

## IV.B.2 Process for the Regeneration of Sodium Borate to Sodium Borohydride for Use as a Hydrogen Storage Source

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### Objectives

- The primary objective of this project is to develop a low cost pathway to sodium borohydride ( $\text{NaBH}_4$ ) in order to meet DOE cost targets.
- Two general approaches are under consideration: (a) lower the cost of sodium metal substantially, which contributes to over 60% of the  $\text{NaBH}_4$  production cost, and (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 R&D 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  $\text{NaBH}_4$  give rise to an equivalent hydrogen cost in the range of \$188-259/kg  $\text{H}_2$ . Regeneration and spent material management are key aspects of the electrochemical synthesis. 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  $\text{H}_2$  goal.
- Interim Target 1: Improved Na electrolysis yields \$50/kg  $\text{H}_2$  via \$10/kg  $\text{NaBH}_4$ .
- Interim Target 2: Incorporation of waste material recycling: \$10/kg  $\text{H}_2$  from \$2/kg  $\text{NaBH}_4$ .
- Interim Target 3: One-pot electrochemical method: \$5/kg  $\text{H}_2$  from \$1/kg  $\text{NaBH}_4$ .

### FY 2007 Accomplishments

- Discovery of several chemical routes that present appealing possibilities for improving the current chemical process to produce sodium borohydride. MCEL has discovered such a route by using a stream of sodium alcohoxide to recover sodium metal value. This step avoids the use of caustic soda and water in the current production process.
- Demonstrated the feasibility of reducing  $\text{NaBH}_4$  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  $\text{NaBO}_2$ ,  $\text{Na}_2\text{B}_4\text{O}_7$ , "spent fuel" from the Hydrogen on Demand<sup>®</sup> 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 ( $\text{NaBO}_2$  and spent fuel) and byproducts ( $\text{NaOCH}_3$ ) of the process itself.
- A current density of 100 mA/cm<sup>2</sup> at 4 V for Na generation from  $\text{NaOCH}_3$  was obtained. This value is sufficient for manufacturing scale production.

- Designed a reactor to carry out  $\text{NaOCH}_3$  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  $100^\circ\text{C}$ . 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  $\text{NaBH}_4$  hydrolysis are among the most promising systems constructed to date. The high relative cost of  $\text{NaBH}_4$ , however, makes its use prohibitively expensive for automotive applications. The purpose of this project is 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  $\text{NaBH}_4$  may be lowered by as much as a factor of 40. This cost reduction would render the purchase price of the  $\text{NaBH}_4$  adequately low for the American consumer to employ the  $\text{H}_2$  generated from it in general transportation applications.

## Approach

Two parallel routes toward achieving a low cost process for the synthesis of  $\text{NaBH}_4$  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.

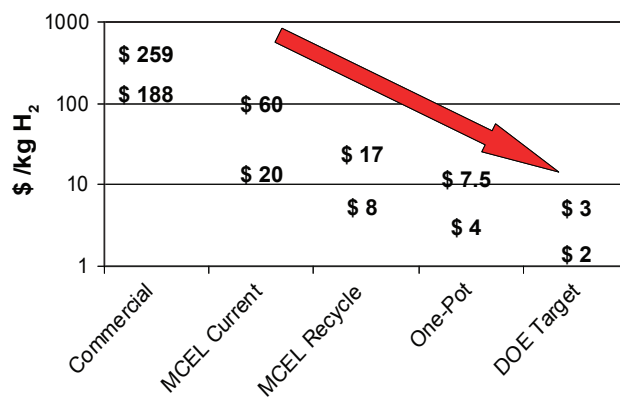
Sodium metal accounts for about two-thirds of the cost in the manufacturing of  $\text{NaBH}_4$ , as well as most of the energy input. In the context of the Schlesinger process, sodium would be generated from the Schlesinger  $\text{NaOCH}_3$  by-product, which provides about 75% of the sodium raw material. Current efforts also include extending the sodium recycling technology from sodium methoxide to sodium borate. Sodium borate contains the remaining 25% of the needed sodium to make sodium borohydride. Between sodium methoxide 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 so far has been the refinement of  $\text{NaBH}_4$  cost predictions, summarized in Figure 1. Building on previous breakthrough of manufacturing Na metal from aqueous (aq.)  $\text{NaOH}$ , further laboratory results for  $\text{NaOH}$  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 1,173.7 mAh of current passed through the electrochemical reactor. In theory, 1,173.7 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  $\text{H}_2$ , which was collected and quantified. Hydrolysis data and weight data show excellent agreement, further verifying the results. By extension, sodium methoxide has been used to produce sodium metal with even better results than those obtained for caustic soda.

Through engineering assessments, economic analysis, and process modeling this breakthrough has been used to make a reliable estimate regarding the future cost of sodium manufacturing, and by extension,



**FIGURE 1.** Cost reduction pathway for hydrogen ( $\text{H}_2$ ) obtained from sodium borohydride ( $\text{NaBH}_4$ ). The left most price range is for today's commercially available product. The 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 future cost of  $\text{NaBH}_4$ . It has been 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 the ones outlined for sodium metal from caustic soda, further developing future price models for  $\text{NaBH}_4$ . Additional information on the  $\text{NaBO}_2$  recycle is included below.

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  $\text{NaBH}_4$  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  $\text{NaBH}_4$  cost structure to the future use of  $\text{NaBH}_4$  as a  $\text{H}_2$  storage medium for transportation applications. Additional information on the one-pot synthesis is included below.

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 a plant. 2) The operating cost of a plant is dominated by electricity usage and this cost appears to be more important than the capital cost of membrane material. 3) The current density requirement is likely to be in the range of  $100 \text{ mA/cm}^2$ . The key assumption in this assertion is that the membrane does not need to be replaced very frequently. The actual current density that optimizes the balance between membrane lifetime and electrolyzer cost was determined for the methoxide process.

Because of this, a major portion of the research this past year was directed towards determining membrane characteristics such as current density and stability. Furthermore, the use of sodium methoxide instead of caustic soda has also been investigated. Although this new route affects the durability of the membrane, in the absence of water, the membrane performs much better.

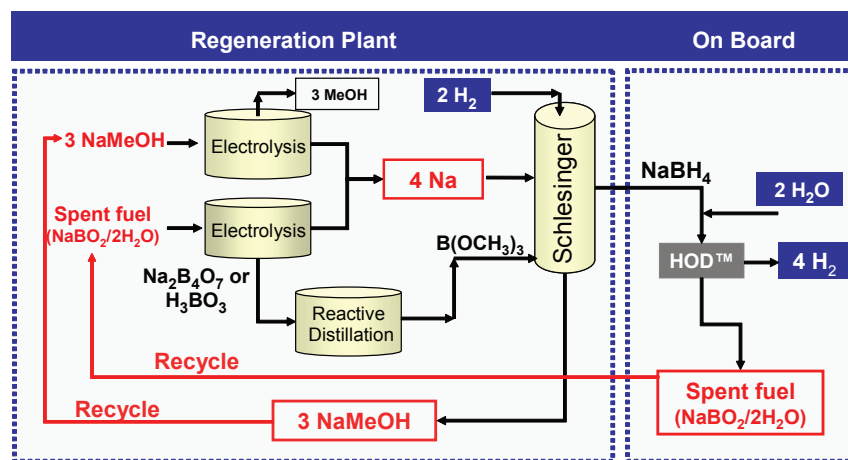
#### Sodium Metaborate Recycle.

To fully recycle  $\text{NaBH}_4$  from its synthesis byproducts and hydrolysis products, borate must be converted to sodium and boric

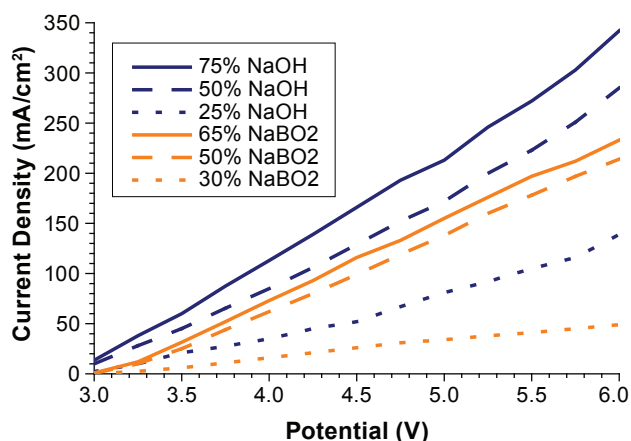
acid. It has been shown that this conversion can be carried out in an electrochemical reactor similar to the one used to synthesize sodium metal from caustic soda. A schematic drawing of the  $\text{NaBH}_4$  synthesis process employing both  $\text{NaOCH}_3$  and  $\text{NaBO}_2$  recycle is shown in Figure 2. Implementation of this recycling process advances the cost goal from the current status to the recycle value, and indicates a cost improvement from today’s price of  $\text{NaBH}_4$  by more than a factor of 10.

#### Current Density and Membrane Performance.

At the heart of the sodium synthesis electrochemical reactor for either  $\text{NaOCH}_3$  or  $\text{NaBO}_2$  recycle lies the sodium  $\beta''$ -alumina ( $\text{S}\beta''\text{A}$ ) membrane. The  $\text{S}\beta''\text{A}$  membrane can be modified to obtain a solid state sodium ion conductor with different physical properties. The performance of a standard sodium  $\beta''$ -alumina ( $\text{s-S}\beta''\text{A}$ ) was compared against the performance of a modified sodium  $\beta''$ -alumina ( $\text{m-S}\beta''\text{A}$ ). Current density measurements for molten  $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$  (melting point  $\sim 60^\circ\text{C}$ ) at about  $120^\circ\text{C}$  show that the maximum current density is achieved with  $\text{m-S}\beta''\text{A}$  membranes rather than  $\text{s-S}\beta''\text{A}$ . The current density for  $\text{NaBO}_2$ , at  $66 \text{ mA/cm}^2$ , is lower than in the caustic soda ( $100 \text{ mA/cm}^2$ ) using the  $\text{m-S}\beta''\text{A}$  membranes. Figure 3 shows a comparison of three different concentrations of caustic soda 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  $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$  compared to caustic soda, and the fact that electrolyte is essentially lost when  $\text{NaBO}_2$  converts into sodium and boric acid ( $\text{B(OH)}_3$ ). However, while there was a difference in the current densities, there was no difference in the current efficiencies for all of the borate and caustic soda melts which were greater than 99% utilizing the alumina membranes.



**FIGURE 2.** Process schematic for recycling all sodium and borate products back into sodium borohydride ( $\text{NaBH}_4$ ). Three sodium atoms come from recycled sodium methoxide ( $\text{NaOCH}_3$ ) and the fourth comes from recycled sodium borate ( $\text{NaBO}_2$ ). Boric acid is also obtained from recycled sodium borate ( $\text{NaBO}_2$ ).



**FIGURE 3.** Current Density Behavior for Different Aqueous Solutions of Caustic Soda and Sodium Borate with Respect to Applied Potential

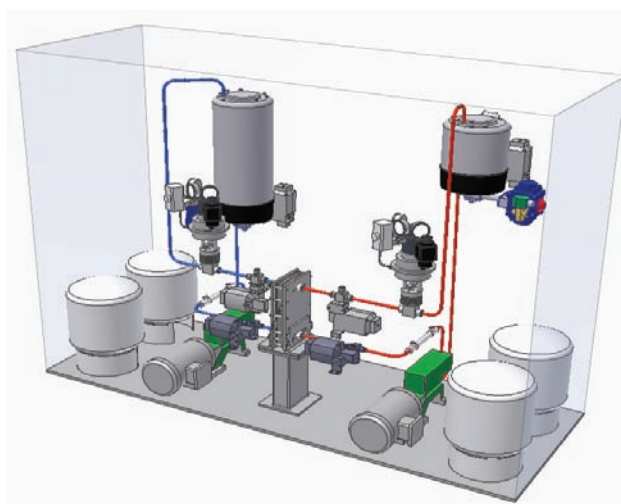
A second important parameter for the scaling up of sodium syntheses from either the  $\text{NaOCH}_3$  or  $\text{NaBO}_2(\text{aq.})$  is the membrane lifetime. Sodium synthesis from  $\text{NaBO}_2$  preserves the membrane for a long time compared with extracting sodium from caustic soda. When sodium methoxide is used, the membrane durability is increased substantially from the aqueous  $\text{NaBO}_2$  results. The most preferable scenario is that the membrane can perform for a year or longer. In caustic soda solutions, the performance lifetime is far short of that time frame, and it is the reason for using  $\text{NaOCH}_3$  rather than  $\text{NaOH}$ . The reason for membrane failure in  $\text{NaOH}(\text{aq.})$  has not yet been determined. It is not simply a chemical break down, as molten  $\text{NaOH}$  does not damage the membrane. However, in 50%  $\text{NaOH}$  evidence of membrane degradation can be observed after a single use. The mechanism of membrane degradation is likely associated with caustic soda, water, and the passage of current. Exposure to steam can also be problematic. In molten  $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$ , which is 47%  $\text{NaBO}_2$  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.

**Reactor Design: 1 kg Na/day.** Caustic soda was chosen for the initial modeling and demonstration scale project because it represents 75% of the sodium value needed to make  $\text{NaBH}_4$ . Further, as caustic soda is a by-product of the borohydride synthesis, it is already present in the  $\text{NaBH}_4$  manufacturing facility. Finally, most of the engineering done for hydroxide electrochemical reactors will be directly applicable to electrochemical reactors employed to make sodium metal from sodium borate, and by extension, to the electrolysis of sodium methoxide ( $\text{NaOCH}_3$ ).

All of the components of the sodium synthesis reactor have been modeled using AspenTech HYSYS. The materials compatibility testing efforts were completed. Selection of processing equipment has also

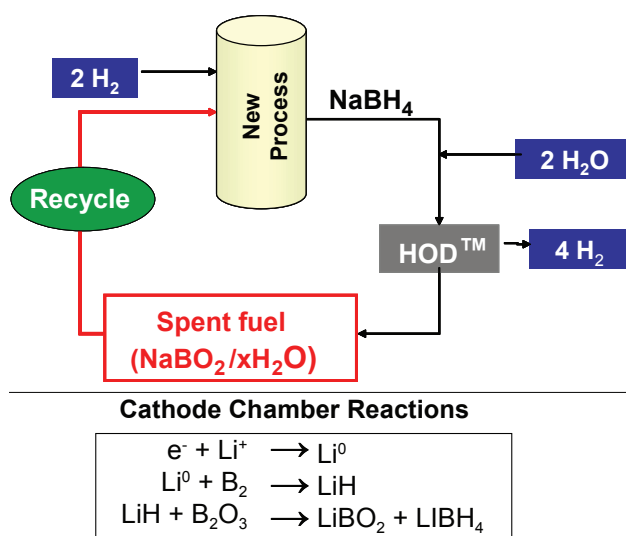
been completed. A scale of 1 kg/day of sodium was selected as first trial in the prototype demonstration process to commercialization. The electrochemical reactors are currently engineered to be stackable, meaning that to increase sodium production one only needs to put additional electrochemical reactors together (either in series or in parallel). Each electrochemical reactor will be capable of generating approximately 1 kg of sodium metal per day. For the initial stage only one electrochemical reactor will be operated, to be carried out in a dedicated pilot plant facility shown in Figure 4. It is designed specifically to handle the hazards associated with bringing together sodium metal and aqueous solutions, although, the use of sodium methoxide minimizes those hazards. The electrochemical reactor 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 reactor in an air environment. The assembly shown in Figure 4 will be placed in a fume hood. The hood has its own fire suppression system, which consists of extinguishers suitable for Class D fires. Construction of this pilot plant was put on hold by direction of the DOE.

**One Pot Electrolysis.** Further investigation of the direct electrochemical formation of B-H species was 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  $\text{LiH}$  with trimethylborate (TMB) in 1-butyl-1-methyl-pyrrolidinium tris(pentafluoroethyl)trifluorophosphate (BMPFPF) gave a strong nuclear magnetic resonance (NMR) signal for  $\text{BH}_4^-$ . That TMB was used successfully as a boron source is a positive development. In the 2005 molten salts work,  $\text{B}_2\text{O}_3$  was used for  $\text{BH}_4^-$ .



**FIGURE 4.** Assembly to Produce Sodium Metal from Caustic Soda ( $\text{NaOH}$ ) or Sodium Methoxide ( $\text{NaOCH}_3$ )

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]. With the formation of  $\text{BH}_4^-$  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  $\text{BH}_4^-$  from hydrogen, borate starting material, and electricity. This scheme is illustrated in Figure 5.



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

## Conclusions and Future Directions

- Current efforts have led to a cost reduction pathway for  $\text{NaBH}_4$  leading to its use as a transportation fuel. The economic models were refined to reflect the improved knowledge.
- Sodium borate ( $\text{NaBO}_2$ ) has been recycled into sodium metal and acidified borate solutions, completing a closed mass balance recycle of products into borohydride. Work showed complete conversion of borate to boric acid, and experimentation on direct synthesis of trimethyl borate in the electrolysis cell.
- Current densities of up to 100  $\text{mA}/\text{cm}^2$  through the ion selective membrane is adequate for scaling up sodium synthesis from caustic soda ( $\text{NaOH}$ ) and sodium methoxide ( $\text{NaOCH}_3$ ). Work duplicated this feat from  $\text{NaBO}_2$ , and improved the membrane lifetime. The selection of  $\text{NaOCH}_3$  over  $\text{NaOH(aq.)}$  has improved the lifetime of membranes in 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  $\text{BH}_4^-$  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).

## References

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