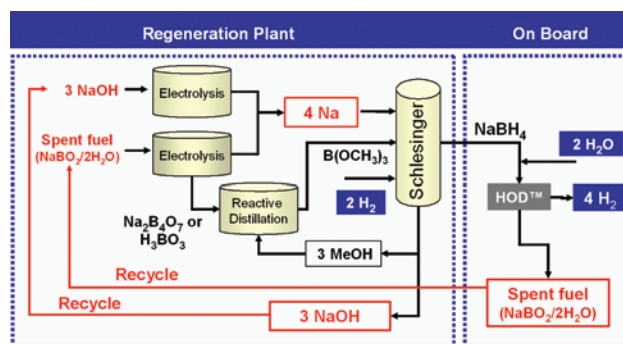


FIGURE 2. Process schematic for recycling all sodium and borate products back into NaBH₄. Three sodium atoms come from recycled NaOH and the fourth comes from recycled NaBO₂. Boric acid is also obtained from recycled NaBO₂.

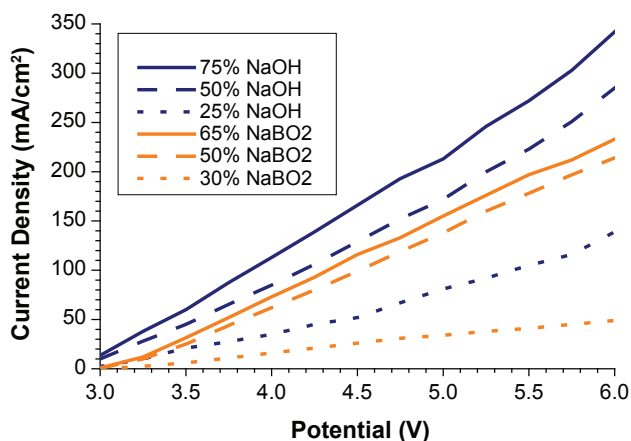


FIGURE 3. Current density behavior for different aqueous solutions of hydroxide and borate with respect to applied potential.

A second important parameter for the scaling up of sodium syntheses from either the NaOH (aq.) or NaBO₂ (aq.) is the membrane lifetime. Sodium synthesis from NaBO₂ preserves the membrane for a substantially longer time compared with extracting sodium from NaOH. The most preferable scenario is that the membrane can perform for a year or longer. In NaOH solutions the performance lifetime is far short of that time frame, and is an area of continuing research. The reason for membrane failure has not yet been determined. It is not simply a chemical break down, as molten NaOH does not damage the membrane. However, in 50% NaOH evidence of membrane degradation can be observed after a single use. The mechanism of membrane degradation is likely associated with NaOH, water, and the passage of current. Exposure to steam can also be problematic. In molten NaBO₂·4H₂O, which is 47% NaBO₂ by weight, different behavior is seen even though a solution such as this one is reasonably basic. No visual evidence of membrane damage is observed after use. The lifetime of the membrane remains unknown, but appears substantially longer than the same membrane in hydroxide solutions.

Reactor design: 1 kg Na/day. Sodium hydroxide was chosen for the initial modeling and demonstration scale project because it represents 75% of the sodium value needed to make NaBH₄. Further, as NaOH is a byproduct of the borohydride synthesis, it is already present in the NaBH₄ manufacturing facility. Finally, most of the engineering done for hydroxide cells will be directly applicable to cells employed to make Na metal from NaBO₂.

All of the components of the sodium synthesis reactor have been modeled using AspenTech HYSYS. The materials compatibility testing efforts are currently underway. Selection of processing equipment is in progress. Construction of this pilot plant will commence in the latter half of calendar year 2006. A scale of 1 kg/day of sodium was selected as first trial in the prototype demonstration process to commercialization. The cells are currently engineered to be stackable, meaning that to increase sodium production one only needs to put additional cells together (either in series or in parallel). Each cell will be capable of generating approximately 1 kg of sodium per day. For the initial stage only one cell will be operated, to be carried out in a dedicated fume hood facility diagrammed in Figure 4, designed specifically to handle the hazards associated with bringing together sodium metal and aqueous solutions. The cell itself is expected to be in its own sub-enclosure, which will contain a nitrogen atmosphere. The nitrogen will prevent ignition of any hydrogen-oxygen mixture that might form were the cell in an air environment. The hood has its own fire suppression system, which consists of extinguishers suitable for Class D fires.

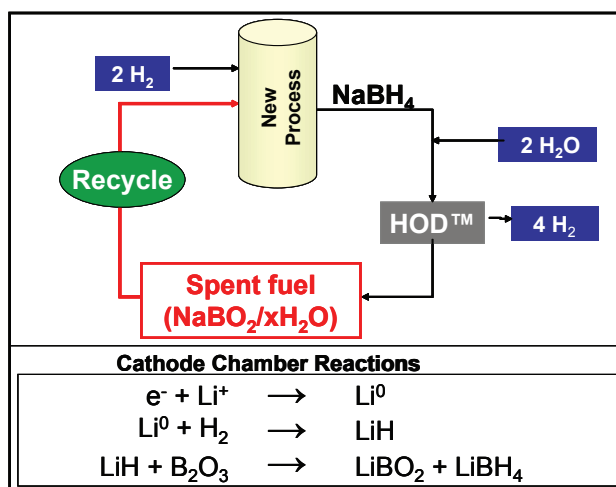


FIGURE 4. Assembly to Produce Sodium Metal from NaOH

One Pot Electrolysis. Further investigation of the direct electrochemical formation of B-H species is being carried out in collaboration with Professor Andrew Bocarsly at Princeton University. The first important experiment was to add lithium hydride to trialkylborate in an ionic liquid solvent. The room temperature reaction of LiH with trimethylborate (TMB) in 1-butyl-1-methyl-pyrrolidinium tris(pentafluoroethyl)trifluorophosphate (BMPFFP) gave a strong nuclear magnetic resonance signal for BH₄⁻. That TMB was used successfully as a boron source is a positive development. In the 2005 molten salts work, B₂O₃ was used for BH₄⁻ generation out of necessity, because the boron source needed to be non-volatile at the reaction temperature of 300°C. The room temperature reaction in ionic liquid allowed the use of TMB. Trimethyl borate has the two-fold advantage of being readily available and therefore less expensive, and being the boron source used currently in the Schlesinger process. Recent work in another laboratory has demonstrated another key reaction for the ionic liquid borohydride synthesis, the electrolytic formation of sodium and lithium metal [1]. The Princeton research team is attempting to reproduce this result. With the formation of BH₄⁻ and the synthesis of alkali metal demonstrated, the only remaining step for the direct synthesis is the generation of the metal hydride from hydrogen and the alkali metal. These three steps take place in the cathode compartment of the one-pot electrolytic cell, and result in the synthesis of BH₄⁻ from hydrogen, borate starting material, and electricity. This scheme is illustrated in Figure 5.

Conclusions and Future Directions

- Current efforts have led to a cost reduction pathway for NaBH₄ leading to its use as a hydrogen carrier for use as a transportation fuel. As more

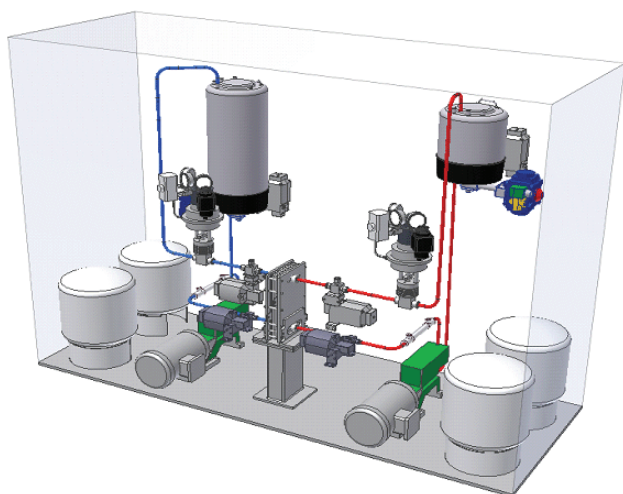


FIGURE 5. Process Summary for the One-Pot Recycling of Borates back into Borohydrides

information is obtained on each of the processes to generate either sodium metal or borohydride directly the economic models will be refined to reflect the improved knowledge.

- NaBO_2 has been recycled into Na and acidified borate solutions, completing a closed mass balance recycle of products into borohydride. Future work will endeavor to show complete conversion of borate to boric acid, and experimentation on direct synthesis of trimethyl borate in the electrolysis cell.
- Current density of 100 mA/cm^2 through the ion selective membrane is adequate for scaled-up sodium synthesis from NaOH. Future work will be to duplicate this feat from NaBO_2 , and to improve the membrane lifetime, particularly in NaOH (aq.) electrochemical systems.

- Pending the go/no-go decision, a task is planned to build the 1 kg of Na/day electrochemical reactor. The knowledge gained from this work will be fed back into the economic model, and used to model the scale-up of the reaction.
- Two of three cathode compartment reactions have been demonstrated for one-pot borohydride ion synthesis. Future work will be to prove the third reaction and complete synthesis of the BH_4^- species.

Special Recognitions & Awards/Patents Issued

1. “Methods and Apparatus for Synthesis of Metal Hydrides” (Patent Pending).
2. “Apparatus and Process for the Production of Metals in Stacked Electrolytic Cells” (Patent Pending).
3. “Processes for Separating Metals from Metal Salts” (Patent Pending).

FY 2006 Publications/Presentations

1. “New Electrolytic Synthesis of Borohydride Anions from Boron Oxide in a Molten Salt Melt” Presentation by Michael T. Kelly at the ACS Fall National Meeting, Washington, D.C., August 28, 2005.
2. “Process for the Regeneration of Sodium Borate to Sodium Borohydride” Presentation by Michael T. Kelly, Jeffrey V. Ortega, Oscar A. Moreno, and Ying Wu at the DOE Annual Program Review, Washington, D.C., May 18, 2006.

References

1. Matsumoto, Zhibin, Sakaebe, and Tatsumi, *J Rare Earths*. 2000, *Spec. Iss.*, p. 26.