Hydrogen Generation Via Sodium Borohydride

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Outline

- Millennium Cell – Company overview / background
- Hydrogen storage via sodium borohydride:
  - Description of hydrogen generation reaction
  - Gravimetric/volumetric storage density
- Technology applications and performance data:
  - Portable/Backup Power
  - Transportation
- Basic approach to regeneration of sodium borohydride:
  - Transportation strategy
- Conclusions
Company Overview

- A development stage, intellectual property company that licenses enabling technologies for the hydrogen economy
  - 8 patents issued to date
  - 36 patent applications submitted to date

- Start-up company founded in 1998, grew to 15 people by early 2000 (5 scientists) with a chemistry / fuel cell focus:
  - NaBH₄ direct electro-conversion fuel cell and hydrogen generation

- Public offering in August 2000 (Nasdaq: MCEL), currently 40 employees located in Eatontown, NJ
  - 27 in Product Development organization, including 10 Ph.D.s

- Organization: Research and development on energy storage falls primarily into three groups:
  - Synthesis Chemistry (Dr. Y. Wu)
  - Catalyst Optimization (Dr. G. Smith)
  - Systems Design/Prototyping/Testing (Dr. R. Mohring)
Hydrogen Generation from Sodium Borohydride (Hydrogen on Demand™ Process)

\[
\text{NaBH}_4 (\text{aq}) + 2 \text{H}_2\text{O} \rightarrow \text{cat} \quad 4 \text{H}_2 + \text{NaBO}_2 (\text{aq}) + \sim 300 \text{ kJ}
\]

- An energy-dense water-based fuel (i.e., 30 wt% NaBH\textsubscript{4} holds 6.7 wt% H\textsubscript{2})
- Proprietary catalyst induces rapid H\textsubscript{2} production
- Pure humidified H\textsubscript{2} delivered to engine or fuel cell
- Borate can be recycled into NaBH\textsubscript{4}
- Exothermic reaction requires no heat input

- Hydrogen is generated in a controllable, heat-releasing reaction
- Fuel is a room-temperature, non-flammable liquid under no pressure
- Generated H\textsubscript{2} is high purity (no CO, S) and humidified (heat generates some water vapor)
- The fuel cell creates water! Optimization of HOD + PEMFC system can allow for use of high concentration (potentially approaching 100%) NaBH\textsubscript{4} fuels
- Higher concentration \(\Rightarrow\) higher volumetric and gravimetric H\textsubscript{2} storage
Hydrogen on Demand™ Schematic

Fuel tank: NaBH₄ solution

Discharged fuel area: NaBO₂

Fuel Pump

Hydrogen on Demand™ Catalyst Chamber

Gas/Liquid Separator

H₂

borate

H₂O

Coolant Loop

Heat Exchanger

Pure Humidified H₂

Fuel Cell

Water from Fuel Cell

Hydrogen + Steam

Oxygen from Air
**Gravimetric Storage Efficiency of SBH**

*Fuel Cell Water Integration*

Calculated Hydrogen Storage Efficiency, 90% Fuel Utilization
(Advanced Engineering: Fuel Cell Water Integration, Slurry/Solids Handling)

<table>
<thead>
<tr>
<th>SBH fuel conc (wt%)</th>
<th>Max theo. H2 (wt%)</th>
<th>90% fuel util w/ 30% BOP (weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>4.3</td>
<td>2.7</td>
</tr>
<tr>
<td>30</td>
<td>6.4</td>
<td>4.0</td>
</tr>
<tr>
<td>40</td>
<td>8.5</td>
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<td>10.7</td>
<td>6.7</td>
</tr>
<tr>
<td>60</td>
<td>12.8</td>
<td>8.1</td>
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<td>70</td>
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<tr>
<td>80</td>
<td>17.1</td>
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<td>19.2</td>
<td>12.1</td>
</tr>
<tr>
<td>100</td>
<td>21.4</td>
<td>13.5</td>
</tr>
</tbody>
</table>

- SBH has the intrinsic energy density needed to be a competitive fuel
- Challenges associated with higher concentrations:
  - Water management
  - Thermal management
  - Fuel/borate handling
Volumetric Storage Efficiency

Volumetric storage efficiency of 30 wt% fuel = ~63 g H₂/L

For comparison:
- Liquid H₂ = ~71 g H₂/L
- 5000 psi compressed = ~23 g H₂/L
- 10000 psi compressed = ~39 g H₂/L

For a practical system, Balance of Plant (both volumetrically and gravimetrically) is key.
Commercial Vehicle Demonstrations

- **Chrysler Town and Country Natrium®**
  - Fuel cell (Ballard Power Systems) electric hybrid minivan
  - Debut at EVAA – Dec 2001, on tour most of 2002
  - FC is ~60 kW primary power plant
  - Estimated 300 mile range for system

- **Peugeot-Citroën H₂O Vehicle**
  - Fuel cell (Hpower) electric hybrid vehicle, fire rescue vehicle concept car
  - Debut at Paris Auto Show – Oct 2002
  - FC is ~5 kW range extender
Hydrogen on Demand™ System
Chrysler Town and Country Natrium®

- Sodium Borohydride Fuel/Borate Tank
- Hydrogen on Demand™ H₂ Generator
- Electric Drive Motor
- Lithium Ion Battery Pack
- DC/DC Converter
- Ballard Fuel Cell Engine
High-Power Hydrogen Generator
Hydrogen on Demand™ Technical Specification

- Hydrogen delivery pressure: Variable from 0 - 13 bar (~0 - 190 psig)
- Rated power output: 0 - 75 kWₑ (up to ~5.5 kg/hr H₂)
- Hydrogen generation system controls integrated into vehicle:
  - Fuel cell output is monitored (demand signal)
  - Independent PLC (Programmable Logic Controller) monitors and controls the HOD system, communicates with vehicle main controller
  - Fuel pump is modulated to vary fuel flow rate
    - Rate of hydrogen generation is proportional to fuel input rate

- Developments on next generation system:
  - Water balance is monitored and dynamically controlled
  - Thermal and water management model of combined HOD + PEMFC system
Volumetric Efficiency of Hydrogen Storage/Generation

Increased Packaging Flexibility

Compressed H₂ cylinders
(x3 @ 5000 psi)

H₂ generation system, fuel and borate tanks
(equals energy storage of ~5 compressed tanks)
High Power Testing/Instrumentation:
Fuel Cell Emulator

- Simulates the $\text{H}_2$ draw of a high power fuel cell or hydrogen engine, up to $>2000\ \text{SLM H}_2$
- Flow schedule entered into computer based on system model of fuel cell device/vehicle
- Mass flow control valve coupled via a PID control loop to a Coriolis flow meter
- Ability to test hydrogen generation systems under true operating conditions, without having a fuel cell
Data taken on MCEL H₂ Internal Combustion Engine Taxi

Flow profile through fuel cell emulator

Compressed H₂ baseline and Hydrogen on Demand™ running shown

Ability to “load follow”, even with aggressive transients

Hydrogen on Demand™ Application
Prototype Backup Power System

- Systems typically run at < 40 psig system pressure, rated at 18 SLM hydrogen, capable of max flows of up to ~45 SLM (~3 kW<sub>e</sub>)
- One-button operation – works as a “black box” hydrogen source that looks like a low pressure hydrogen cylinder
Backup Power System, Load Following Characteristic

15 sec Interval Flow Testing, 0 – 18 SLM H₂ (~ 0 – 1.4 kWₑ), P₀ = 28 psig
Backup Power System, Variable Flow Rate
Flow Step Testing, 0 – 18 SLM H₂ (~ 0 – 1.4 kWₑ), P₀ = 28 psig
Transportation Fueling/Recycling Strategy

- Infrastructure envisioned such that borates will be recycled into borohydride at centralized facilities.

- Current production process is geared towards specialty chemical applications of sodium borohydride, and is expensive and inefficient.

- Chemical research at Millennium Cell is targeting a better regeneration process that will allow SBH to become a commodity chemical. This is necessary in order to access markets such as transportation.

- Markets such as backup power are less sensitive to fuel price; incremental process improvements go a long way…
Current NaBH₄ Process (Schlesinger Process)

- Many by-products generated in the overall process
- **Large amounts of Na metal needed** – energy intensive to make
- Overall process is not energy efficient
- CO₂ emission significant in electrolytic production of Na metal
- Results in high cost of NaBH₄
R&D Strategy for Developing New NaBH₄ Synthesis Process

**Multi-Step vs. One-Step Approach**

**Multi-Step Approach:**
The constituent reaction steps are more likely to be feasible than one-step. Process chemistry of separation and purification has to be addressed.

**One-Step Approach:**
Conceptually simple, but requires large energy input in a single step. Technically challenging; reaction feasibility yet to be demonstrated. Possibly achievable via electrolysis routes.
Reactions A and C have been demonstrated in our facilities (next slides)

Reaction B is currently a focus of synthesis research; preliminary results to be presented at a later date
Reaction A: Boron Ester from Borax or Metaborate and CO₂

\[
\text{Na}_2\text{B}_4\text{O}_7 + 12 \text{CH}_3\text{OH} + 2 \text{CO}_2 \rightarrow 4 \text{B(OCH}_3\text{)}_3 + 2 \text{NaHCO}_3 + 5 \text{H}_2\text{O}
\]

- 70 °C, low pressure
- 20% B conversion to trimethyl borate

\[
\text{NaBO}_2 + \text{CO}_2 + 3 \text{CH}_3\text{OH} \rightarrow \text{B(OCH}_3\text{)}_3 + \text{NaHCO}_3 + \text{H}_2\text{O}
\]

- 100 °C, 450 psig
- best result: 67% conversion

B(OC₄H₉)₃ has also been prepared in this manner

*patent application has been filed on both reactions
Reaction C: Diborane to NaBH₄ by Na₂CO₃ Reaction

\[
2 \text{B}_2\text{H}_6 (g) + 2 \text{Na}_2\text{CO}_3 (s) \xrightarrow{0 \degree \text{C}} \xrightarrow{\text{H}_2\text{O}} 3 \text{NaBH}_4 (s) + \text{NaBO}_2 (s) + 2 \text{CO}_2 (g)
\]

\[\Delta G = -37.3 \text{ kcal/mol, Yields up to 25 %}\]

Competing reaction: \[\text{B}_2\text{H}_6 + 6 \text{H}_2\text{O} \rightarrow 2 \text{B(OH)}_3 + 6 \text{H}_2\]
\[\Delta G = -144.1 \text{ kcal/mol}\]

\[
2 \text{B}_2\text{H}_6 (g) + 2 \text{Na}_2\text{CO}_3 (s) \rightarrow 3 \text{NaBH}_4 (s) + \text{NaBO}_2 (s) + 2 \text{CO}_2 (g)
\]

Batch ball-mill reactor, or flow Parr reactor

Highest yield: 47%, when using diglyme suspension

Competing reaction: NaBH₄ + CO₂ can be minimized by carefully selecting reaction conditions

*patent application has been filed on both reactions
NaBH₄ Product Characterization

**IR Spectroscopy**

Product from Ball-Mill

NaBH₄ standard

**XRD**

[CJ0027.MDI] 102201-02 <2T(0)=−0.09-0386> NaBH₄

2-Theta(°)

Intensity(Counts)

**NMR**

**¹H NMR**

J₉-H = 82 Hz

**¹¹B NMR**

J₉-H = 82 Hz
- Cathode reaction:
  \[ \text{BO}_2^- + 3\text{H}_2 + 2e^- \rightarrow \text{BH}_4^- + 2\text{OH}^- \]

- Anode reaction:
  \[ 2\text{OH}^- + \text{H}_2 - 2e^- \rightarrow 2\text{H}_2\text{O} \]

- Important considerations:
  - Electrolyte, electrode choices
  - Membrane separators
  - Cell Current efficiencies
  - Product separations

- Electrolytic reactions can often take place closer to chemical equilibrium, achieving higher energy efficiency.
Conclusions

- Millennium Cell is pursuing the use of sodium borohydride (SBH) as a hydrogen storage medium
- SBH has a relatively high intrinsic gravimetric and volumetric hydrogen storage density, which can yield practical hydrogen generation systems with proper engineering
- Hydrogen on Demand™ technology has been successfully demonstrated over a wide range of hydrogen delivery flow rates and pressures
- Progress is being made on research to improve current SBH synthesis technology so that markets such as transportation can be accessed
- The path is defined, but there is certainly more work ahead of us!
  - Continued improvements in regeneration technology
  - Systems design and engineering to access higher energy densities
The BCl₃ reaction has been demonstrated on the pilot scale @ 750 °C in early 1960’s. The B(OR)₃ reaction requires validation and further understanding.