

Process for the Regeneration of Sodium Borate to Sodium Borohydride

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*DOE Annual Program Review
Washington, D.C., May 16-19, 2006*

*Project ID #: STP 22
Contract #: DE-FC36-04GO14008*

This presentation does not contain any
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Overview

Timeline	Barriers
<ul style="list-style-type: none">▪ Project start date:<ul style="list-style-type: none">▪ Fiscal Year 2004▪ Project end date:<ul style="list-style-type: none">▪ Fiscal Year 2006▪ Percent complete:<ul style="list-style-type: none">▪ 65%	<ul style="list-style-type: none">▪ A. Cost▪ C. Efficiency▪ G. Life Cycle and Efficiency Analyses▪ Q. Regeneration for Irreversible Systems▪ R. By-Product Removal▪ Other: Applicable to Off-Board Delivery and Storage
Budget	Partners
<p>Total funding: \$4.5 MM, 3 yrs DOE share: \$3.6 MM MCEL share: \$0.6 MM APCI share: \$0.4 MM Funding received in FY05: \$0.75 MM Funding for FY06: \$0.91 MM</p>	<ul style="list-style-type: none">▪ Millennium Cell - Na/B Separation, Engineering, Membrane development▪ Air Products - Economic assessment▪ Rohm and Haas - Process engineering▪ Princeton - Direct borate electrolysis

Objectives

Barrier	Project Objectives
A. Cost	Develop regeneration process for NaBH_4 that significantly lowers its cost
C. Efficiency	Improve overall energy efficiency; Demonstrate feasibility of achieving ~50% “well-to-tank” efficiency.
G. Life Cycle and Efficiency Analyses	Conduct a high-level energy efficiency assessment based on the newly-developed re-generation process.
Q. Regeneration Processes for Irreversible Systems	Develop energy efficient and cost effective process for off-board regeneration of NaBH_4 .
R. By-Product Removal	Develop a process that re-uses the by-product NaBO_2 , thereby completing the recycling loop.

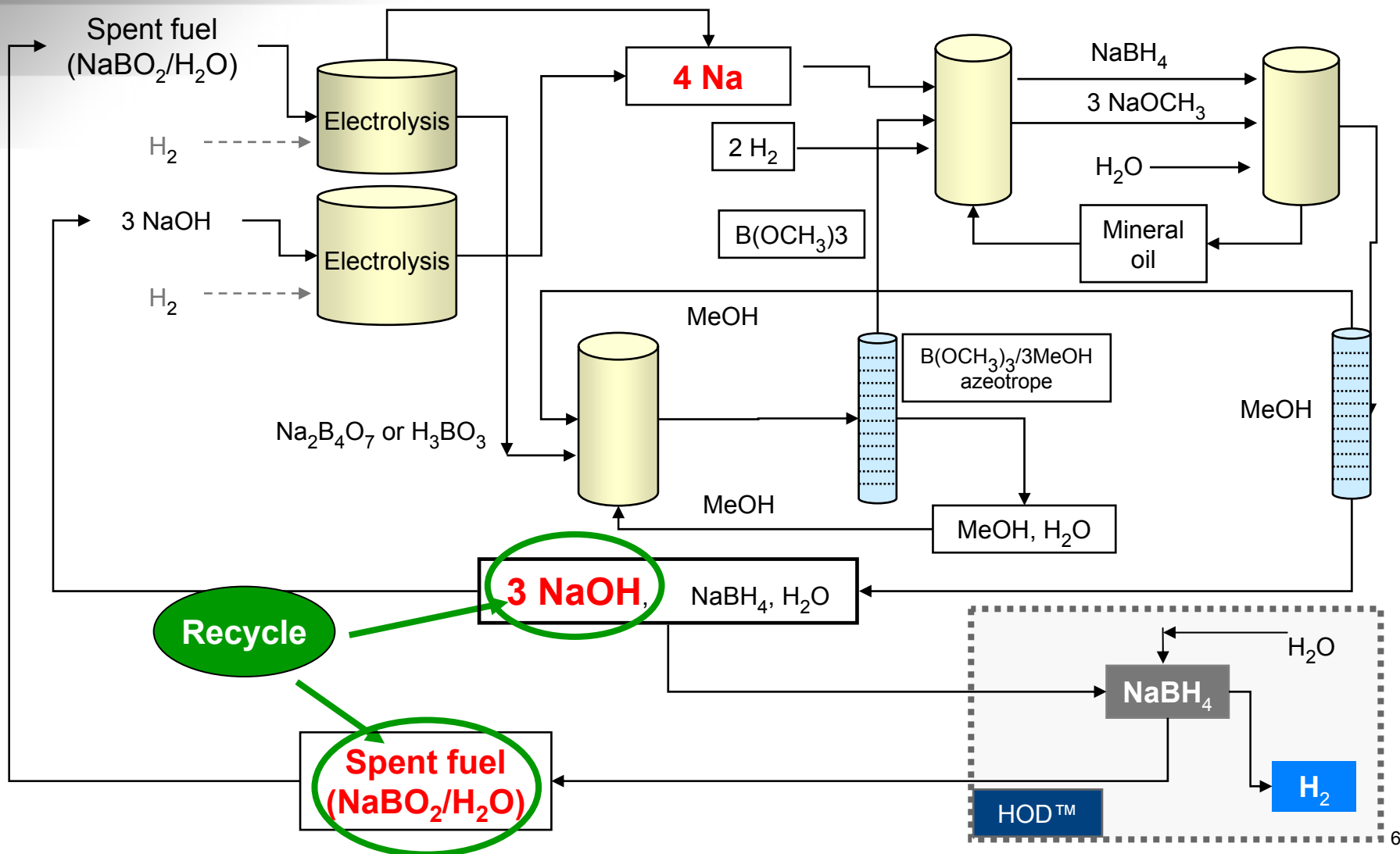
Status Against DOE Targets

- Objective:
 - Reduce SBH cost
- Status:
 - Current SBH: **\$40-60** /kg purchased
 - Reported in May 2005: estimated ~\$7/kg production cost when NaOH electrolysis is implemented
- Further cost reduction:
 - Co-production of Na and Boric acid from recycled borate
 - One-pot reaction from borate to SBH.
- DOE Target:
 - \$2-3/kg H₂ is equivalent to \$0.40-0.50/kg SBH.

- **Use Electrochemical process to achieve high energy efficiency**
 - Highly efficient pathway to key precursor for SBH.
 - Direct electrolysis of spent fuel
 - One-pot electrolysis for SBH synthesis
- **Reduce number of steps in regeneration process**
 - Eliminate costly and inefficient separation and purification steps
- **Couple engineering development with bench scale testing**
 - Safety and cost considerations
- **Multi-discipline approach that includes chemistry, materials science, and engineering**
 - Reaction kinetics studies
 - Materials compatibility and durability studies
 - Reactor and process designs

Approach

- utilizing recycled material



Reaction Chemistry

- Measured current density in NaOH and NaBO₂ electrolysis
- Demonstrated that precursors to NaBH₄ synthesis can be made from the direct electrolysis of spent fuel
- Showed the feasibility of synthesizing BH₄ in ionic liquids at room temperature (current commercial NaBH₄ process: 275°C)

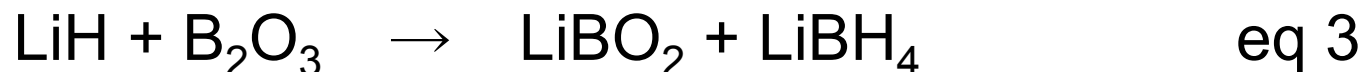
Preliminary Engineering Assessment

- Completed preliminary engineering:
 - PFDs, P&IDs, Equipment List, Equipment Specs
- Materials performance testing for reactor:
- Process modeling using HYSYS: 40% complete
- Safety and hazard assessment: 40% complete

Preliminary Cost Assessment

- Established plant scale
- Gathered initial information on electrolyzer cost

“One-Pot” Borohydride Electrochemical Generation



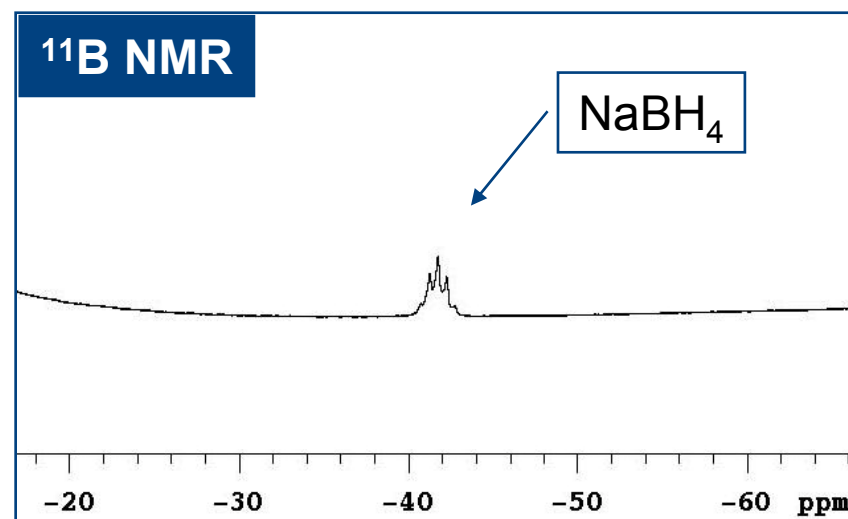
- Reaction sequence takes place in one pot, with no need for separations
- Yield is currently low (<10%), most likely due to the low solubility of H₂ in the melt at reaction temperature (275 °C).
- Work at subcontractor (Princeton) **focused on utilizing melts with higher H₂ solubility**
- **Status:**
 - **1st Step:** Demonstrated the hydride transfer chemistry with commercially available hydrides and borate
 - **2nd Step:** Will Attempt electrochemical synthesis of hydride when the chemistry and analysis methods are in hand

“One-Pot” Borohydride Electrochemical Generation

One-pot SBH synthesis in ionic liquids

Ionic Liquids	M.P. (°C)
1-butyl-1-methyl-pyrrolidinium tris(pentafluoroethyl)trifluorophosphate	-50
Trihexyl-tetradecyl-phosphonium tris(pentafluoroethyl)trifluorophosphate	-50
1-butyl-2,3-dimethylimidazolium chloride	89

- **Step 1: successfully demonstrated the synthesis of NaBH_4 in the first two ionic liquids at room temperature, with hydride starting material.**
- **Remain to be shown: same reactions can take place with electrochemically generated hydride**



“One-Pot” Borohydride Electrochemical Generation

2-Compartment E-Chem Cell



- **Experimental Focus:**
 - electrochemical generation of hydride with subsequent formation of BH_4^- in the same cell.
 - Trimethyl borate species has been shown to be electrochemically activated at Pt and Li electrodes
- **Results so far:**
 - In the absence of Li or Na as counter cations to the hydride, B-O species was converted into B-F species.
 - Conversion of B-O to B-F occurs only with applied voltage indicating electroactivity.
- **Future experiments:**
 - will include addition of H_2 at cathode as well as Li or Na to make borohydride.

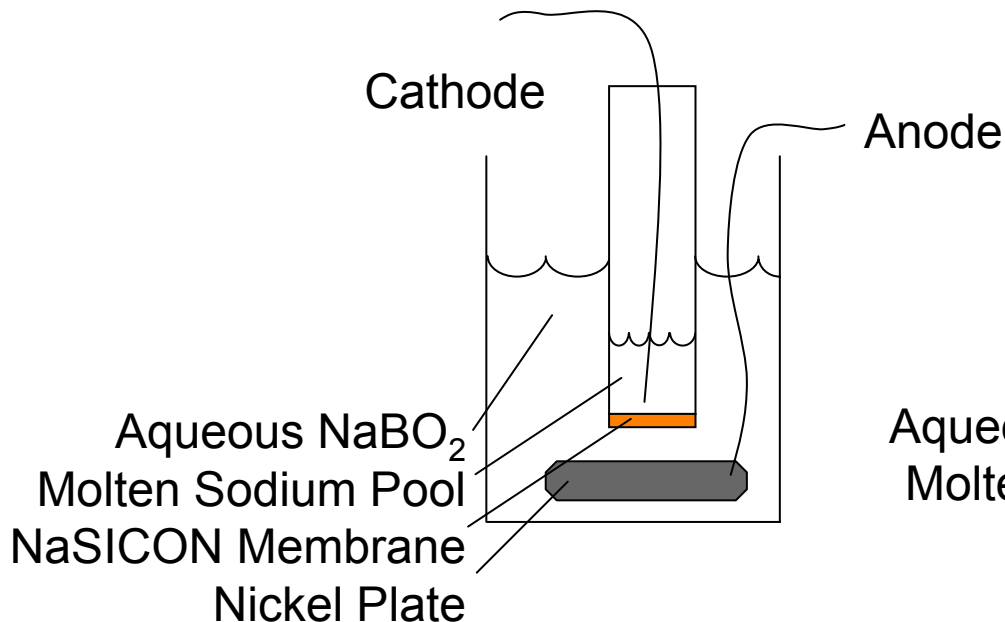
Sodium and Boron Separation

Method:

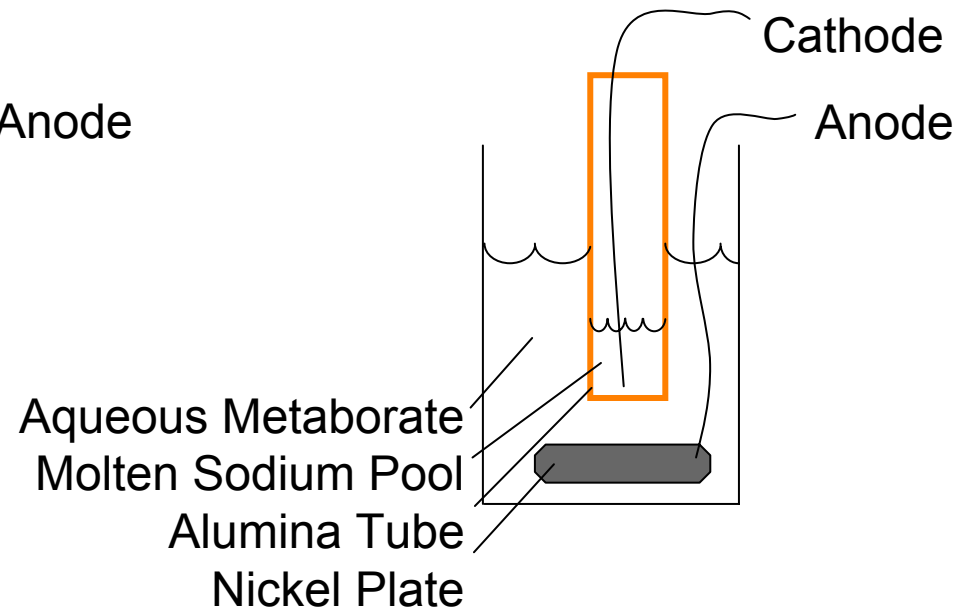
Direct recovery of Na metal and borate from NaBO_2 spent fuel, for use in SBH synthesis

Experimental Set-up

NaSICON membrane

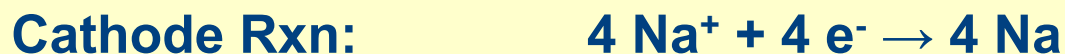


Na- β'' -alumina membrane



Sodium and Boron Separation

- Effect of Applied Potential

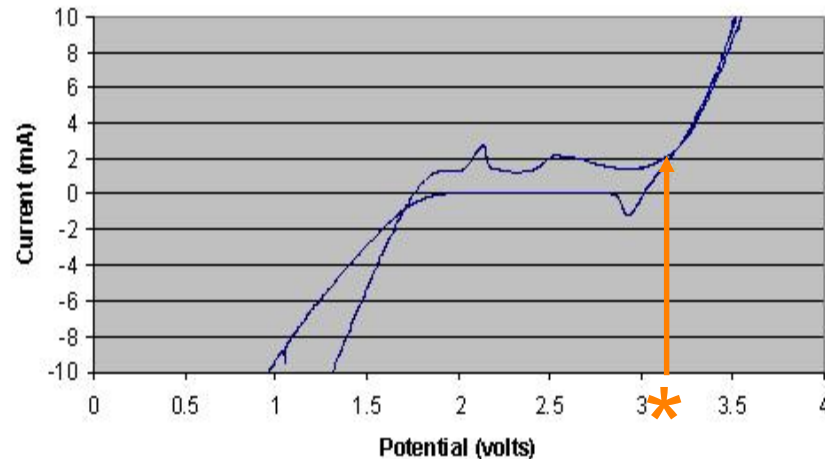


- Onset potential = 3.2 V
- Higher potential required to achieve sufficient reaction rate

Example Experimental Results

	Potential (V)	Current (mA)	Yield
Run A	3.5	4.8	85%
Run B	5.0	125	96%

Cyclic Voltammogram of NaBO₂·4H₂O



Sodium and Borate Separation

Na Synthesis from Various Aqueous Solutions

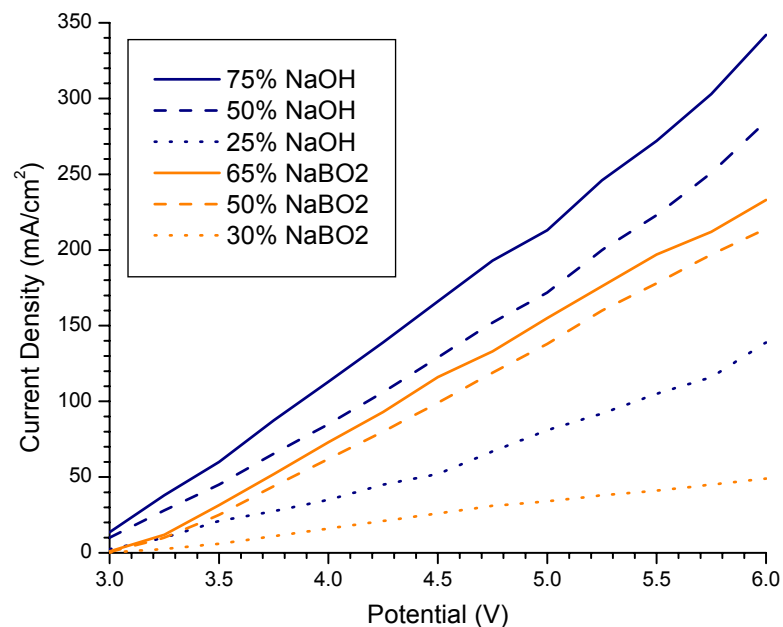
Aqueous Solution	Na- β "-alumina	NaSICON
NaBO ₂ (concentrated)	100% Current Efficiency	No reaction
NaBO ₂ (dilute)	Failed – 0% yield	60-70% yield
NaOH (concentrated)	100% Current Efficiency	No reaction
NaOH (dilute)	<i>To be tested</i>	Partial rxn, membrane damaged
Borax (concentrated)	100% Current Efficiency	<i>To be tested</i>
Borax (dilute)	<i>To be tested</i>	30-35% yield
“Spent Fuel” from HOD®	100% Current Efficiency	Failed, membrane damaged

Initial Experiments Appear to Indicate:

- Na- β "-Alumina is more effective with concentrated solutions while NaSICON is more effective with dilute solutions
- Further experimentation needed to obtain additional insight

Current Density Determination

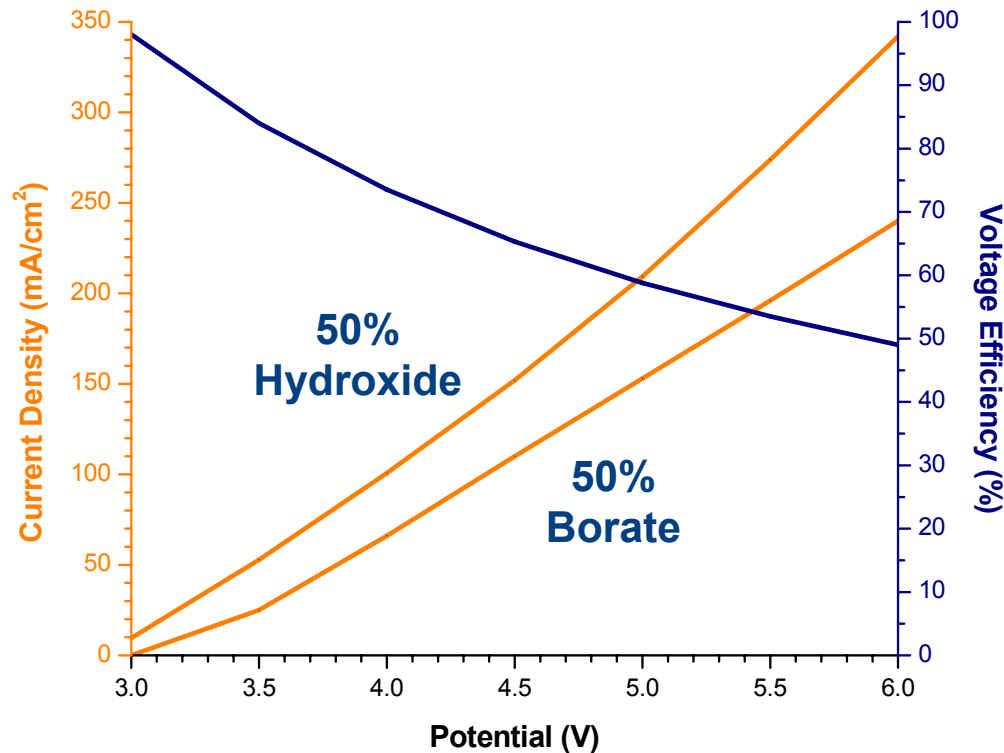
- Higher current densities were achieved in hydroxide solutions than in the corresponding borate solutions
- Membranes exhibited better stability in borate solutions
- Use of β'' -alumina allowed 99+% current efficiencies in both the borate and the hydroxide melts tested.



Note: β'' -Alumina membranes with Ni counter electrode

Optimized Current Density

Measured Current Density vs. Voltage Efficiency

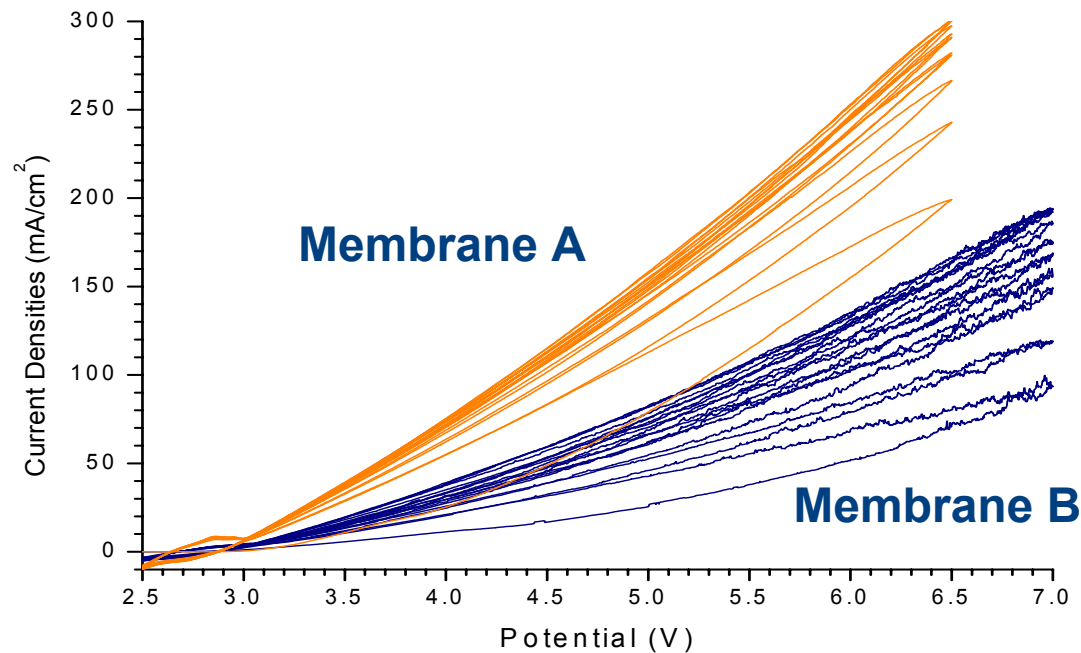


- Increasing applied potential increases current density but also decreases the voltage efficiency

Theoretical Minimum Potential = 2.94 V at 115 °C

Effects of Membrane Composition

Of the two types of β'' -membranes tested, Membrane A exhibits higher current densities and is more resistant to failure than Membrane B



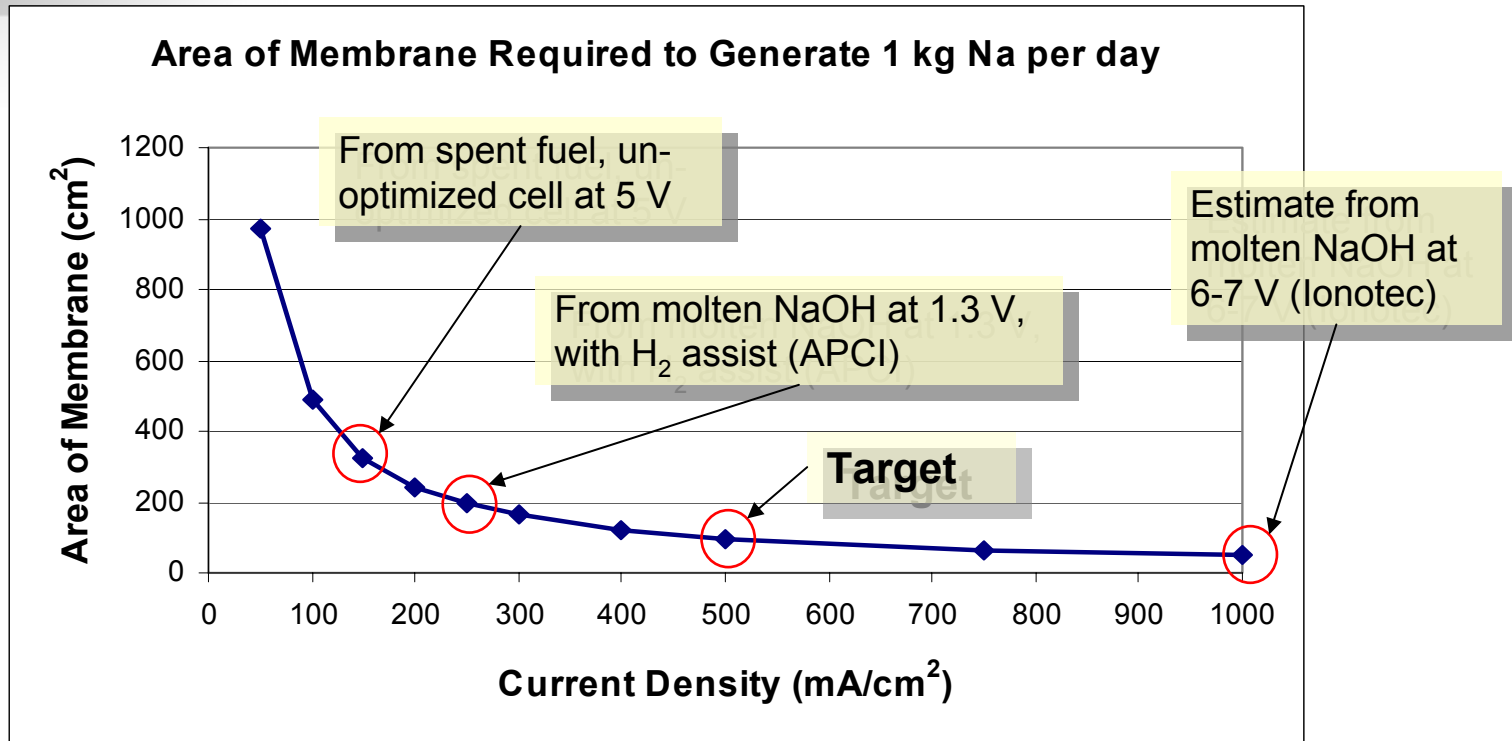
Tasks

- Based on results generated from bench scale experiments, design a process for scale up operation and cost estimates
- Determine materials of construction for components of electrochemical reactor.
- Verify physical properties of membrane.
- Design of electrochemical reactor for continuous flow operation.
- Perform safety and hazard analysis (e.g. FMEA)

Accomplishments

- Established basic Process Flow Diagram (PFD)
- Started to generate equipment list and equipment specifications
- Developed Piping and Instrumentation Diagram (P&ID)
- Completed preliminary mass balance
- Process simulation (modeling) using Aspen HYSYS software

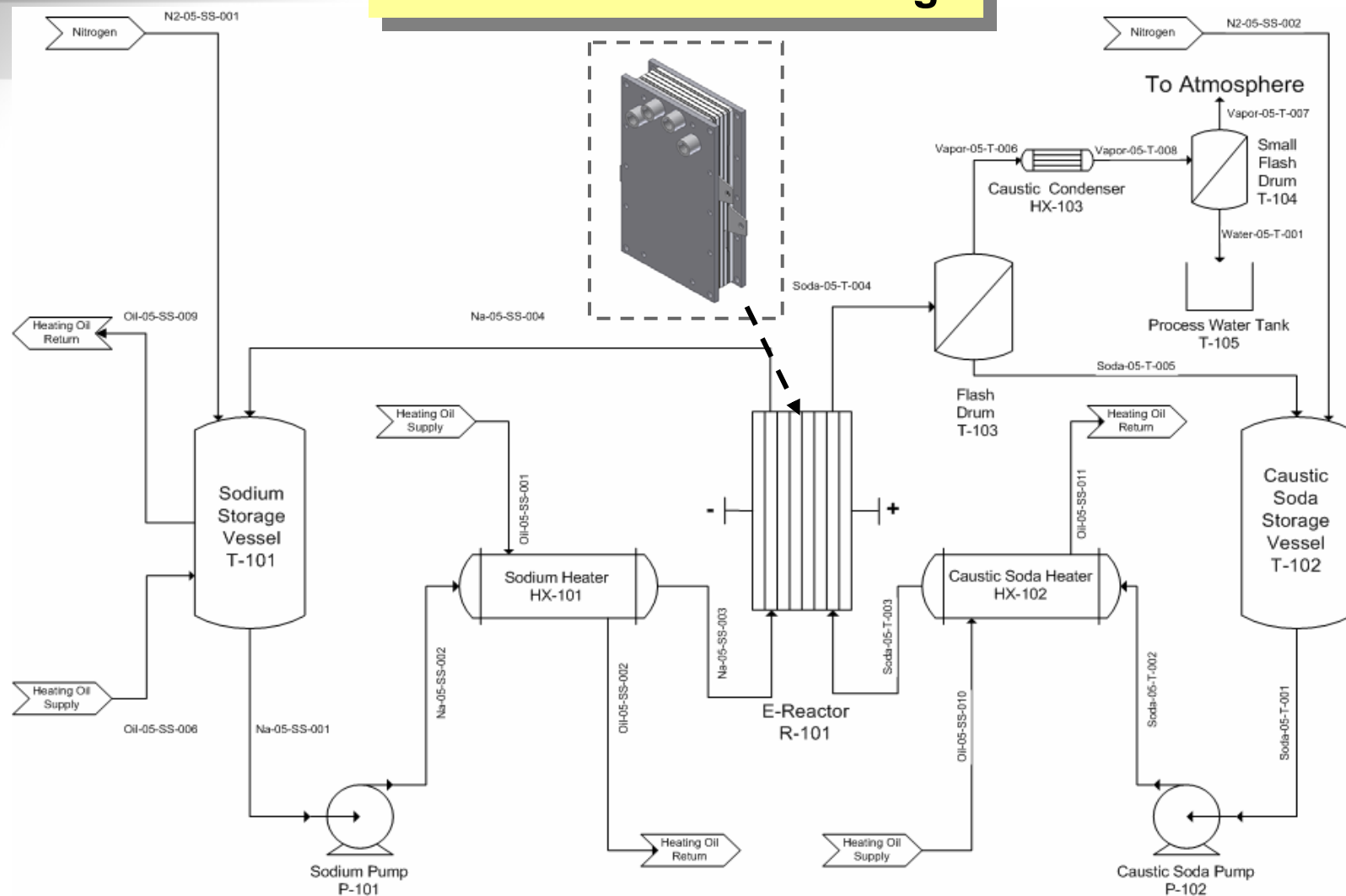
Preliminary Engineering



- Molten salt electrolysis requires converting spent fuel to anhydrous starting materials – high cost
- Aqueous electrolysis allows the direct use of spent fuel – low cost
- Trade-off: lower current density, therefore more membrane required

Process Flow Diagram

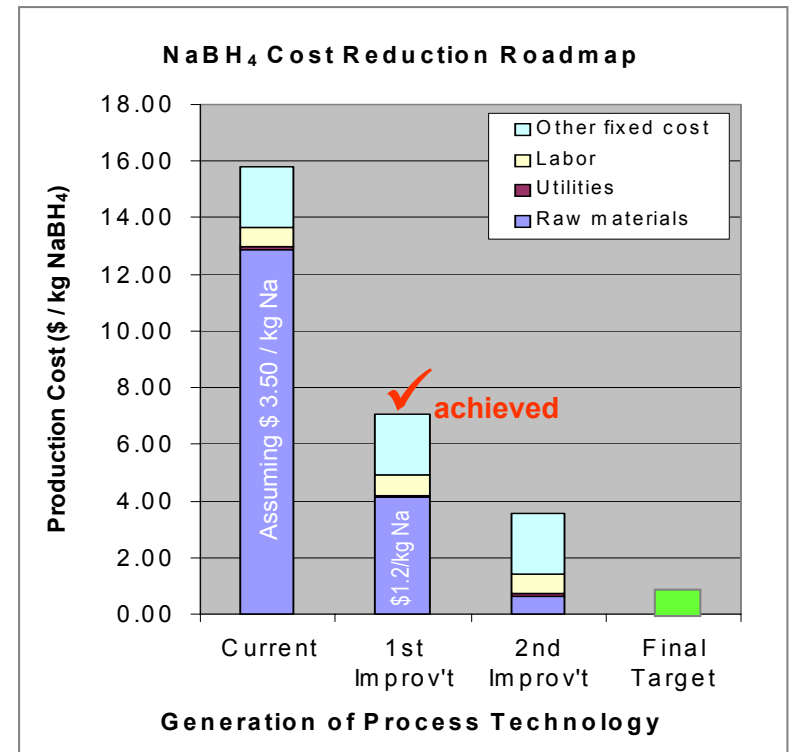
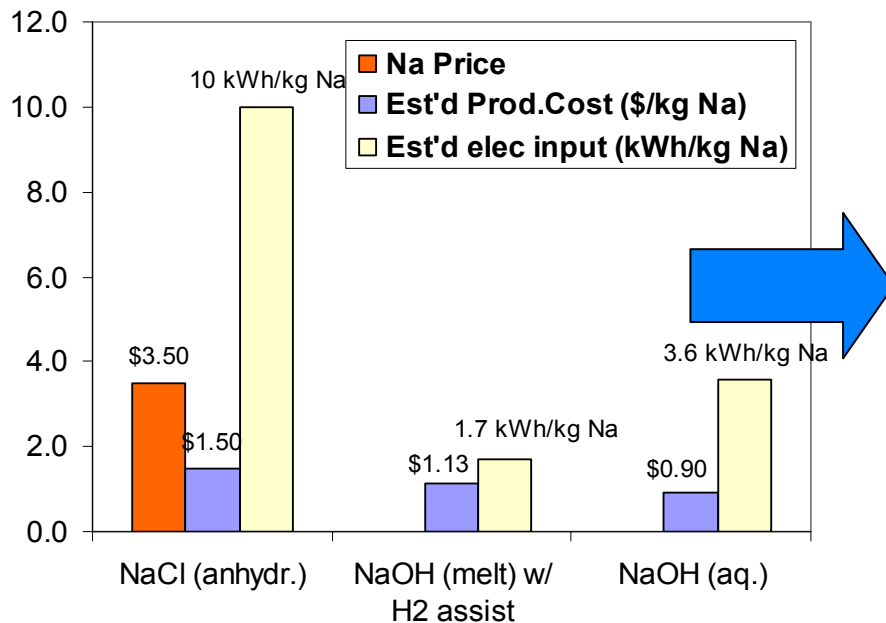
Initial Process Flow Design



Cost Reduction Summary

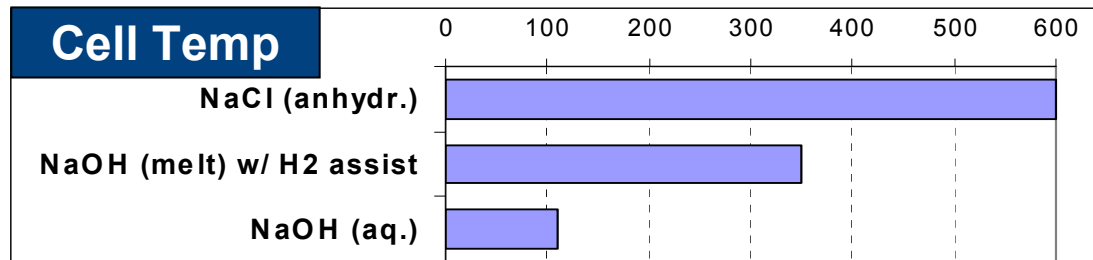
- Of the 3 options investigated, only the route via Na cost reduction is mature enough to allow for a reasonable preliminary cost analysis
- For the Na/B co-production route and the direct BH route, more data is needed on reaction yields and electrolytic efficiency before conducting cost analysis

Na Metal Production Cost via electrolysis of NaOH or NaCl



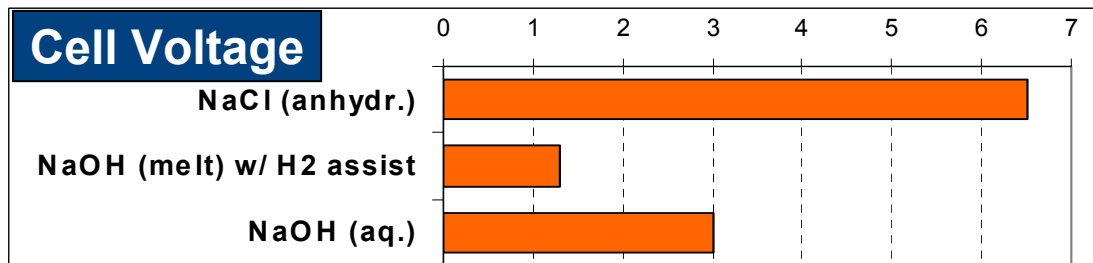
Improvements in Efficiency

Producing Na from NaOH instead of NaCl is more energy efficient

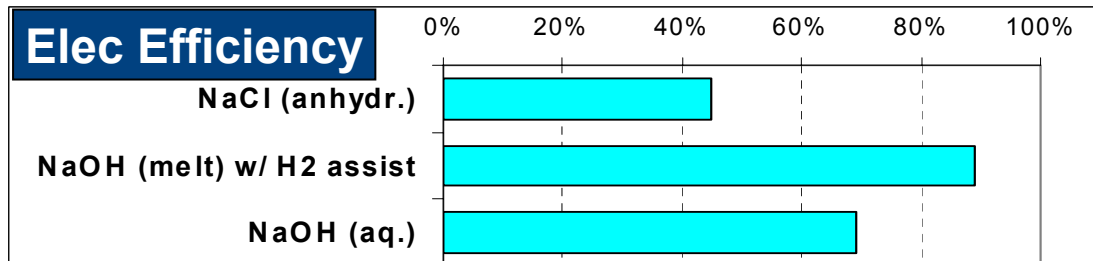


NaOH Electrolysis is

Lower in Temperature



Lower in Voltage



Higher in Efficiency

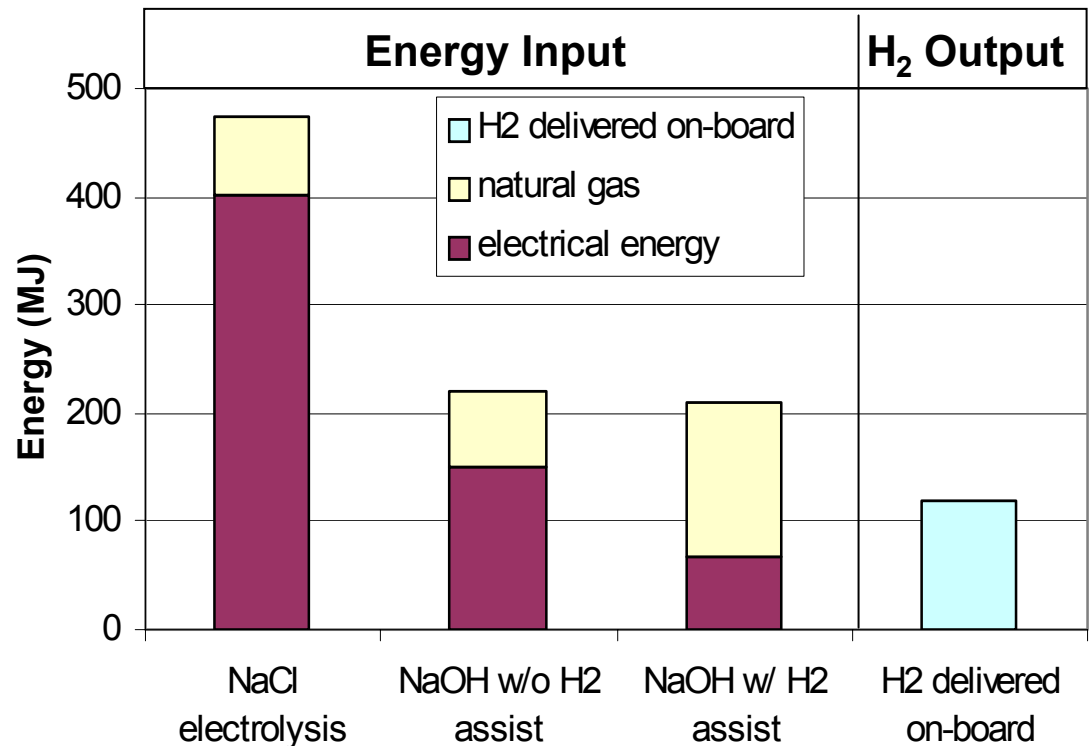
Comparison of Electrical Energy Input

	NaCl (anhydrous)	NaOH (Anhydrous)	Aqueous NaOH
Current efficiency	80 %	100 %	100 %
Voltage efficiency	56 %	90% (with H ₂ -assist)	70 %
Overall electrical efficiency	45%	90%	70%
Temperature	600 ° C	350 ° C	110 ° C
Cell Operating Voltage	6 - 7 V	2.8	4.2
Electrical energy input per kg Na produced	10 kWh/kg	1.6 – 3.6 kWh/kg	2.4 – 4.2 kWh/kg
Estimated Na production cost	\$ 1.57 /kg	\$1.22 /kg	\$0.90 /kg

Well-to-Tank Efficiency

Energy Input for the Production of NaBH_4 via 3 different methods of Na production

- The majority of the energy input is in the Na production*
- Producing Na by H_2 -assisted electrolysis dramatically reduced the upfront energy input in the NaBH_4 manufacturing process.*
- US production of Na metal uses hydro-electric energy almost exclusively, resulting in very little CO_2 emission.*



W-t-T Efficiency: 25% 54% 60%

Preliminary Engineering Assessment

- Continue materials chemical compatibility tests
- Complete HYSYS process modeling for the process
- Complete safety and hazard assessment

Membrane Testing

- Explore methods to increase current densities in borate electrolysis
- Additional experiments using other inexpensive sodium salts, e.g. borax or borate-caustic mixtures
- Long-term stability tests
- Equivalent quantitative experiments with NaSICON membranes
- Explore new electrochemical cell configuration

Preliminary Cost Assessment

- Complete cost assessment associated with electrolysis of borate
- Coordinate with TIAX

Project Go/no-go Decision with DOE

Summary

- After demonstration SBH regeneration cost reduction via NaOH electrolysis last year, further demonstrated feasibility of direct electrolysis of spent fuel (NaBO_2) to obtain precursors to SBH synthesis, namely Na metal and non caustic borates.
- Expanded the one-pot reaction of borohydride synthesis in medium temperature halide melt to room temperature ionic liquids.
- Initiated process engineering assessment in order to establish cost estimates of SBH regeneration
- Gained significant insight into the concentration sensitivity of the electrolytic processes, particularly its effect on various membranes
- Continue down the path of cost reduction and efficiency improvement

Highlights from the Safety Plan

- **Project hydrogen hazards:**
 - Use of hydrogen gas in laboratory-scale quantities
 - Explosive hazard due to improper cylinder handling and storage
 - Flammable gas leak hazard from hydrogen lines and delivery manifolds
 - non-pressurized use
 - fire hazard
- **Project safe-guards to deal with the hazards are:**
 - Regular and routine equipment inspection
 - Safety reviews prior to any new experiments
 - Cylinders are stored and used in well-ventilated areas separated from cylinders containing compressed oxygen or other oxidants
 - Utilize stainless steel manifolds that pass proper pressure and leak tests prior to use
 - Use only commercially-obtained pressure vessels in good condition, with suitable overpressure-relief valves
 - Air/oxygen will be purged from any vessel before hydrogen is added

Response to Previous Year Reviewers' Comments

- They need to make a system and run it using waste products and show us the full scope of energy and materials added. Then we will have evidence of progress.
 - During this past year, we have shown that our system does indeed run utilizing several sodium-containing waste products including: hydroxide, borate, and hydroxide-borate mixtures. We have also quantified the examples for hydroxide and borate.
- Cost of NaOH and impurities in NaOH should be considered. Investigate possible effects of impurities in NaOH.
 - The most common impurities found in NaOH are: Fe, Mg, Cl, K, and Na₂CO₃.
 - The effect of these impurities has already been considered. The ion selective membranes currently under study were partly chosen because they will not be 'clogged' by these impurities. Currently, these impurities do not detrimentally affect our process.
 - We also have the option to choose between vendors/suppliers which offer NaOH with either different or less impurities. The variation in cost will also depend on volume, demand, competition, market, and transportation. Therefore the current cost estimates for NaOH are adequate.

Response to Previous Year Reviewers' Comments

- Determine total energy required for "one-pot" synthesis. Any use for Br?
 - Premature to conduct total energy calculation
 - However, a crude calculation may be performed using a cell voltage between 4–5V at ϕ 5-8/kWh with a current efficiency of 95%. Electricity will cost \$0.75-1.20/kg SBH. Assuming that hydrogen feed costs between \$0.80/kg and \$1.20/kg H₂, adding \$0.09-0.13/kg SBH, giving a cost range of \$0.98/kg – \$1.33/kg SBH.
 - The Br is less important. We can choose different anode redox couples such as O₂. New results from using ionic liquids rather than the bromide melt will alleviate the need to consider bromine.
- It is recommended to bring up the go/no-go decision point once the system analyses work is completed. It is also recommended to give the system analyses work on this concept a higher priority to accelerate the decision point.
 - Estimated to be completed by August 2006.
 - TIAX is conducting regeneration cost analysis in a separate effort
- Complete the project scope as stated, especially economic feasibility study relevant to the processes developed.
 - Currently underway.

Response to Previous Year Reviewers' Comments

- Please clarify the hydrogen storage capabilities of sodium borohydride.
 - $1 \text{ NaBH}_4 \rightarrow 4 \text{ H}_2$, therefore, H_2 generated is equivalent to 21.3% of NaBH_4 's weight.
 - With consideration of water: $1 \text{ NaBH}_4 + 2 \text{ H}_2\text{O} \rightarrow 4 \text{ H}_2$, therefore, H_2 generated is 10.9% of the total borohydride + water weight
 - Other concentrations: 20 wt% \rightarrow 4.2% H_2 , 30 wt% \rightarrow 6.4% H_2 .
 - On the system storage level: 3.9% demonstrated, 4.5% targeted for now
- Need to correct well-to-tank analysis. Suggest using overall US mix for electrical generation efficiency/ CO_2 .
 - Currently TIAX and Argonne National Laboratory have been tasked by the DOE to provide accurate up-to-date energy efficiency and economic investigation and validation. We are working closely with them.
- Even though the energy and economic analysis was reported out to DOE, a summary of that analysis should be included in future presentations.
 - A summary of the energy and economic analysis reports would require significant effort to generate. We have chosen instead to focus our effort on the tasks committed in the Statement of Work. However, a very brief summary is included in this presentation (page 24).

Filed Patent Applications

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

Presentations

1. “New Electrolytic Synthesis of Borohydride Anions from Boron Oxide in a Molten Salt Melt” Presentation by Michael Kelly, Ph.D. ACS Fall National Meeting, Washington, D. C., August 28, 2005

Critical Assumptions and Issues

- **Cost of electricity**
 - The cost of electricity may vary, assumed to be \$0.05-0.08/kWh in present study.
- **Energy efficiency**
 - Upon scale-up, it will be important to keep the efficiency optimized and not lose any energy as a result of the system engineering.
- **Cost reduction**
 - Assumed same performance results will be obtained upon scaled-up.
- **Materials compatibility and stability**
 - Assumed that materials under current study will not require unreasonable frequent replacement.
 - Assumed currently identified process safety risks can be managed without exorbitant costs
- **Isolation/separation and utilization of products**
 - Isolation and separation steps and their costs have not been considered in detail.
 - Further process simplification and integration are expected to reduce the need for such steps.

Acknowledgements

- DOE
 - Grace Ordaz, James Alkire, Sunita Satyapal
- Air Products and Chemicals
 - Edward Heydorn, Jianguo Xu
- Princeton
 - Andrew Bocarsly, Jonathan Mann (Student)
- TIAX
 - Steve Lasher, Stefan Unnasch, Mark Marion