

III.B Chemical Hydrides

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

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Objectives

- Develop an electrolysis-based process for the reduction of borates to borohydrides to meet 2010 DOE cost targets of \$1.50/kg H₂ and \$4/kWh for the hydrogen storage system.
- 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. Life Cycle and Efficiency Analyses
- Q. Regeneration Processes for Irreversible Systems
- R. By-Product Removal

Approach

- Test different electrolytic-based methods leading to reduced cost of sodium borohydride.
- Down-select from the various methods the most promising for economic analysis.
- Conduct economic analysis to estimate the lowest possible cost for sodium borohydride.
- Build a laboratory-scale synthesis demonstration unit, pending outcome of go/no-go decision point.

Accomplishments

- Demonstrated electrolysis of sodium metal from sodium hydroxide at 80% electrolytic efficiency, with an electricity savings of over 75% compared with industrial methods (sodium metal is the most expensive raw material of sodium borohydride manufacture, contributing roughly 60-65% of the total cost).
- Discovered a stable molten hydroxide system in which sodium borate might be directly reduced to borohydride.
- Developed analytical methods for detecting sodium borohydride in hydroxide melts.

- Completed a summary report of all known thermochemical processes for the synthesis of sodium borohydride.

Future Directions

- Down-select the approach most likely to meet DOE cost targets from the three electrolysis methods being explored.
- Conduct an energy efficiency and economic analysis of the selected regeneration process, projecting the cost of sodium borohydride.
- Build a laboratory demonstration scale production unit to demonstrate the viability of borate regeneration in year three, based on the outcome of the go/no-go decision point.

Introduction

At the present time, there are no hydrogen storage technologies that can be used to implement a transportation infrastructure that employs hydrogen as its consumable fuel. The barriers to commercialization differ for nearly all of the technology options. Chemical storage represents one class of potential solutions to the storage problem. The combination of relatively high volumetric and gravimetric storage densities makes chemical hydrides an attractive answer to the hydrogen storage dilemma. However, one of the largest hurdles that must be overcome for chemical hydrides to be desirable for transportation applications is the cost of chemical hydrides. Currently, no chemical hydride can be synthesized at a sufficiently low cost for use as a mass consumer fuel.

Millennium Cell proposes using sodium borohydride (NaBH_4) to store hydrogen,¹⁻³ and is considered a leader in the development of chemical hydride storage systems. After extensive analysis at Millennium Cell and Air Products, it appears that the synthesis methodology most likely to result in substantial cost reduction of a chemical hydride like NaBH_4 is to use electrolysis techniques. The key to advancing this technology is to find an electrolysis process wherein borates (fully oxidized boron species) are directly reduced to borohydrides using electricity. Also important would be an electrolysis route to make sodium metal that both uses less energy and is less capital intensive, which would make the current process more cost-effective. Sodium metal is the highest-cost raw material used in the present manufacturing process for NaBH_4 . By

our estimation, approximately 60-65% of the cost of NaBH_4 is Na metal.

Approach

We believe that electrolytic techniques to manufacturing chemical hydrides are the most likely to result in substantial cost savings over present methods.⁴ Borates, the oxidized forms of boron compounds, are inert electrochemical species in water. In other solvent media, however, borates may prove more active. The work herein will take place in molten salt media, where a number of key electrolytic parameters can be controlled. Initial work focuses on molten hydroxide systems. Borohydride is stabilized in basic solution, and hydroxide melts are very basic. Hydroxides also provide solubility for both borate reagents and borohydride products. This system also excludes water, the presence of which is likely to cause electrolysis of water as well as hydrolysis of borohydride back to borate. Re-hydrolysis of borohydride (a back-reaction) by water undoes the synthetic work performed on the borate and wastes energy, so water exclusion is highly desirable.

When looking at sodium generation, electrolysis of sodium hydroxide requires considerably less energy than similar electrolyses in sodium chloride (NaCl). Sodium hydroxide is also a side product of the present synthesis of NaBH_4 and would thus recycle itself back to the beginning of a synthetic cycle for NaBH_4 based on electrolysis of sodium hydroxide to make sodium. Efficient sodium production also has a potentially wider impact than NaBH_4 because many chemical hydrides are exchangeable. Sodium hydride, for

example, can be used to make magnesium hydride. Thus, a breakthrough in hydride synthesis is potentially applicable to all chemical hydride cost reduction efforts.

Results

In the effort of direct borate reduction to borohydride, we completed two studies in the 3 months since project inception:

- Selection of mixed melt for borohydride stability
- Development of product analysis methods by titration and nuclear magnetic resonance (NMR)

An early test shows that NaBH_4 is not stable in molten sodium hydroxide. The temperature is too high for the hydrides on boron to remain stable in the presence of the protons in hydroxide. A typical cyclic voltammogram (CV) showing the decomposition of NaBH_4 in sodium hydroxide (NaOH) melt at 350°C is shown in Figure 1. It is important that NaBH_4 have reasonable stability in the selected melt environment in order to detect, and more importantly, isolate the product when it is formed.

Our work has demonstrated that in a mixed melt containing both NaOH and potassium hydroxide (KOH), NaBH_4 is stable. The key parameter is temperature – at the eutectic composition of NaOH and KOH , the melting point of the solids is below 190°C . At 200°C , sodium borohydride hydrolysis proceeds at a sufficiently slow rate that borohydride decomposition is minimal.

An effective method to assay sodium borohydride is needed. Electrochemical detection of NaBH_4 has proven to be difficult in a mixed hydroxide melt even when a substantial quantity of borohydride is deliberately added to the melt. The electrochemical signal for oxidation of borohydride is weak. Therefore, alternative methods of detection are needed. It was learned that the cathodic portion of the melt, amounting to about 0.5-2 grams of NaOH-KOH , could be cooled to room temperature and then dissolved in a minimum of water, often 10 milliliters or less, without destroying any borohydride ions that may be present. Once dissolved in water, the solution could be titrated for sodium borohydride,⁵ or the borohydride could be observed spectroscopically by boron (^{11}B) NMR.

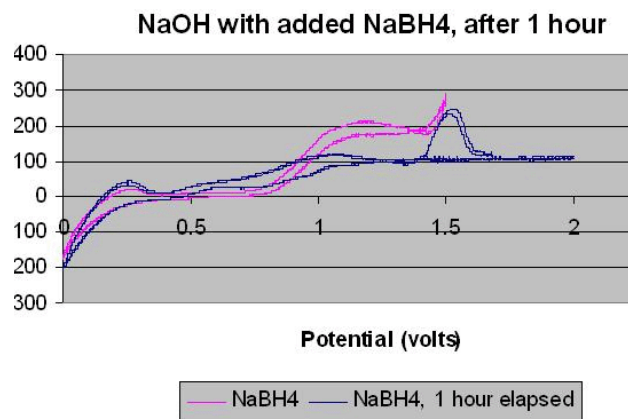


Figure 1. Cyclic Voltammogram Showing Loss of NaBH_4 in Molten NaOH at 350°C (The limiting current between about 1.0 and 1.5 V is proportional to the concentration of sodium borohydride. After 1 hour, the limiting current drops from 200 mA to 100 mA, so it can be estimated that 50% of the sodium borohydride has been hydrolyzed.)

Both techniques are quantitative and result in good assessment of electrolytic yield of the reaction.

In the effort to improve the energy efficiency of sodium production and therefore reduce the raw material cost for the manufacture of NaBH_4 , we have made the following progress: .

- Achieved 80% electrolytic efficiency in the electrolysis of molten NaOH
- Demonstrated efficacy of hydrogen-assisted electrolysis and resultant efficiency improvement
- Based on experimental data, completed a comparison of energy efficiency of hydrogen-assisted electrolysis with standard Na manufacturing methods from molten NaCl

Figure 2 shows the free energy change of each reaction step during the process of making sodium borohydride. As the figure indicates, the free energy input during the electrolysis of sodium is more than the energy required to make borohydride. When NaCl is electrolyzed to make sodium, more than 50% of the energy is wasted. The inset shows the same step when sodium hydroxide is electrolyzed, with the efficiencies demonstrated at Millennium Cell. The required energy input is reduced six-fold, and the energy loss is reduced by over an order of magnitude. These changes have a substantial impact on the overall energy consumption and efficiency of the

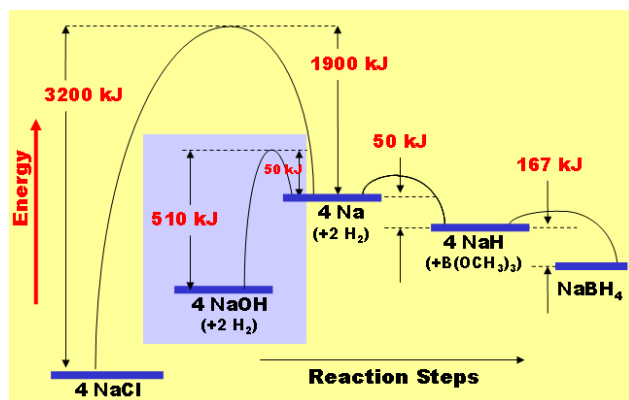


Figure 2. Reaction Step Diagram for the Manufacture of Sodium Borohydride, Including Free Energy Change (Free energy is given for the temperature at which that step is carried out. Temperatures are not the same for each step. Energy levels are not to scale. Inset shows proposed sodium hydroxide electrolysis.)

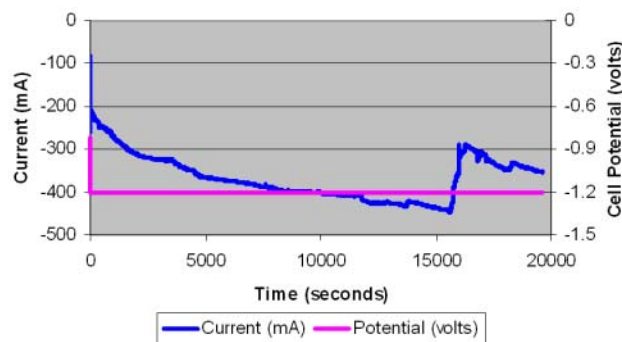


Figure 3. Current and Cell Potential Profiles Shown as a Function of Time for the Hydrogen-Assisted Electrolysis of Sodium Hydroxide to make Sodium (Reaction temperature is 360°C. Electrolytic yield for this run is 80%. Theoretical voltage for the reaction is 1.08°V.)

process. Figure 3 shows an actual electrolysis of sodium hydroxide to make sodium, wherein 80% electrolytic efficiency is obtained. Electrolytic efficiency is calculated by multiplying the voltage efficiency (theoretical voltage divided by actual voltage) and the current efficiency, which is the theoretical yield determined by the number of coulombs passed divided by the actual product yield, as shown in equation (1).

$$\text{Electrolytic Eff.} = \frac{\text{Theoretical Voltage}}{\text{Actual Voltage}} \times \frac{\text{Expected Yield}}{\text{Actual Yield}} \times 100\% \quad (1)$$

The main advantages of NaOH electrolysis over NaCl electrolysis for the production of sodium metal are summarized in Table 1.

Table 1. Comparison of Molten NaCl Electrolysis and Molten NaOH Electrolysis

Reaction Medium	Molten NaCl	Molten NaOH
Operating Temperature	600°C	350°C
Anode Product	Chlorine (Cl ₂)	Water (H ₂ O)
Theoretical voltage	3.42 V	1.07 V
Actual voltage	~ 5.5 V	~1.2 V
Separator	Porous ceramic membrane	Selective sodium ion conducting ceramic membrane

The reason that such high efficiency can be achieved is attributed to hydrogen-assisted electrolysis. In the standard electrolysis of NaOH, it is split into sodium metal and oxygen gas, leaving water as a byproduct. Oxygen electrochemistry is known to have substantial overvoltage, which causes the additional voltage over the theoretical required to activate and drive a reaction. Overvoltage contributes to lowered voltage efficiency. In a hydrogen-assisted electrolysis, hydrogen gas is supplied to the anode, where it is oxidized to protons, which react with hydroxide to make water. The sodium reduction reaction at the cathode is unchanged from standard electrolysis. Hydrogen is known to exhibit little overvoltage, so oxidation of hydrogen can be much more efficient than any typical electrochemistry involving oxygen.

Conclusions

This newly started project addresses key issues to determine the feasibility of using sodium borohydride as a hydrogen storage medium. Conclusions from work done in the first three months of the project are as follows:

- Sodium metal can be manufactured with substantially less energy than it is presently.
 - Lowered energy usage translates into a more environmentally benign process.
 - Lowered energy usage translates into a less expensive synthesis.
- The conditions under which sodium borohydride is stable in molten hydroxide have been determined.
- The ability to detect and quantify the amount of borohydride has been developed.
 - Stability and detection provide the necessary conditions under which direct synthesis can be explored.

References

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