Hydrogen Storage via Sodium Borohydride

Current Status, Barriers, and R&D Roadmap

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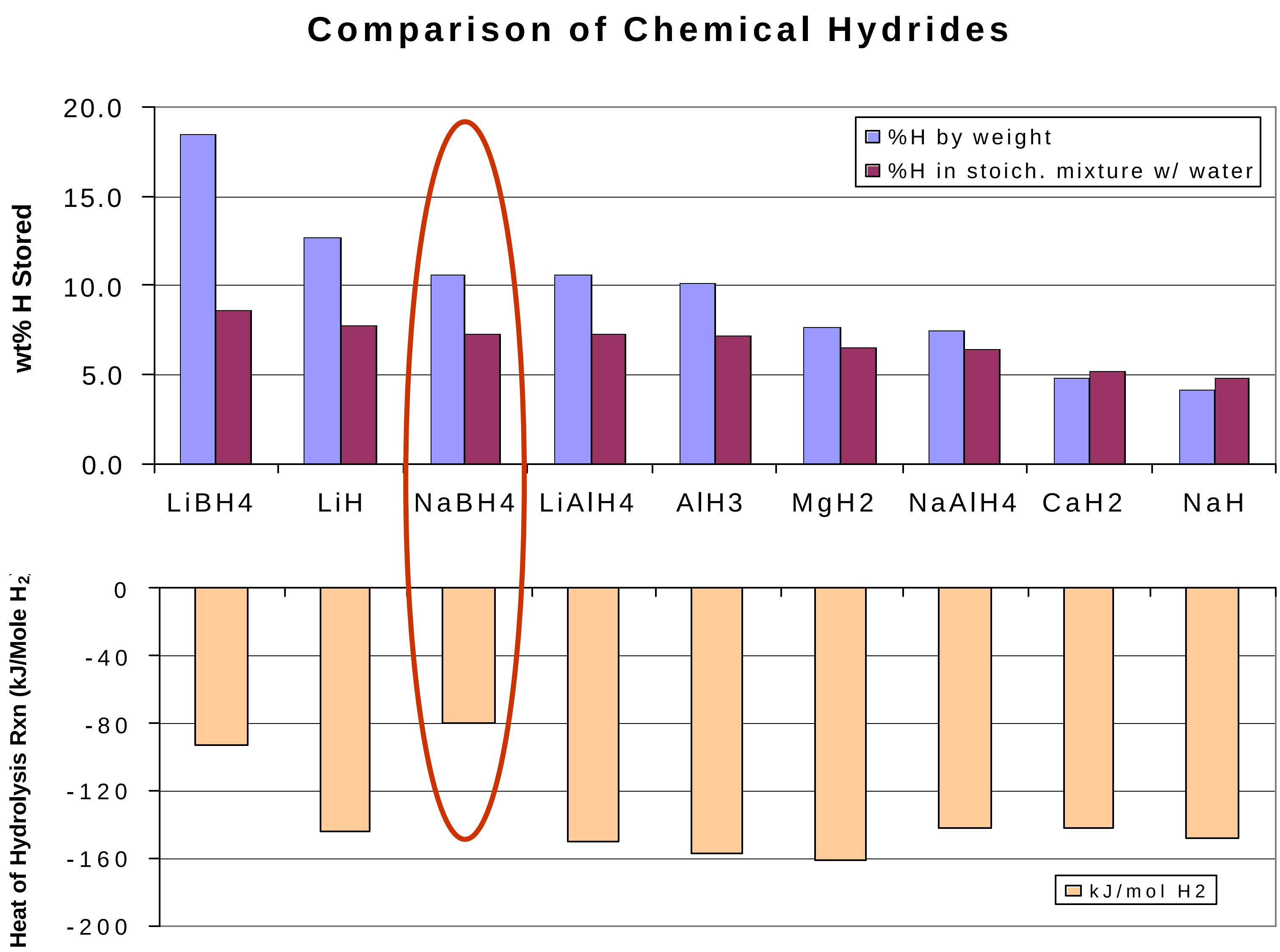
Outline

- Introduction: hydrogen storage via sodium borohydride
- Current Status: portable and vehicular applications
- Barriers to commercialization
- Research issues and on-going efforts
- Summary

Choice of Chemical Hydrides



Hydrogen Generation from Sodium Borohydride
(Hydrogen on Demand™ Process)

$$NaBH_4 + 2\,H_2O \xrightarrow{cat} 4\,H_2 + NaBO_2\,(aq) + \sim 300\ kJ$$

$NaBH_4 + 2\,H_2O$	→ (cat)	$4\,H_2$	$NaBO_2$ (aq)	~300 kJ
An energy-dense water-based fuel (i.e., 30 wt% $NaBH_4$ holds 6.7 wt% H_2)	Proprietary catalyst induces rapid H_2 production	Pure humidified H_2 delivered to engine or fuel cell	Borate can be recycled into $NaBH_4$	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**
- **No side reactions or volatile by-products.**
- **Generated H_2 is high purity (no CO, S) and humidified (heat generates some water vapour)**

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Groups Investigating Borohydride and Related Systems

- **Millennium Cell** – Hydrogen on Demand™ Systems and SBH Synthesis;
  - Partners: U. S. Borax, Air Products and Chemicals
- **Manhattan Scientifics/R.G. Hockaday** – Portable SBH systems
- **Hydrogenics** – System integrator, HyPORT™ power generator using SBH as source of H_2
- **Prof. S. Suda** (MERIT/KUCEL) – Hydrogen generation method, and SBH synthesis from MgH_2.
- **Toyota Motor Company** – Japanese patents on H_2 generation from SBH, methods for SBH synthesis.
- **Dr. Peter Kong, INEEL** – Nuclear energy assisted synthesis of SBH, recently acquired funding
- **Prof. M. A. Matthews**, Univ. South Carolina – SBH hydrogen generation systems (steam hydrolysis)
- **Prof. A. Zuttel**, Univ Fribourg, Switzerland – $LiBH_4$, thermo-decomposition

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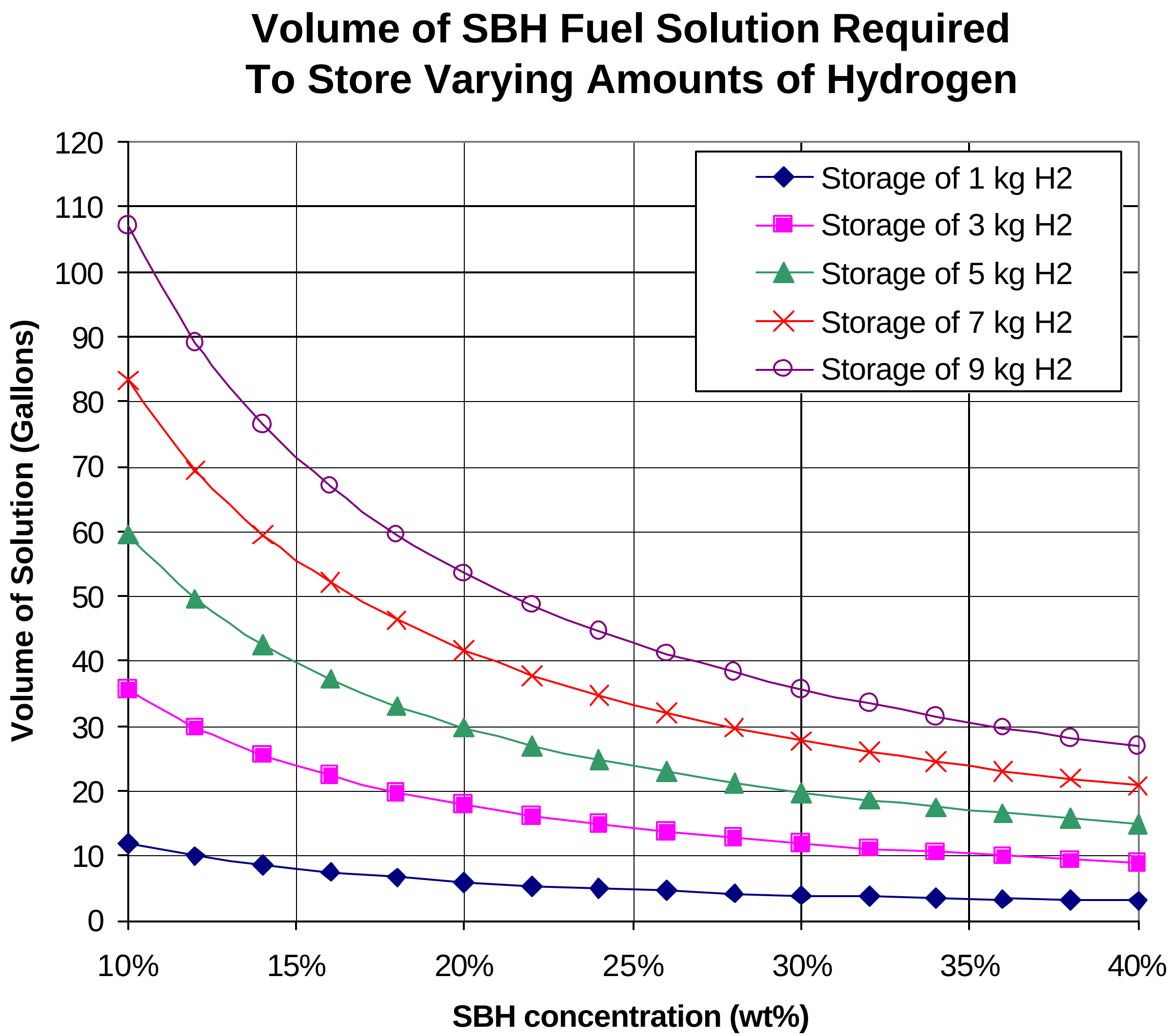
Volumetric Storage Efficiency



Volumetric storage efficiency of 30 wt% fuel = ~63 g H_2/L

For comparison:

- **Liquid H_2 = ~71 g H_2/L**
- **5,000 psi compressed = ~23 g H_2/L**
- **10,000 psi compressed = ~39 g H_2/L**

For a practical system, Balance of Plant is key

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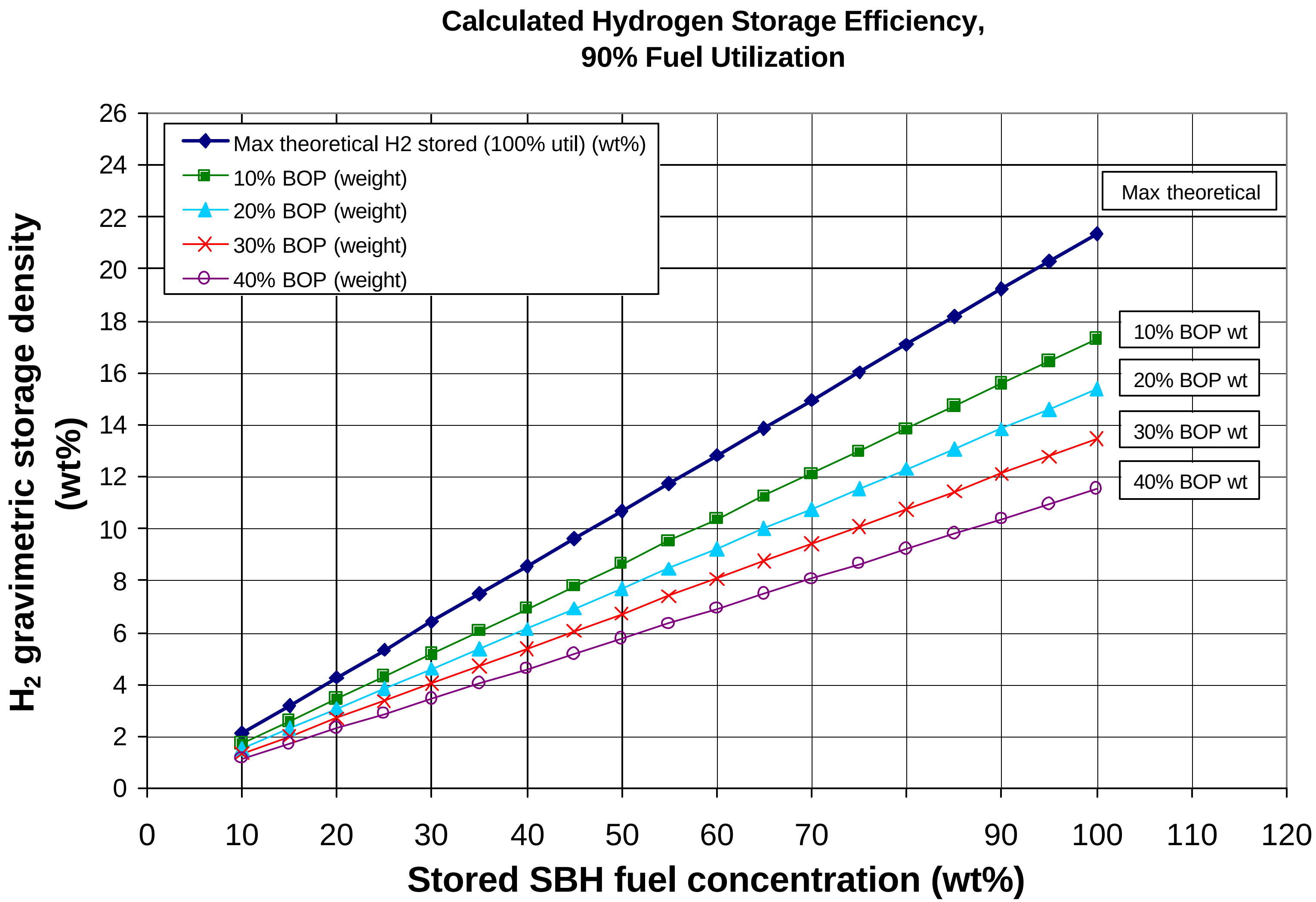
Gravimetric Storage Efficiency of SBH, with BOP



SBH has intrinsically high storage density for H, which can yield practical hydrogen generation systems with proper engineering

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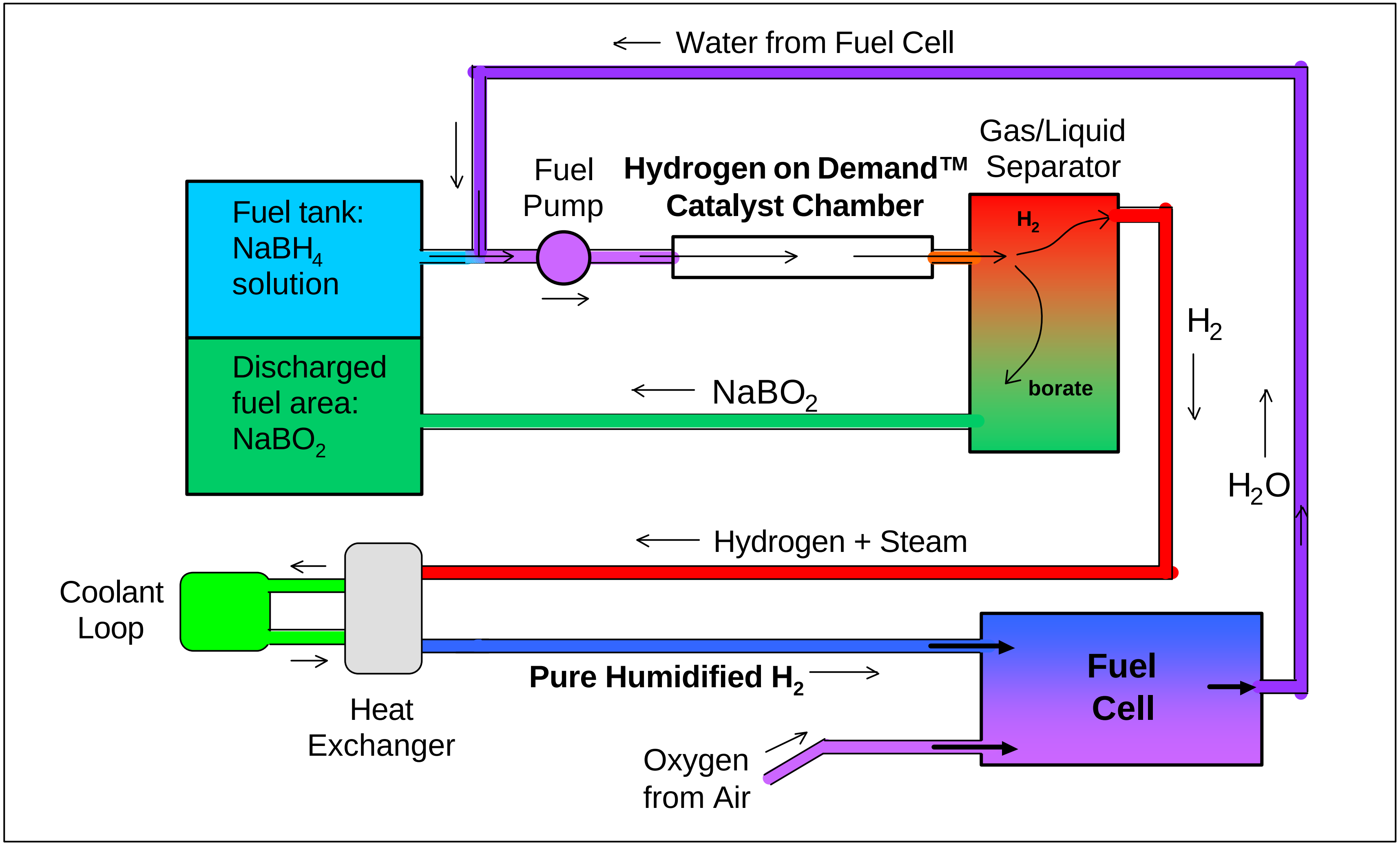
Practical Hydrogen on Demand™ Schematic



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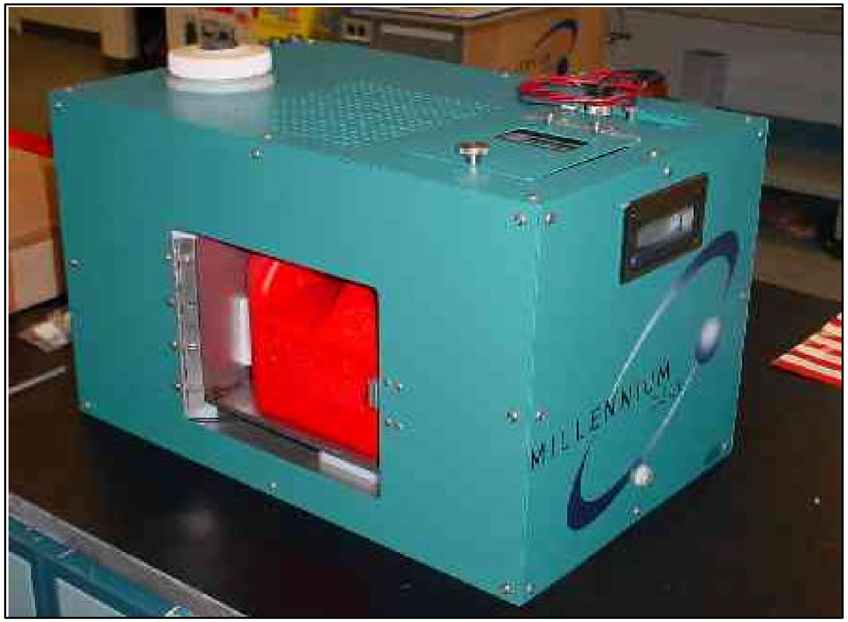
Hydrogen on Demand™ Applications

Prototype Backup Power System - 1.2 kW hydrogen generation 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_e)
- One-button operation – works as a "black box" hydrogen source that looks like a low pressure hydrogen cylinder

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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 H_2O 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

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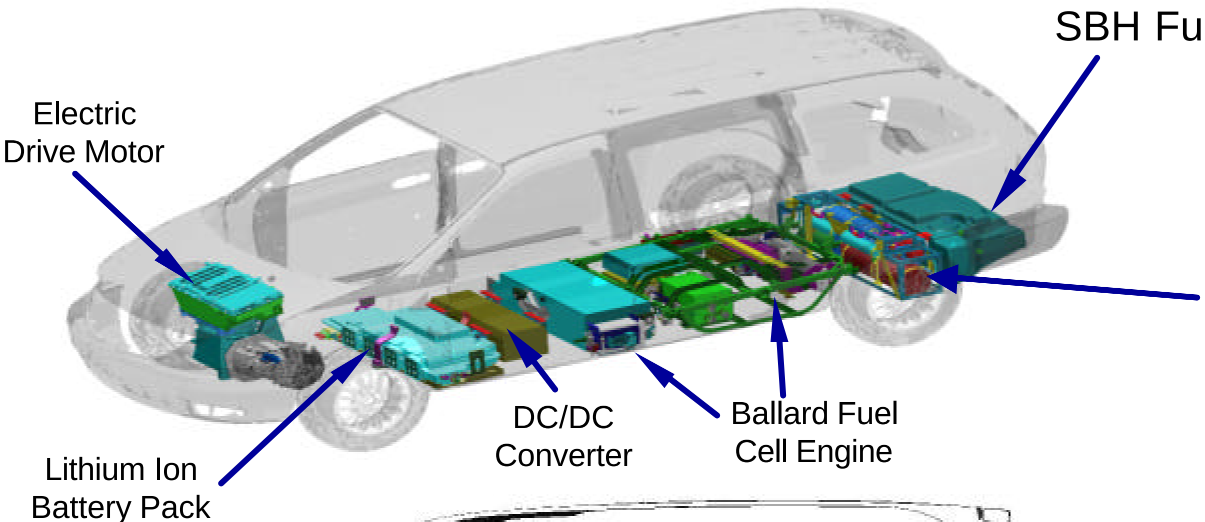
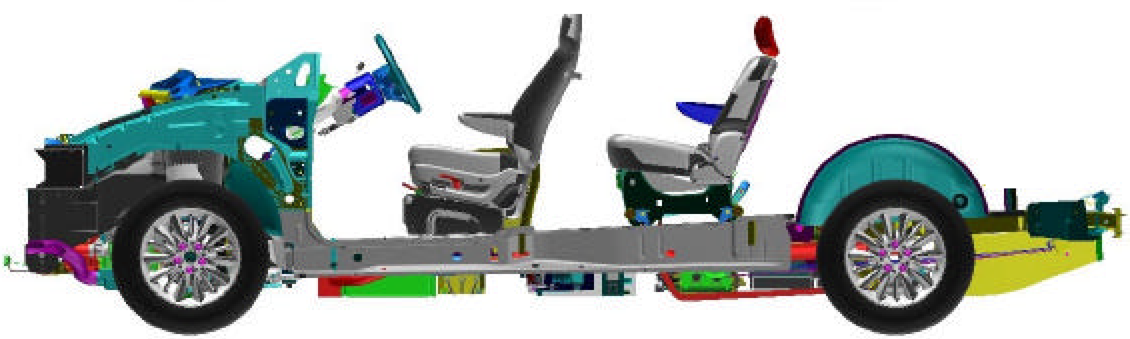
Volumetric Efficiency of Hydrogen Storage and Generation

Increased Packaging Flexibility



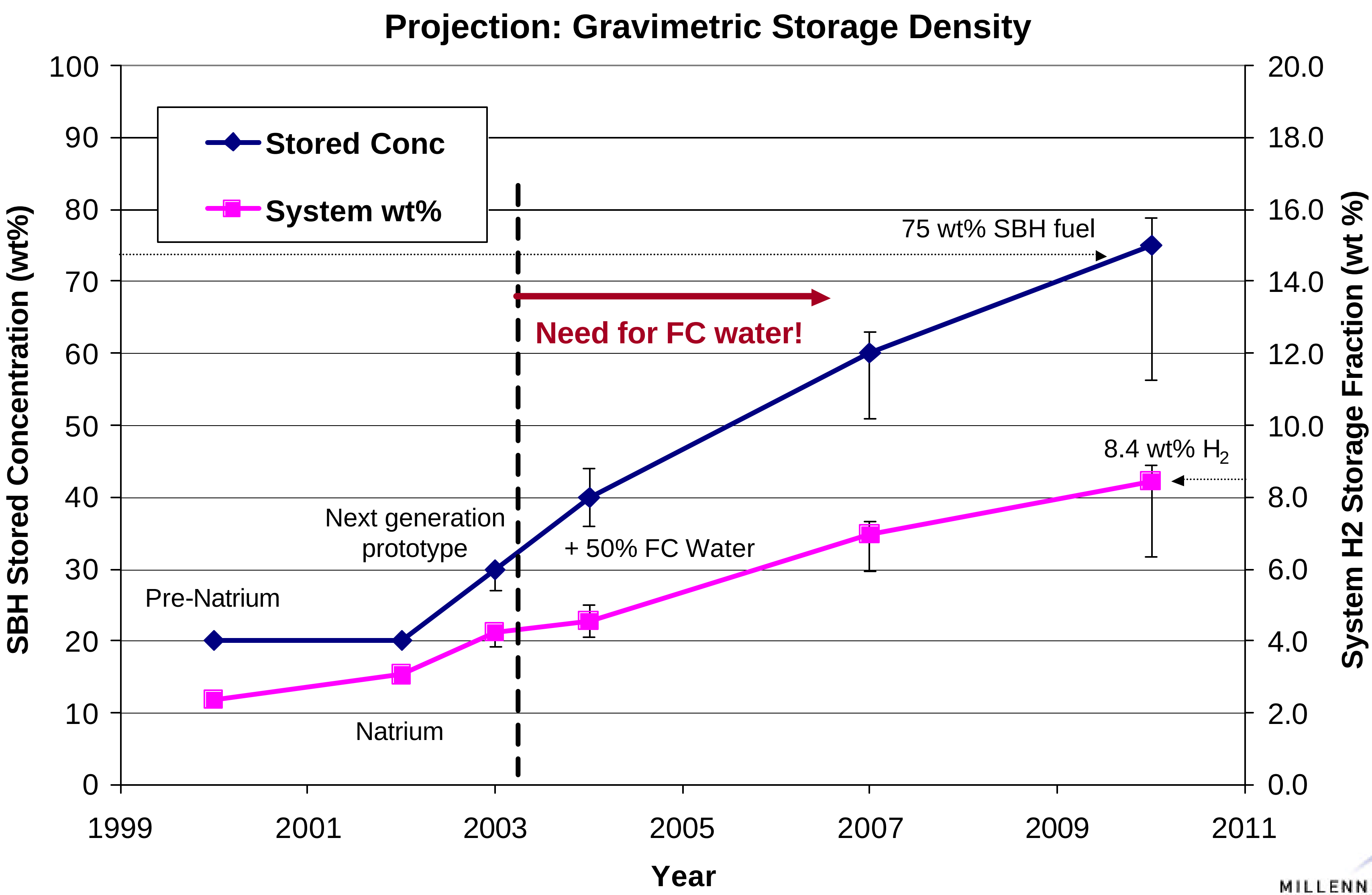
Hydrogen on Demand™ H_2 Generator

3 cylinders @ 5000 psi



Transportation / Stationary: Projected Target

Gravimetric Projection (50-75 kW, 7.5 kg stored H_2)



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Current Status of H_2 Storage Technologies

Hydrogen Storage Technology	Current Volumetric Storage Density ($g\ H_2/L$)	Current Gravimetric Storage Density (wt %)	+ of Storage Technology	– of Storage Technology
5000 psi (350 bar)*	~12.5 g H_2/L = 1.5 MJ/L	~ 2.7 wt%	Known Technology	H_2 under pressure, g H_2/L, Infrastructure, H_2 not humidified
10000 psi (700 bar)*	~24.2 g H_2/L = 2.9 MJ/L	~ 3.3 wt%	Known Technology	H_2 under pressure, g H_2/L, Infrastructure, H_2 not humidified
Liquid*	~37.0 g H_2/L = 4.4 MJ/L	~ 5.0 wt%	Known Technology	Boil Off, Infrastructure
Solid Metal Hydrides	?	?	?	
Hydrogen on Demand™ $NaBH_4$ Chemical Hydride	~> 22 g H_2/L = > 2.5 MJ/L	> 4.0 wt%	H_2 is not under pressure, system design, Infrastructure	Regeneration, Fuel Handling Strategy

*Taken from: GM Website, specifications of Hywire and HydroGen3 Vehicles:
http://media.gm.com/about_gm/vehicle_tech/fuel_cell/monaco/hydrogen/index.htm
http://media.gm.com/about_gm/vehicle_tech/fuel_cell/hywire/index.html

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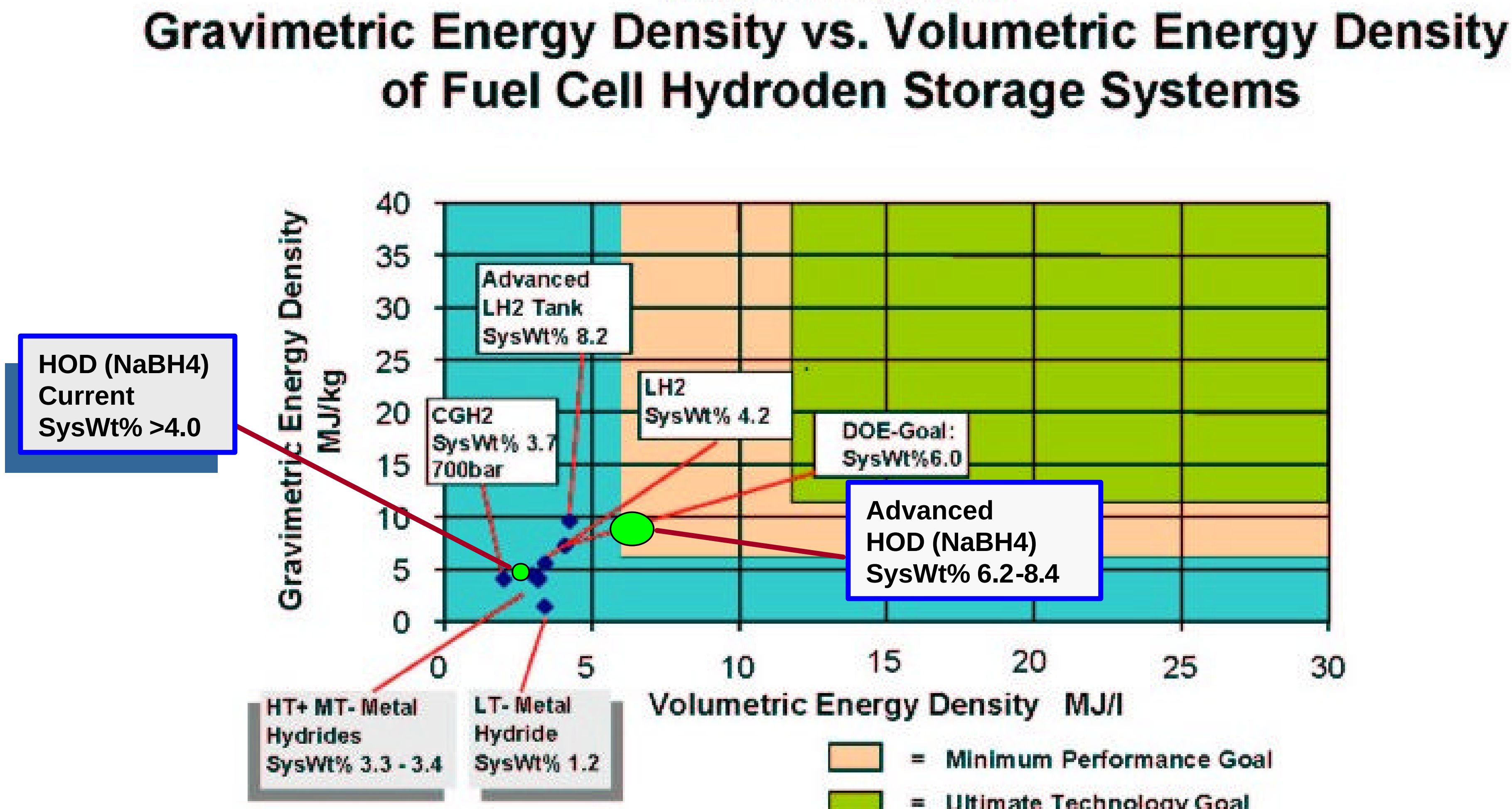
Hydrogen Storage Targets



Taken from: Brenstoffzellen - Fahrzeuge von GM/Opel – Technik und Markteinfuehrung, Dr. G. Arnold, Jan 22-23, 2003

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Increase the Gravimetric and Volumetric Energy Density

- Two main approaches:
  - Directly increasing the fuel concentration:
    - Physical characteristics issues
    - Chemistry issues (e.g., max concentration in catalyst bed)
  - Improving system design:
    - Recycle H_2-stream condensate
    - Recycle fuel cell water
    - Higher concentration ➔ higher volumetric and gravimetric H_2 storage
- Fuel properties and fuel chemistry are important across a range of high concentration fuels
  - Physical properties
  - Stability, solubility, viscosity
  - Freezing points

⇒ A number of these issues are already being addressed at MCEL

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Fuel Cost Reduction

Why is $NaBH_4$ costly to produce?

- Need 4 electrons, stored in 4 B-H bonds, used to reduce H_2O and form H_2
- Need to combine 3 different elements + electrons + energy

  Na + B + H + electrons + energy (substantial entropic and enthalpic barriers)
- The complexity of the system leads to a stepwise process for SBH production.
- The $NaBH_4$ price will always be driven by the price of primary energy
- Energy efficiency is key; any process has to be optimized to minimize wasted energy.

Particular Challenge for Transportation Applications

- Convert a multi-component, high energy, high purity specialty chemical into an everyday commodity fuel
- Difficult to compete with the current cost of gasoline, ***but*** could compare favorably with other hydrogen storage technologies.

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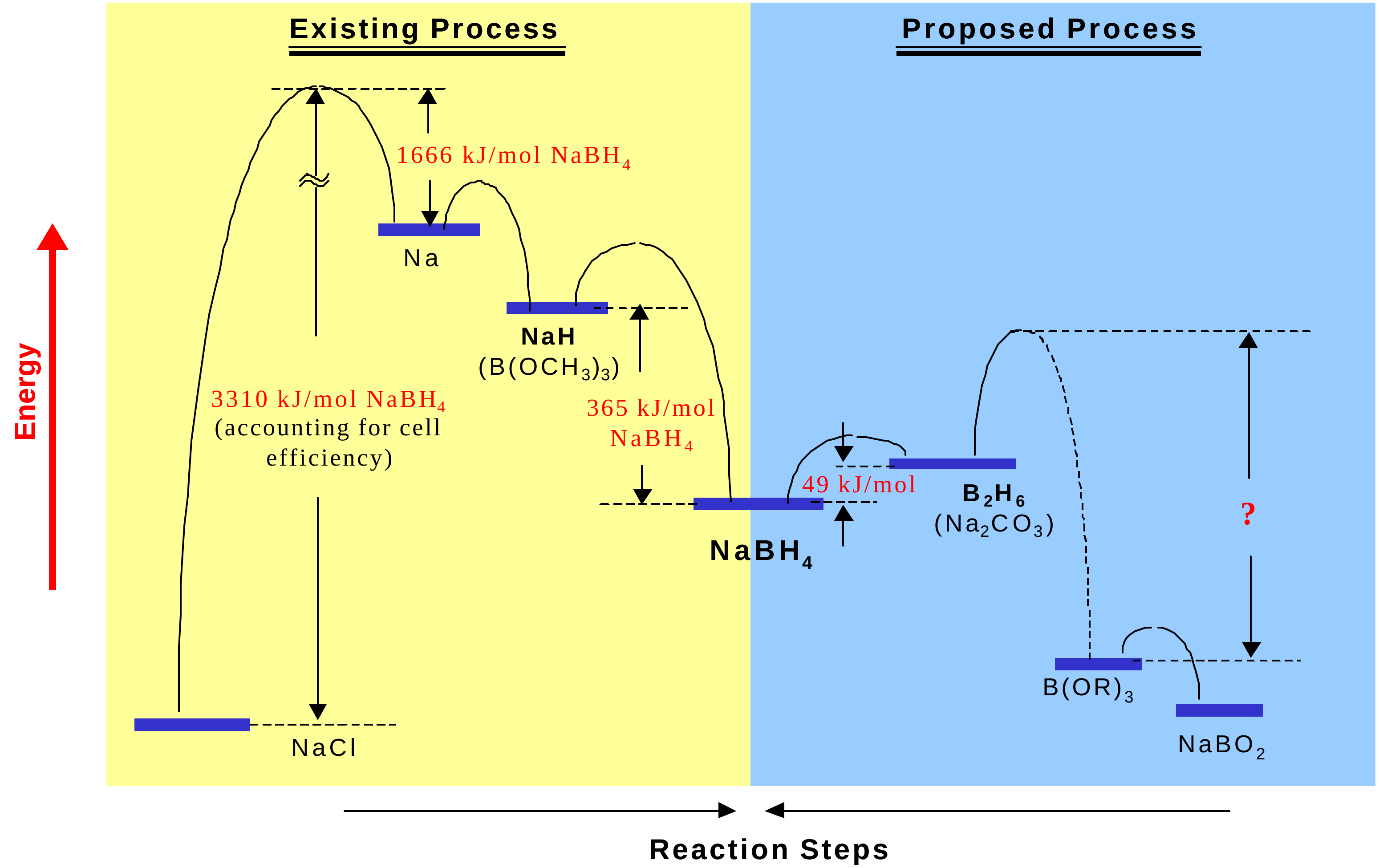
Can B_2H_6 be better than NaH as an Intermediate ?



- Production of Na is < 50% energy efficient
- Further energy losses to convert Na to $NaBH_4$

- Utilize alternative intermediate B_2H_6.
- Need appropriate energy input to efficiently produce B_2H_6.

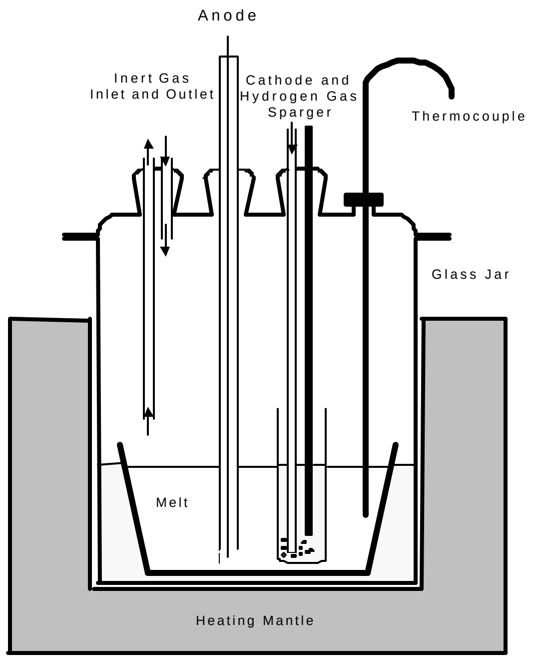
We are currently investigating both electrochemical and chemical pathways

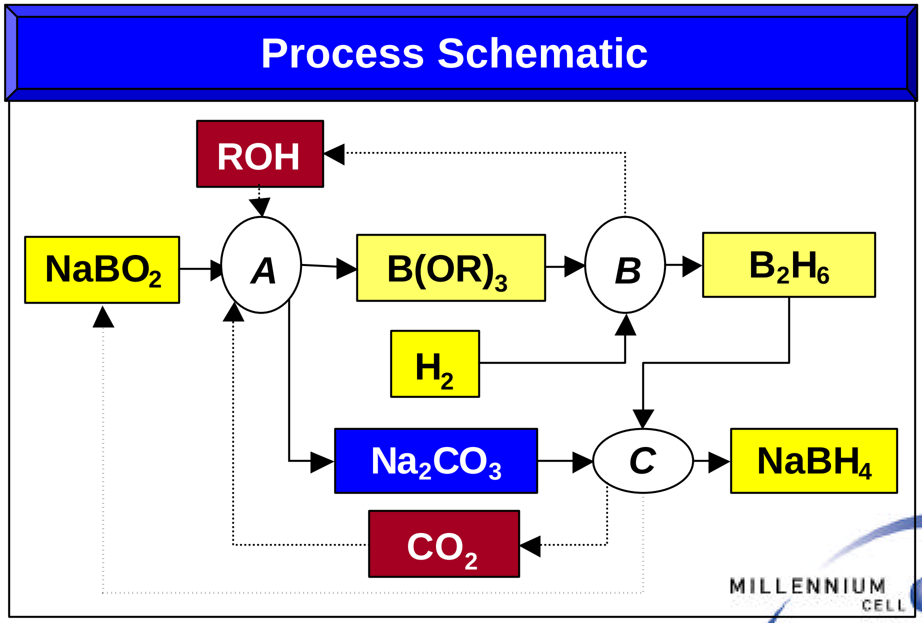
Electrochemical Pathway

- More efficient electrochemical synthesis of Na
- Direct electrochemical conversion of borate to borohydride
- Molten salts and/or ionic liquids as reaction medium

Thermochemical Pathway

- Conversion of $B(OR)_3$ to B_2H_6
- Studied BCl_3 to B_2H_6 as a model reaction system
- Reaction yield is key.





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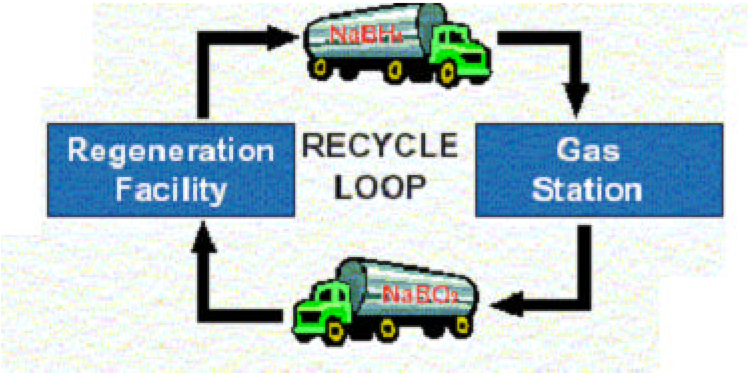
Infrastructure - Transportation Fueling/Recycling Strategy

- Supply and Demand
  - Current production process is geared towards specialty chemical applications of sodium borohydride, and is expensive and inefficient.
  - Markets such as backup power are less sensitive to fuel price; incremental process improvements can go a long way
- Infrastructure envisioned, such that borates will be recycled into borohydride at centralized facilities
- Chemistry research is targeting an improved synthesis and regeneration process that will allow SBH to become a commodity chemical. This is necessary in order to access markets such as transportation.



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Summary

- SBH has 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.
- Studies are being carried out to integrate thermal and water management between the SBH fuel sub-system and the FC sub-system
- Progress is being made to improve current SBH synthesis technology aimed at reducing manufacturing cost.
- 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

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Research Opportunities

- Hydrogen Delivery System
  - Intelligent controls for the fuel system.
  - Increase gravimetric and volumetric storage density
  - Advanced catalyst development and novel catalyst bed development
- Solve the SBH cost reduction and recycling issue
  - Basic research in boron chemistry
  - Chemical engineering and chemical process development
  - Develop fueling infrastructure
- Integrate renewable energy sources and/or non carbon-based energy sources

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Thank You

Questions, comments, and further discussions,

Please contact wu@millenniumcell.com