

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

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# Overview

Project Team	Barriers
<p><b><u>Millennium Cell</u></b>            Ying Wu, Ph.D.            Mike Kelly, Ph.D.            Jeffrey Ortega, Ph.D.            Todd Randall</p> <p><b><u>Air Products and Chemicals</u></b>            Jianguo Xu, Ph.D.            Xiaoping Gao, Ph. D.            Guido Pez, Ph.D.            Sergei Ivanov, Ph.D.            Keith Campbell</p> <p><b><u>Consultant</u></b>            Andrew Bocarsly, Ph.D.            Princeton University</p>	<p><b>A.</b> Cost  <b>C.</b> Efficiency  <b>G.</b> Life Cycle and Efficiency Analyses  <b>Q.</b> Regeneration Processes for Irreversible Systems  <b>R.</b> By-Product Removal  <b>Other:</b> Applicable to Off-Board Delivery and Storage</p> <p style="text-align: center;"><b>Budget</b></p> <p>Total project funding: \$4.5 MM, 3 yrs            DOE share: \$3.6 MM            MCEL share: \$0.6 MM            APCI share: \$0.4 MM</p> <p>Funding received in FY04: \$1.1 MM            Funding for FY05: \$1.2 MM (\$ 0.5 MM obligated)</p>

# Overview of Project Objectives

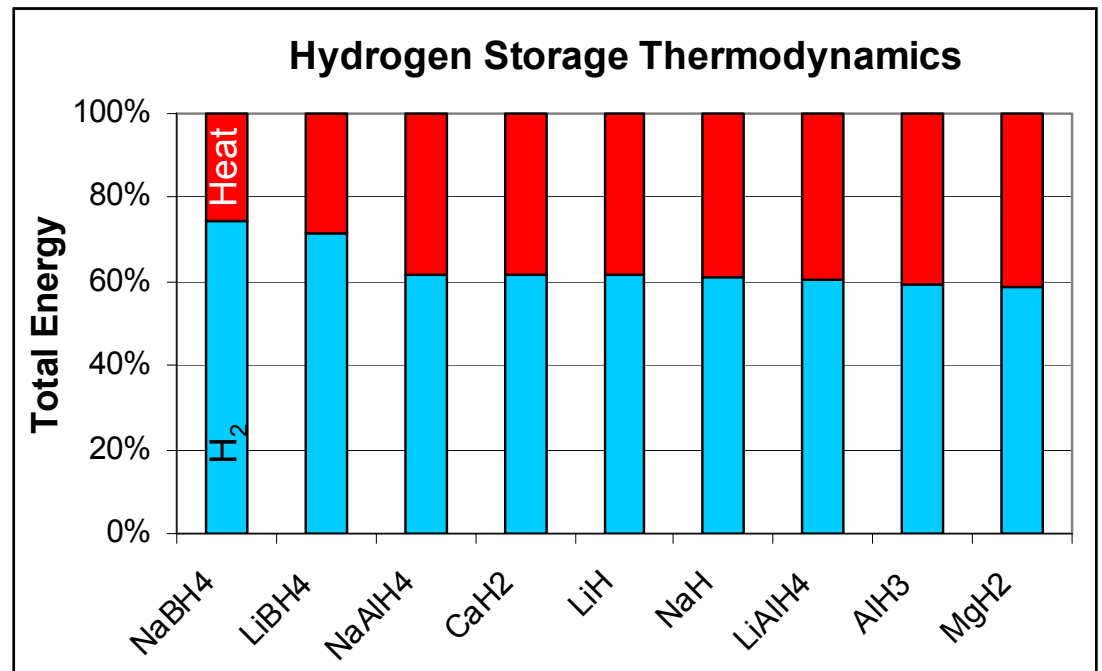
Barrier	Project Objectives
A. Cost	Develop a reliable regeneration process for NaBH <sub>4</sub> that significantly lowers its cost and meet DOE Cost Targets
C. Efficiency	Improve overall energy efficiency by developing a more thermo-neutral re-generation pathway. Demonstrate feasibility of achieving ~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 <sub>4</sub> .
R. By-Product Removal	Develop a process that re-use the hydrogen generation by-product NaBO <sub>2</sub> , thereby completing the recycling loop.

# NaBH<sub>4</sub> Hydrolysis Has the Lowest Heat of Reaction Among Many Common Hydrides

More favorable thermodynamics compared to hydrolysis of other common chemical hydrides

A higher percentage of stored energy is converted to H<sub>2</sub>

NaBH<sub>4</sub> can also be considered for off-board H<sub>2</sub> storage



Storage Capacity				
	20% solution		solid	
	Material-only	System	Material-only	System
Grav. (wt%)	4.3 wt%	1.2-2.2 wt%	21.6 %	TBD
Vol. (g/L)	42 g/L	14-20 g/L	148 g/L	TBD

# Project Timeline

Tasks	Jan. 1, 2004 – Dec. 31, 2004				Jan. 1, 2005 – Dec. 31, 2005				Jan. 1, 2006 – Dec. 31, 2006			
	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
<b>Task 1.0</b> Assessment of Options	■		7/31/04									
<b>Task 2.0</b> Investigate 3 pathways		■										
<b>Down-select Decision:</b> Select best pathway to proceed												
<b>Task 3.0</b> Prelim. Eng. and Econ. Study						■						
<b>Go/No-go Decision:</b> Select best pathway to proceed												
<b>Task 4.0</b> Lab Prototype Demo Unit									■			
<b>Task 5.0</b> Project Mgmt and Reporting		■										



## Criteria:

Technical feasibility to reduce  $\text{NaBH}_4$  production cost by  $> 2x$

Sufficiently address technical and engineering risks;  
Satisfy economic assessment criteria for commercialization.



# Year-1 Objectives Were Achieved by Investigating 3 E-chem Pathways to Lower NaBH<sub>4</sub> Manufacturing Cost

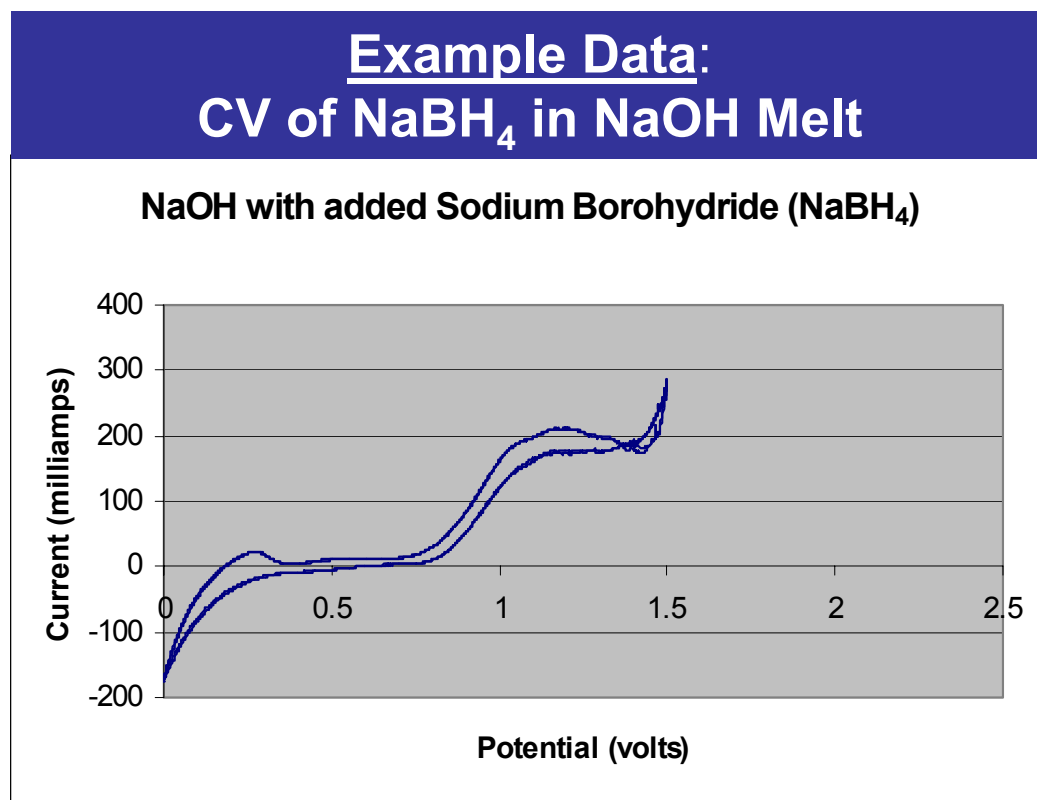
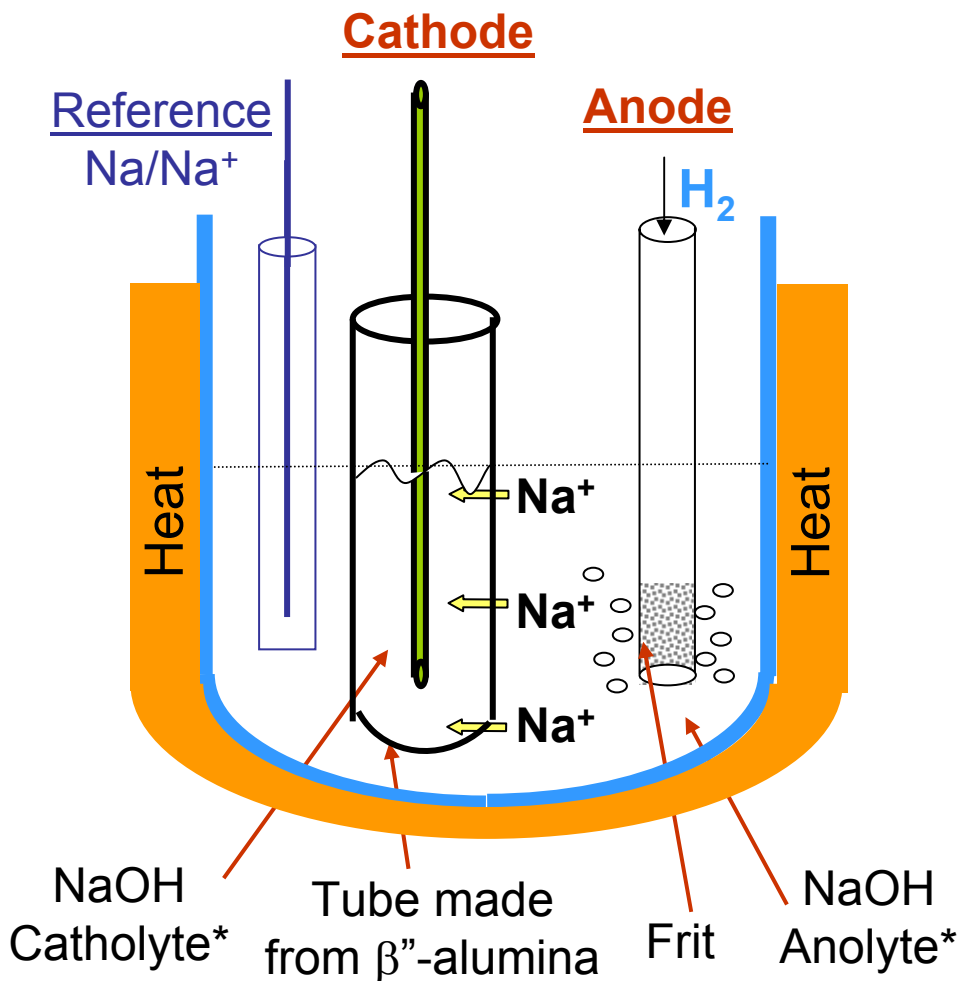
## Summary of Technical Approach

1. Direct borate reduction
  - Direct electro-synthesis of B-H from B-O
  - Hydride transfer electro-catalysts
2. Na cost reduction effort to lower raw material cost
  - Hydrogen-assisted electrolysis
  - Cell and Electrode design optimization
3. Na and H<sub>3</sub>BO<sub>3</sub> co-production effort
  - Extensive process integration to lower cost

## Summary of Year-1 Accomplishments

- Achieved one-pot synthesis of NaBH<sub>4</sub> from borate starting materials
- Demonstrated a highly efficient Na production process that will lower NaBH<sub>4</sub> production cost by a factor of ~ 3
- Demonstrated feasibility of Na metal synthesis from inexpensive, recycled aqueous NaOH
- Developed a number of NMR, IR methods for the characterization and quantitative determination of NaBH<sub>4</sub> and other boron-containing compounds

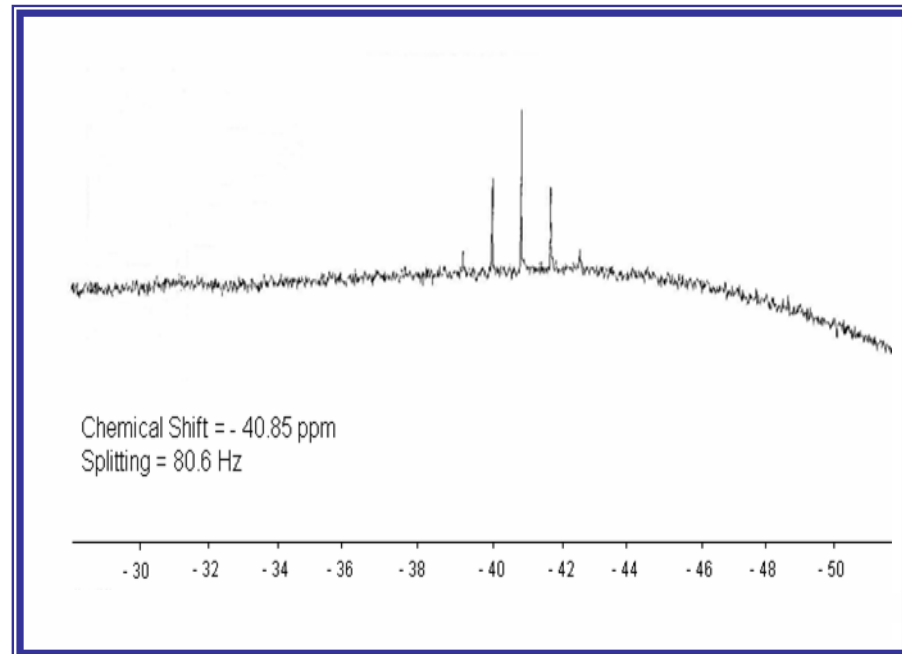
# Schematics of the Experimental Cell



Note: Catholyte and anolyte may contain other species

# Pathway #1: One-Pot Synthesis of $\text{NaBH}_4$ Was Achieved in a Bromide Melt

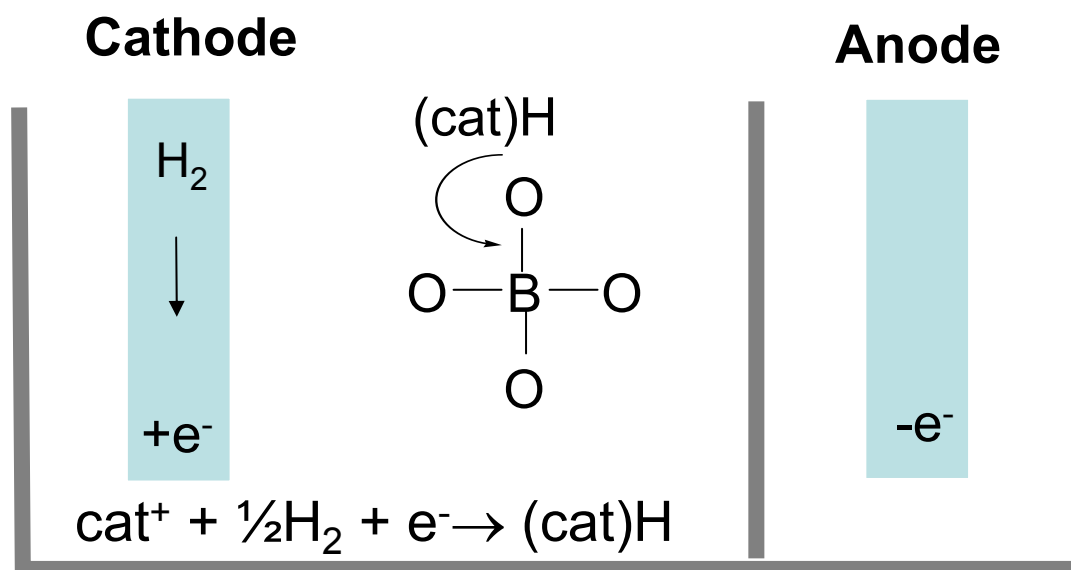
- Previous failure to make B-H in molten hydroxides led us to consider a less basic melt system more conducive to borate reduction
- A molten halide electrolyte containing  $\text{Li}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$  was used as the reaction medium.
- Simultaneous application of  $\text{H}_2$  gas and suitable potential generates LiH in the cathode compartment *in situ*
- When borate is also present in the catholyte, the reaction between LiH and the borate species results in  $\text{BH}_4^-$
- Net Reaction:  $2 \text{B}_2\text{O}_3 + 2 \text{H}_2 + 4 \text{LiBr} \rightarrow \text{LiBH}_4 + 3 \text{LiBO}_2 + 2 \text{Br}_2$
- **Best yield to date is 8.3%, based on current efficiency**
- **$\text{BH}_4^-$  Synthesis in Bromide Melt was Verified by  $^{11}\text{B}$  NMR**





# Alternative Hydride Transfer Electro-Catalyst Scheme Was Investigated

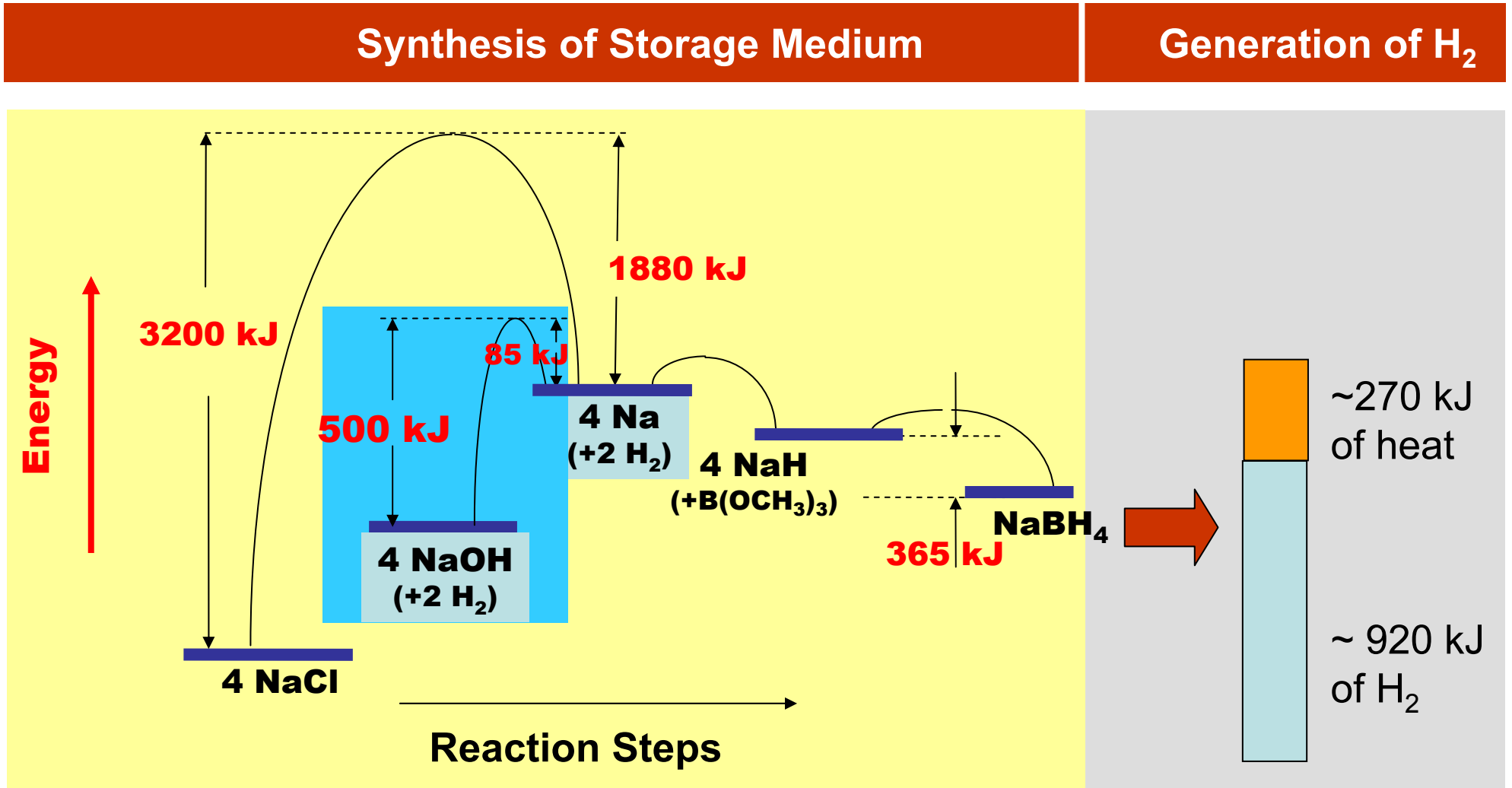
- Direct conversion of B-O to B-H
- Reducing agent is made *in situ* directly from H<sub>2</sub> gas
- Hydride transfer from the catalyst to boron occurs in the catholyte
- Catalyst regeneration occurs at the cathode using H<sub>2</sub> and e<sup>-</sup>
- Reaction performed in either a molten salt or organic solvent
- Monitor reaction products by <sup>11</sup>B and <sup>1</sup>H NMR



# Experimental Feasibility of Hydride Transfer Catalyst Scheme Remains Elusive

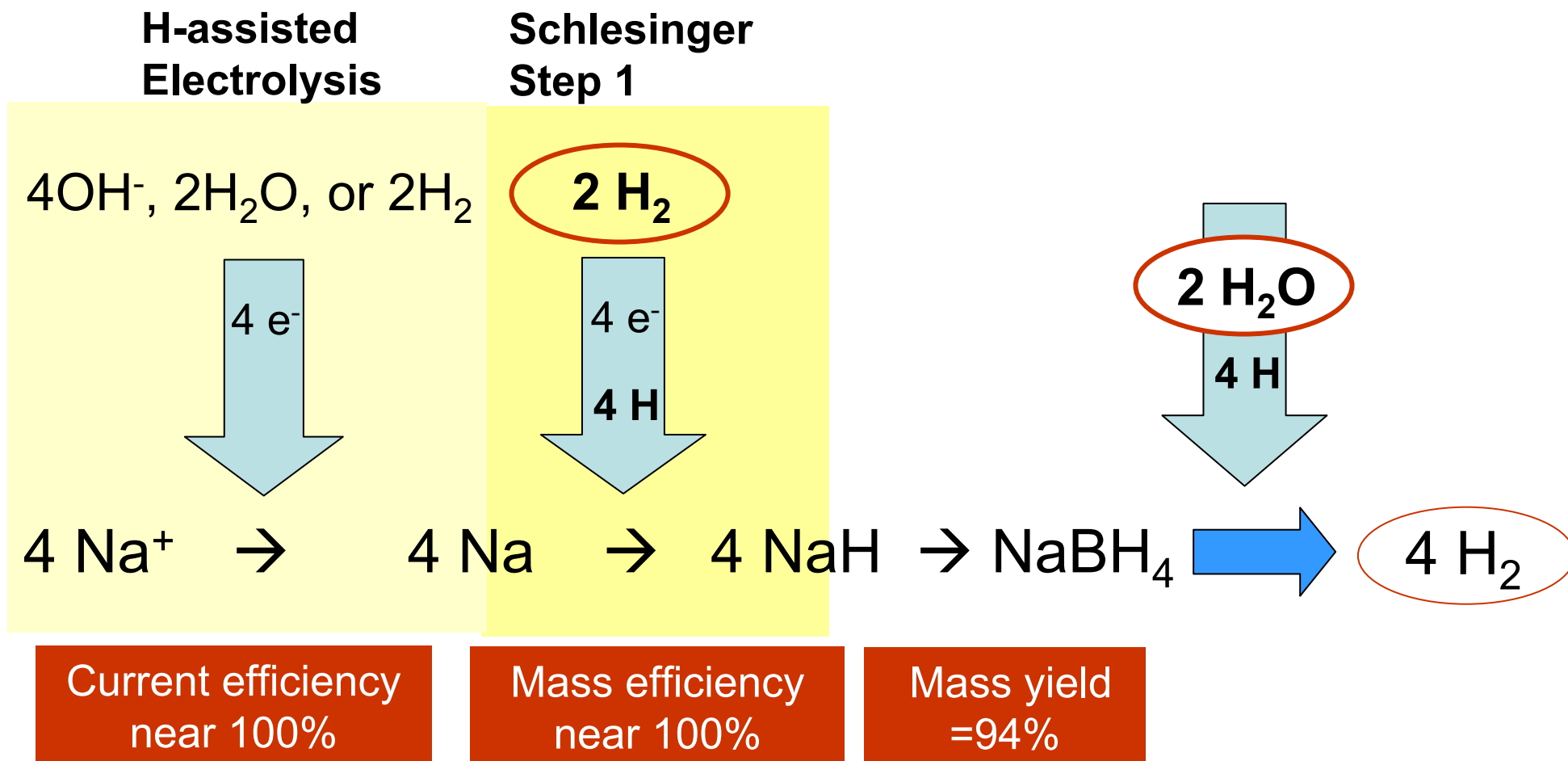
- A handful of catalyst candidates have been screened to date; reaction chemistry as well as electrochemistry are complex
- MCEL employed mostly NMR techniques to analyze products post reaction, while APCI developed an IR (ATR) method to detect B-H products *in situ*.
- Organic solvent presents significant limitations on conductivity in the cell
- Corresponding anode reaction proved challenging to characterize

# Pathway 2: Indirect Route via More Efficient Na Production Process



In order to store 4 moles of H<sub>2</sub>, one needs 4 H<sub>2</sub> + 500kJ of electricity.

# H and Electron Balance

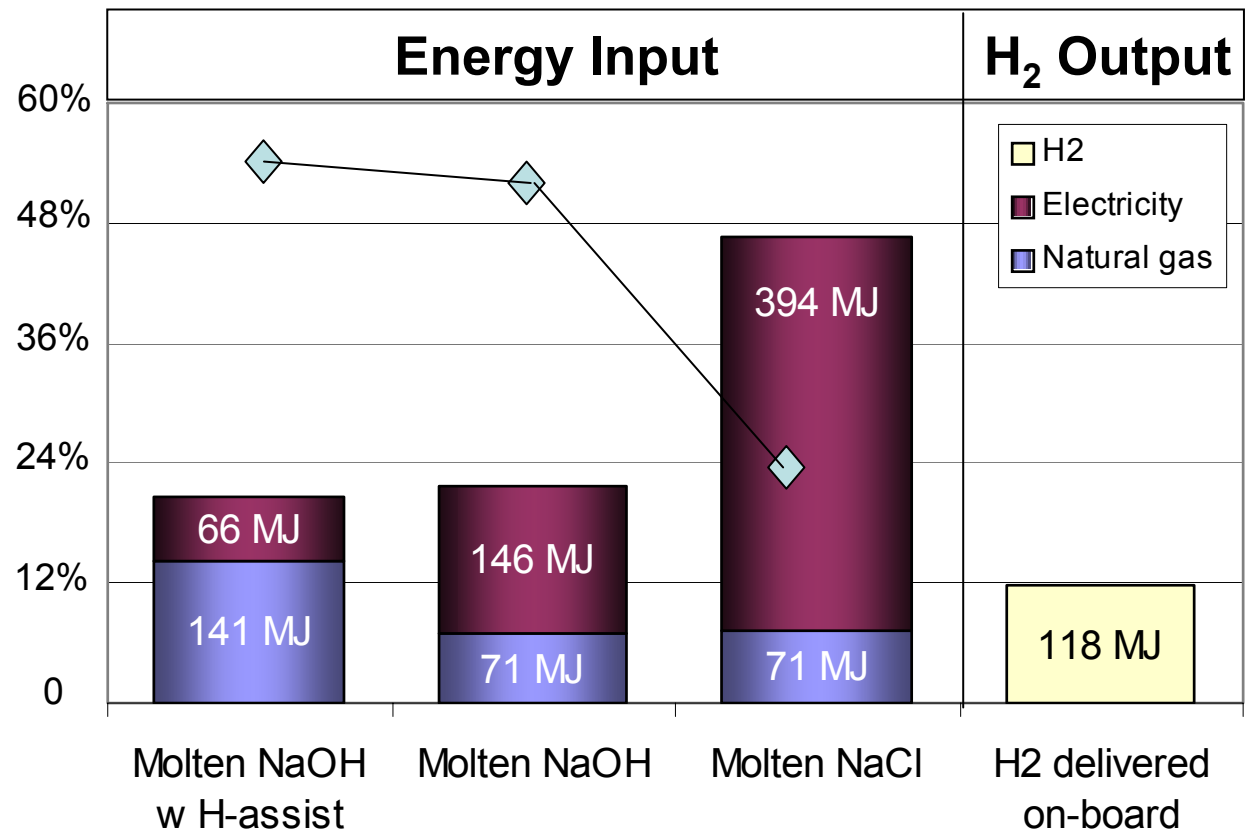


- If H-assisted electrolysis is not employed, the first 4 e<sup>-</sup>'s come from 4OH<sup>-</sup> or 2H<sub>2</sub>O within the melt or aqueous solutions respectively.
- In all cases, electricity is used to increase the energy of electrons.

# Well-to-Tank Efficiency Analysis

## Energy Input for the Production of NaBH<sub>4</sub> via 3 different methods of Na production

- *The majority of the energy input is in the Na production*
- *Producing Na by H<sub>2</sub>-assisted electrolysis dramatically reduced the upfront energy input in the NaBH<sub>4</sub> manufacturing process.*
- *US production of Na metal uses hydro-electric energy almost exclusively, resulting in very little CO<sub>2</sub> emission.*

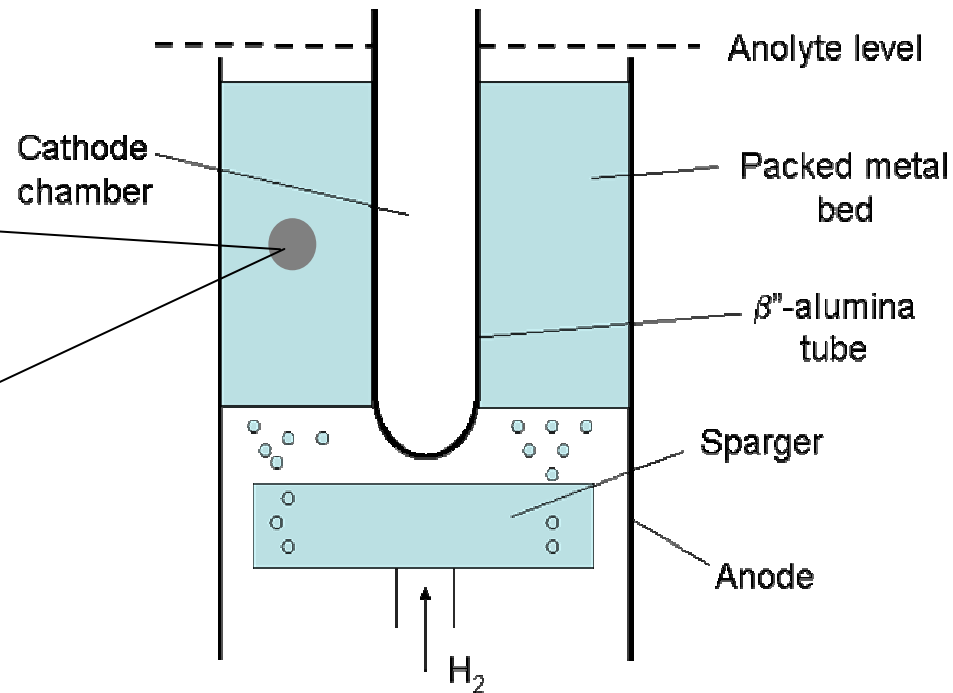
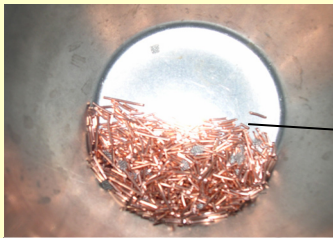


**W-t-T Efficiency: 57% 54% 25%**

# High Reaction Efficiencies Were Achieved by Improving Cell and Electrode Design

Last year, we demonstrated experimental feasibility

Metal packing to optimize 3-phase mixing

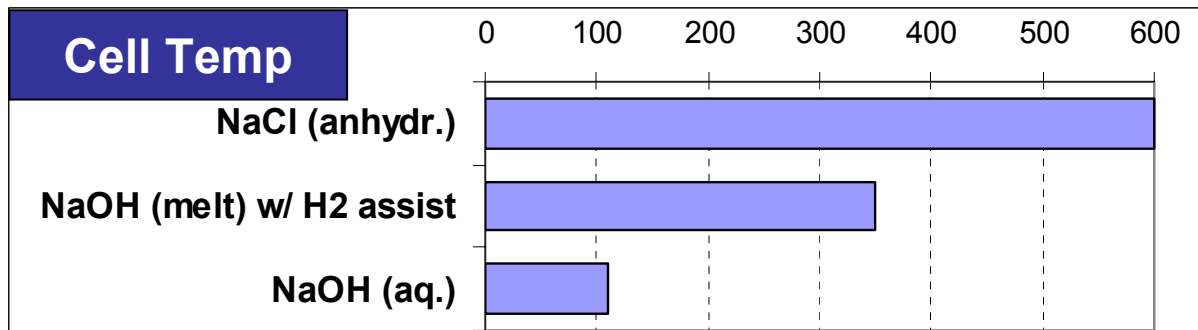


This year, we achieved improved current efficiency, voltage efficiency, and current density was determined to establish commercial feasibility

- Current Efficiency : 96-100%
- Voltage Efficiency: 90%
- Current Density = 240 mA/cm<sup>2</sup>  
(measured at 83% voltage efficiency)
- The experimental results allowed for realistic evaluation of energy requirements for Na production, and thus for NaBH<sub>4</sub> production

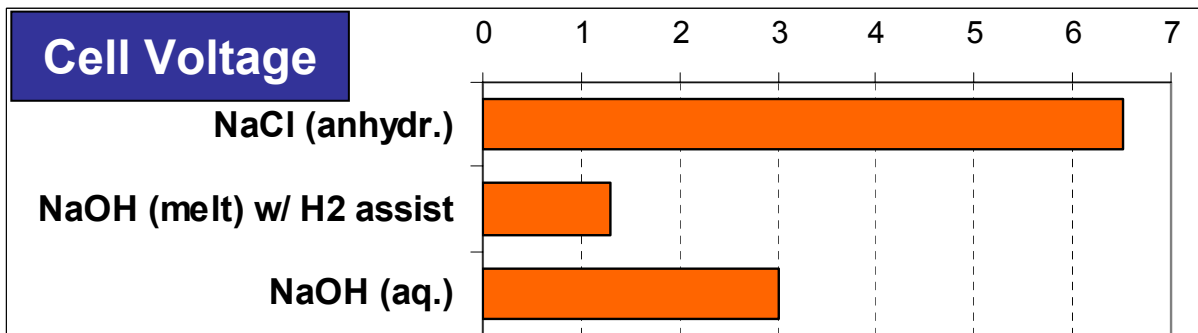
# Reaction Parameter Comparisons

Producing Na metal from NaOH instead of NaCl results in significantly lower electricity consumption with much improved energy efficiency

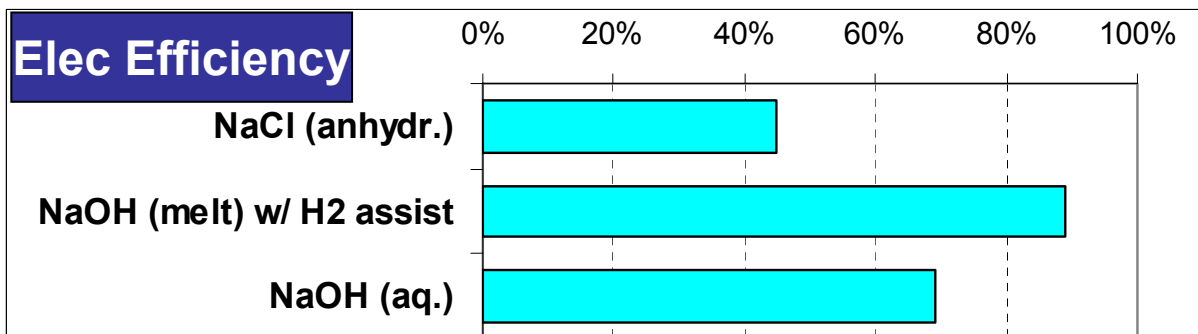


NaOH Electrolysis is

Lower in Temperature

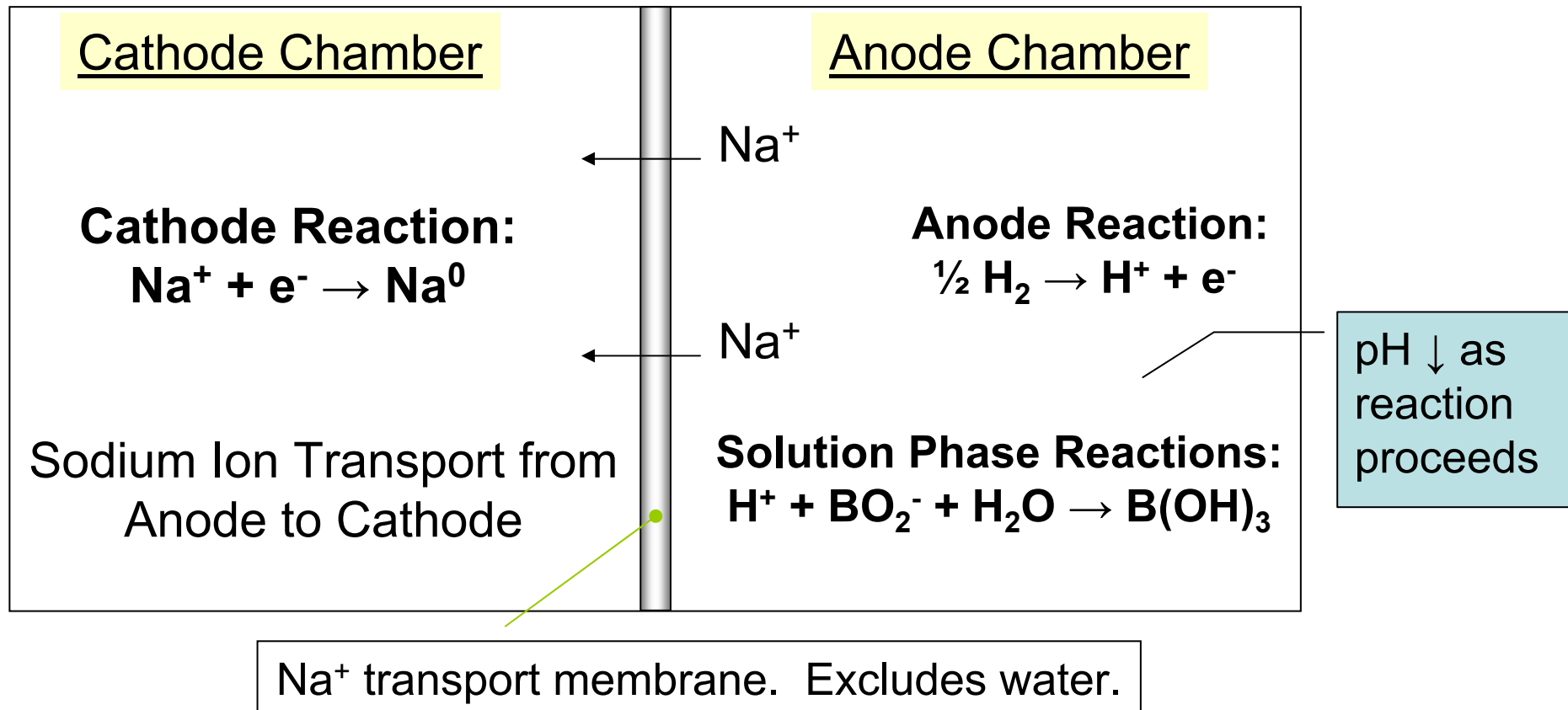


Lower in Voltage



Higher in Efficiency

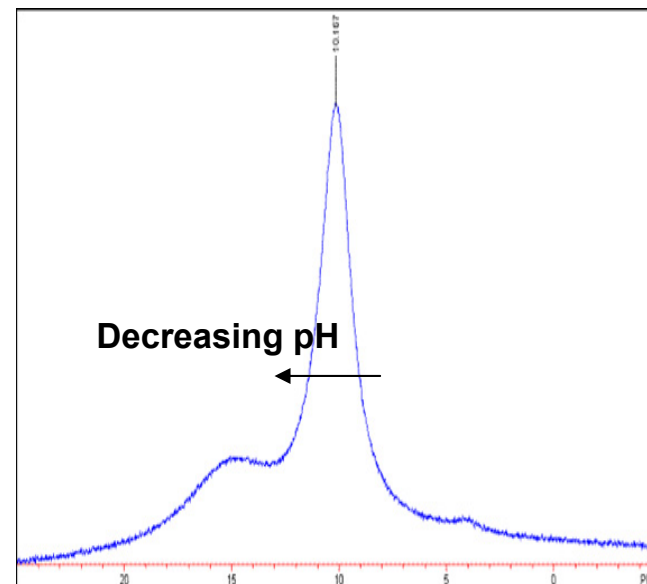
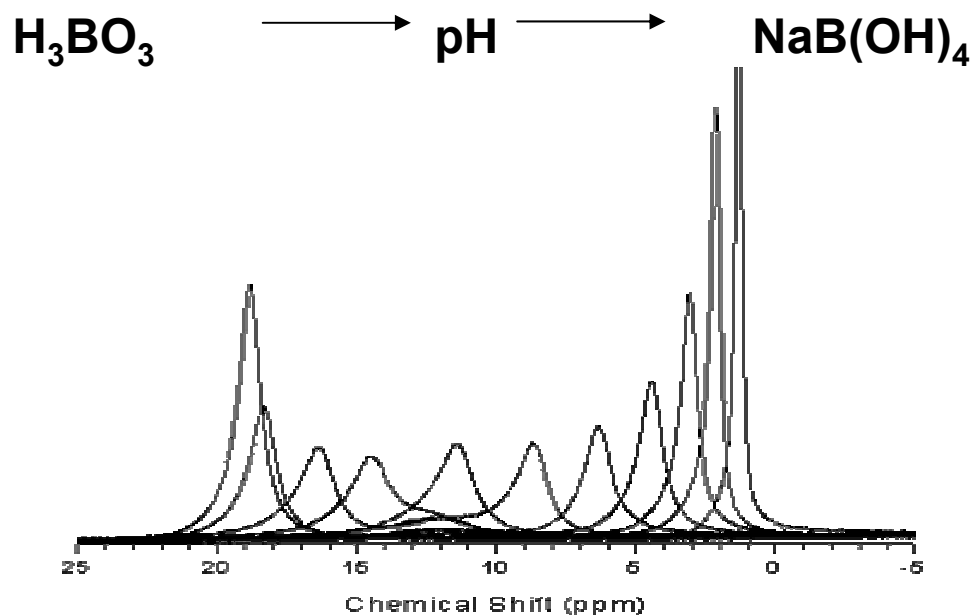
# Pathway #3: Further Process Cost Reduction Can Be Achieved by Co-Production of Na and B(OH)<sub>3</sub>



Data collection in progress to quantify magnitude of cost reduction



# Formation of Low-pH Borates Was Characterized by Shift in $^{11}\text{B}$ NMR Peaks



Chemical shift of borate species as a function of basicity. A calibration curve allows the quantitative determination of anode product and current efficiency

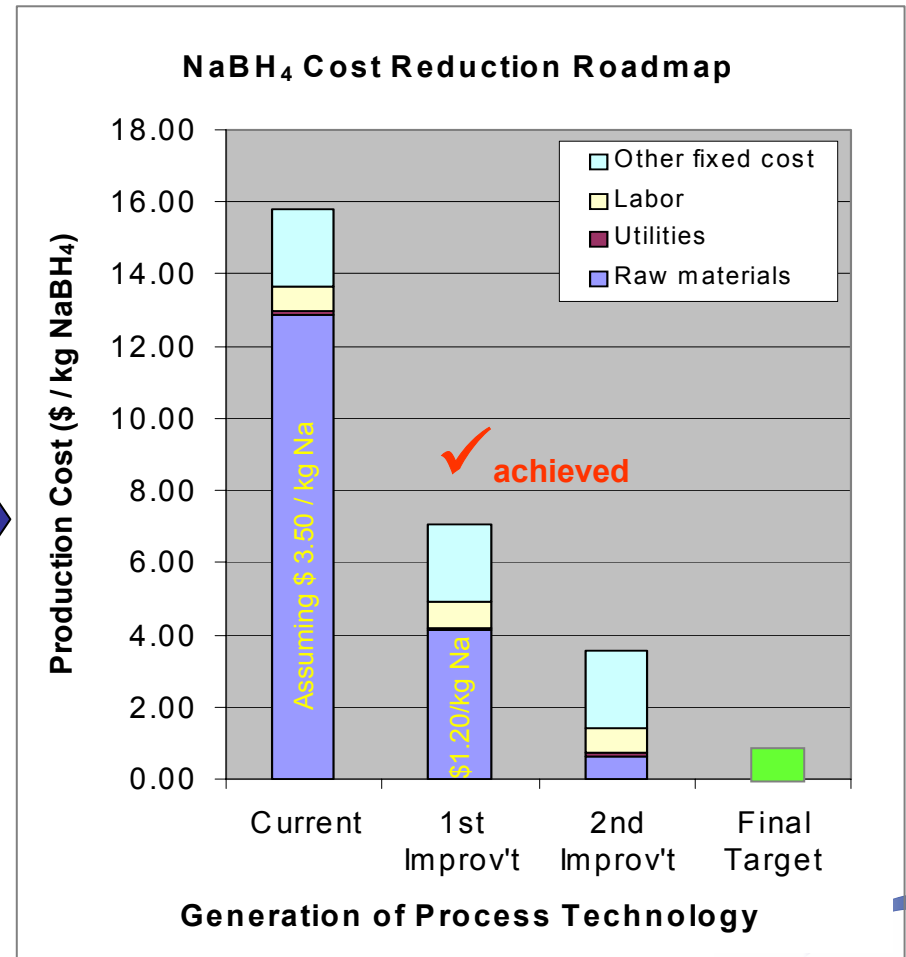
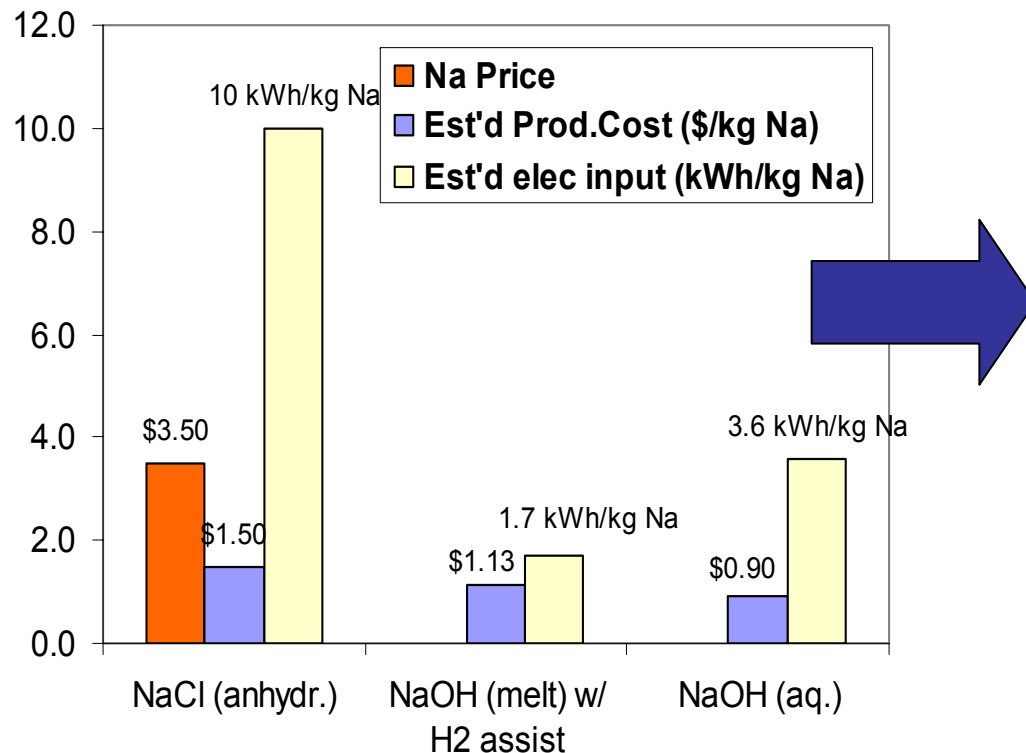
A sample of solution taken after electrolysis using sodium selective membrane shows conversion of  $\text{NaB}(\text{OH})_4$  into  $\text{B}(\text{OH})_3$

When the reaction was stopped at 50% theoretical conversion point, product analysis from NMR indicates 54% conversion, and coulometry suggests 49% conversion.  $\rightarrow$  **High Efficiency**

# Cost Reduction in Na leads to Significant Savings in NaBH<sub>4</sub> Regeneration Cost

- 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



# Project Status Summary

Experimental Pathways		Issues	Action/Plan
1	Na Improvements NaOH melt, H <sub>2</sub> assisted NaOH, aq.	<ul style="list-style-type: none"> <li>Cell and electrode designs to maximize current density and performance</li> <li>Long-term membrane stability</li> </ul>	Combine Efforts and Continue with Engineering R&D, Economic Analysis
2	Na/B Separation Molten Aqueous	<ul style="list-style-type: none"> <li>Demonstrate Na metal production at low temperature</li> <li>Long-term membrane stability</li> </ul>	
3	B-O to B-H Ionic Liquids Organic solvents	<ul style="list-style-type: none"> <li>Only small amounts of B-H formation was observed in inorganic melt system.</li> <li>No B-H formation was observed in organic solvent systems.</li> </ul>	Stop

# Future Work – Year 2 (FY05) of Project

- Investigate technical uncertainties still outstanding
  - Membrane material stability
  - Electrode material stability
  - Optimize hydrogen gas electrode
  - Determine product purity, etc.
- Conduct Preliminary Engineering Study
  - Develop process specification
  - Develop process flow diagrams
  - Develop Process Demonstration Unit (PDU) designs for Year 3
- Conduct Economic Feasibility Study
  - Develop assumptions and inputs to the economic study
  - Establish criteria and key parameters
  - Conduct scenario analysis and sensitivity analysis

# Reviewers' Comments

2004 DOE APR

- ... **May need to consider changing the direction from electrolytic regeneration of borate to borohydride to using a completely different approach for the regeneration.**
- *Electrochemical Regeneration Pathways were chosen after careful evaluation of a large number of thermochemical pathways.*
- *We also investigated a number of electrochemical options and arrived at the conclusion that more energy and cost efficient raw materials production has the highest potential to realize real and significant cost reduction in  $\text{NaBH}_4$*
- *Electrochemical methods DO provide improved energy efficiencies. Our analysis on overall energy efficiency demonstrates the efficiency advantage of our approach. our current project direction is sound.*
- ... **to provide specific estimates on overall energy efficiency of regeneration cycle: theoretical and measured**
- ... **Need to develop an accurate estimate of the full fuel cycle efficiency and cost**
- ... **Figure out the energy cost of hydrogen in the Na process so you know exactly where you have to lower the voltage to equal the existing process.**
- ... **Need to include the energy contained in the  $\text{H}_2$  at the anode in the efficiency calculations.**
- ... **Needs overall energy balance - need to include energy required to make input  $\text{H}_2$  and electricity.**
- *Completed, and results reported.*

# Reviewers' Comments

2004 DOE APR

- ... Perform experiments that might disprove the one step process early so resources are not wasted if this is indeed an unlikely path.

- ... Need to demonstrate direct reduction in one step.

*One-pot reaction in the halide melt proved the feasibility of a more direct pathway to  $BH_4^-$ , but low yields prevent us from declaring it a clear winner;*

*Electrolytically generated hydride transfer catalyst route has shown some indication of B-H formation with a suitable catalyst, but more confirmation is needed before it can be considered conclusive*

*We have shown that direct reduction of borate in a hydroxide melt was not likely to be a fruitful path;*

- ... They need to have partners whose core business is in  $NaBH_4$  regeneration from sodium borate.

- ... Consider realigning this program with the work executed at the Chemical Hydride Center of Excellence.

*Continued discussions with Rohm and Haas, world's largest producer of  $NaBH_4$ ,  
Collaboration under the DOE Center of Excellence for Chemical Hydrogen Storage*

# Reviewers' Comments

- Tech Team Review -

- ... Why did MCEL chose the NaOH melt first and should have known the issues, rather than going with the bromide right away? Are there other issues?

*We did not start with the bromide system because we anticipated that bromine generation would be an issue. It made sense to start with NaOH because it was a NaBH<sub>4</sub> stabilizer in the aqueous solution. We did not know from the start that borohydride was not stable in NaOH melt. However, the stability issue was solved. It was not predictable in the beginning that the B center was not electrochemically accessible in the NaOH melt. It was a good learning process to go through the NaOH melt first. Also the spent fuel contains hydroxide, so to be able to carry out the electrolysis in a hydroxide melt has some advantages.*

- ... The discrepancy in the cost reduction slide (bar chart)- showing a low percent reduction in Na cost leading to a large reduction in overall cost was also discussed. Please show the labor/capital costs and resolve this discrepancy.

*The cost reduction in Na shown on the slide was from ~\$1.50/kg to ~\$0.70/kg, or roughly a 2x reduction. The cost reduction in NaBH<sub>4</sub> started with Na raw material costing \$3.50, which is the purchasing price a borohydride manufacturer would pay, not the production cost shown in the first slide. Because of this added profit margin, there is a larger than 2x reduction in borohydride cost when Na manufacture is integrated with borohydride manufacture. There are other differences in capital cost assumptions that affected the calculations.*

# Reviewers' Comments

- Tech Team Review -

- ... There was more discussion on the efficiency questions- efficiency reported is not exactly well to tank efficiency (efficiency for making electricity needed was not shown).
- *learn from the assumptions used by people studying electrolyzers.*
- ... Also, the point about how much electrical energy input per H<sub>2</sub> (i.e., for one molecule, how many electrons required) and balancing the electrochemical equation came up again. Showing energy and material balance is essential.
- *Addressed earlier in this presentation*
- ... It was suggested that all PIs consider the slides shown by Safe H<sub>2</sub> breaking down key steps/components line by line (for both capacity and efficiency) and present similar information.
- *Process efficiency from primary energy to NaBH<sub>4</sub> synthesis was reported in the quarterly report dated Oct.31, 2004.*



# Supplemental Slides

# Patent Applications Filed Under this Cooperative Agreement

- “Hydrogen-Assisted Electrolysis Processes” (MCEL, APCI)
- “Synthesis of Borohydride in Halide Melt” (MCEL)
- “Process for the Production of Alkali Metals in Stacked Electrolytic Cells” (MCEL)
- “Electrolytic Process for the Separation of Boron and Sodium” (MCEL)
- “Synthesis of Boron Hydrides in Ionic Liquids” (MCEL)

# Hydrogen Safety

The most significant hydrogen hazard associated with this project is:

Utilization 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

# Hydrogen Safety

Our approach to deal with these 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 documented manufacturer's pressure rating and temperature limits, and suitable overpressure-relief valves
- ❖ Pressure of hydrogen admitted to vessels will be limited to 80% of the rated pressure at the temperature of use
- ❖ Air/oxygen will be purged from any vessel before hydrogen is added
- ❖ Pressurization and venting operations will be performed in a well-ventilated hood with all ignition sources and other flammable materials removed
- ❖ Apparatus for admitting hydrogen to any vessel will be designed so that the hydrogen flow can be interrupted by a valve, which makes any fire self-extinguishing without risk of flashback or "sucking back" air to make an explosive mixture