

Sodium borohydride for solid-state green hydrogen export

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Future Energy Exports CRC Annual Conference

11 May 2023

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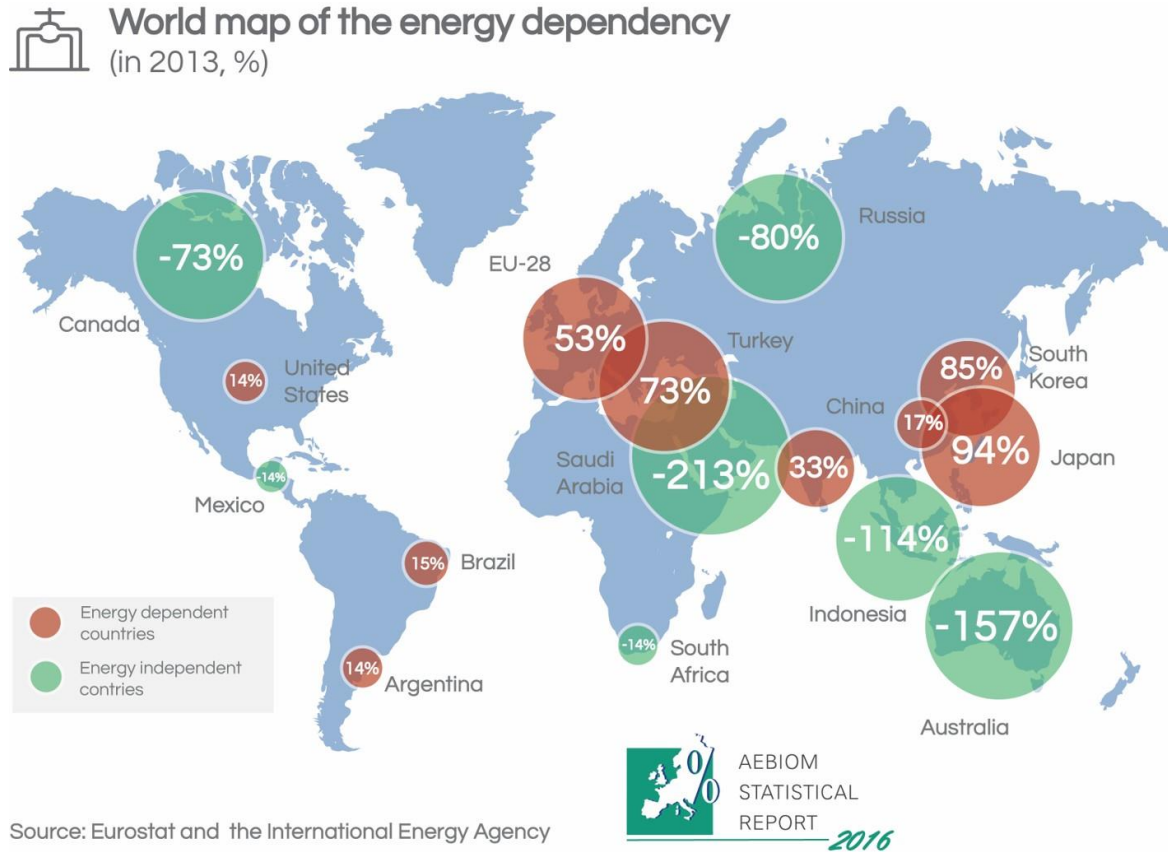


HSRG
Hydrogen Storage Research Group



Curtin University

Hydrogen Energy Export



Why export hydrogen?

- Net zero by 2050
- Growing hydrogen economy
- Meet world energy demands

Global hydrogen demand from Australia:

- 2 - 9 million tonnes by 2030
- 20 - 230 million tonnes by 2050

Hydrogen Energy Storage

How is hydrogen stored?

- High pressures
- Cryogenic temperatures
- Physisorption
- Liquid organic hydrogen carriers
- Chemical or metal hydrides

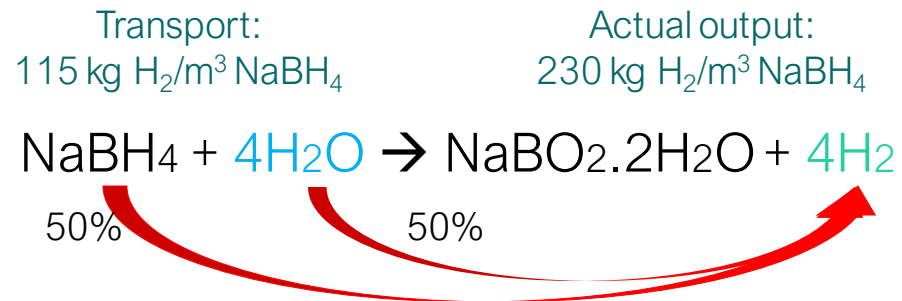


Table 1: Comparison of hydrogen export materials

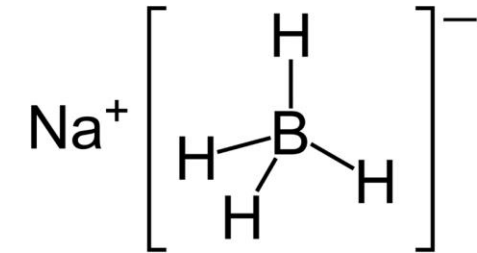
Hydrogen carrier	Export temperature (°C)	Export pressure (bar)	Volumetric density of H ₂ (kg/m ³)
H ₂ (gas)	20	700	39.7
H ₂ (liquid)	-253	1	71.1
NH ₃ (liquid)	20	10	107
LOHC - methylcyclohexane (liquid)	20	1	47.4
NaBH ₄ (solid)	20	N/A	69 - 137

Sodium borohydride (NaBH₄)

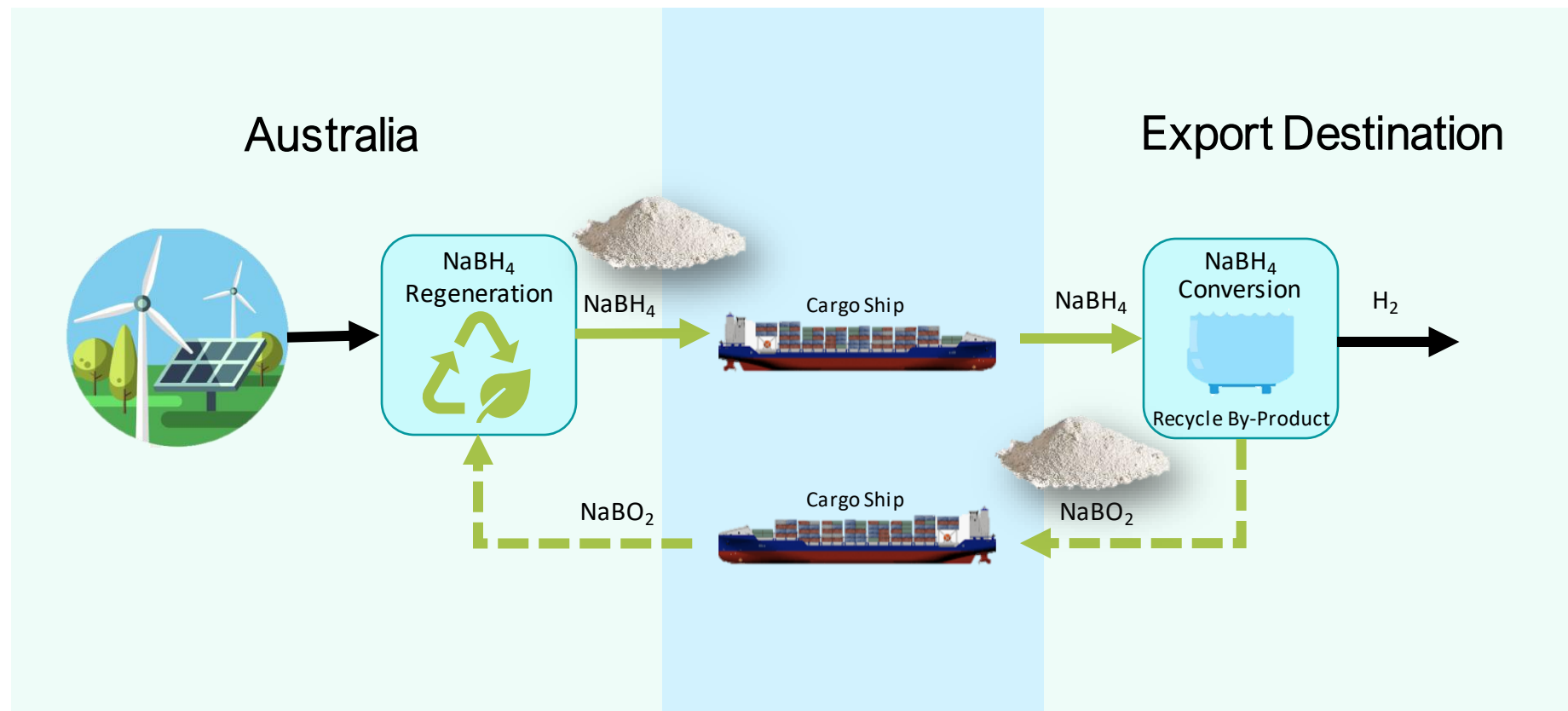
- Metal hydride
- White powder, solid state RTP
- High hydrogen content ≈ 10.7 wt%
- Easy and safe to transport on regular ships
- No heat or energy input upon arrival at export destination
- Controlled hydrogen generation at RTP using metal catalyst
 - Effectively 21.4wt% H₂ by reaction with water



Half the hydrogen comes from water at export destination!



NaBH₄ Hydrogen Export Cycle



How is NaBH₄ Regenerated?

Table 2: Comparison of existing NaBH₄ chemical regeneration methods

	Thermochemical [1-3]	Mechanochemical [4-7]	Electrochemical [8-12]
Temperature	500 – 650 °C	Ambient	Ambient
Pressure/ atmosphere	3-7 MPa H ₂	1 atm Ar or 3-7 MPa H ₂	N/A
Reductant or working electrode	Metal (Mg) or metal hydride (MgH ₂)		Transition metals (Pd/Pt/Au/Ag/Zn)
NaBO ₂ form	Dehydrated	Hydrated or dehydrated	Hydrated
Time	1-2 h	1 – 36h	0.5 - 48h
NaBH ₄ yield	Up to 98%	60-90%	Up to 17%

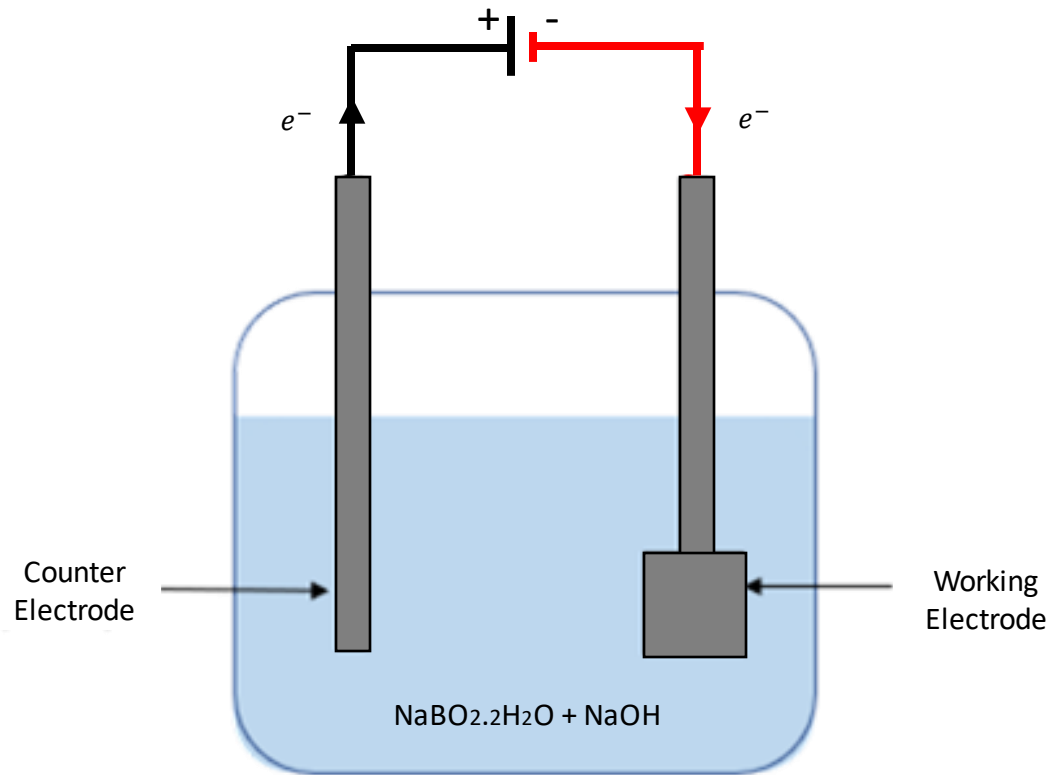
Current issues:

- \$US 50/kg NaBH₄
- High energy or low yield
- Not commercially sustainable

Project approach:

- Electrochemical Regeneration
- Hydrated by-product NaBO₂·2H₂O
- Electrodes reused
- Only input electricity

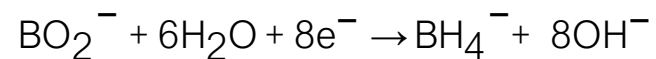
Electrochemical cell set up



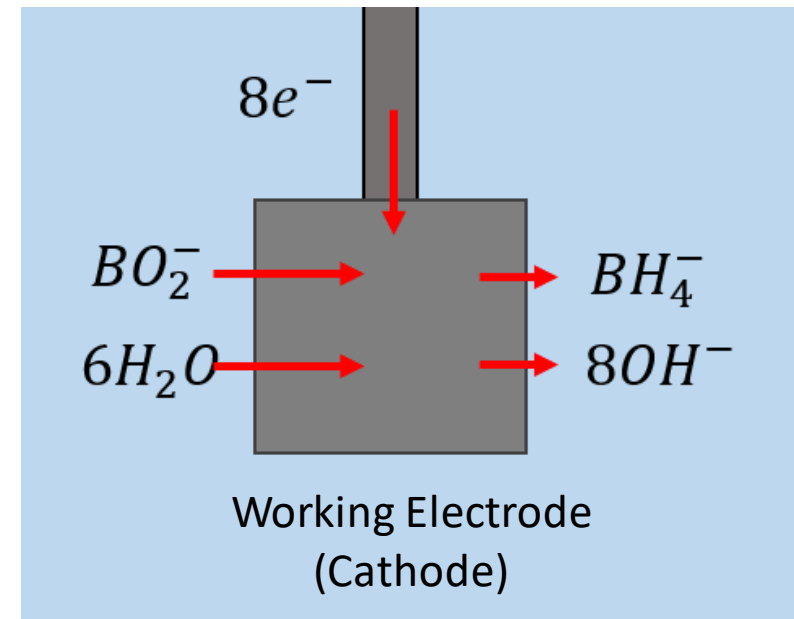
Oxidation:



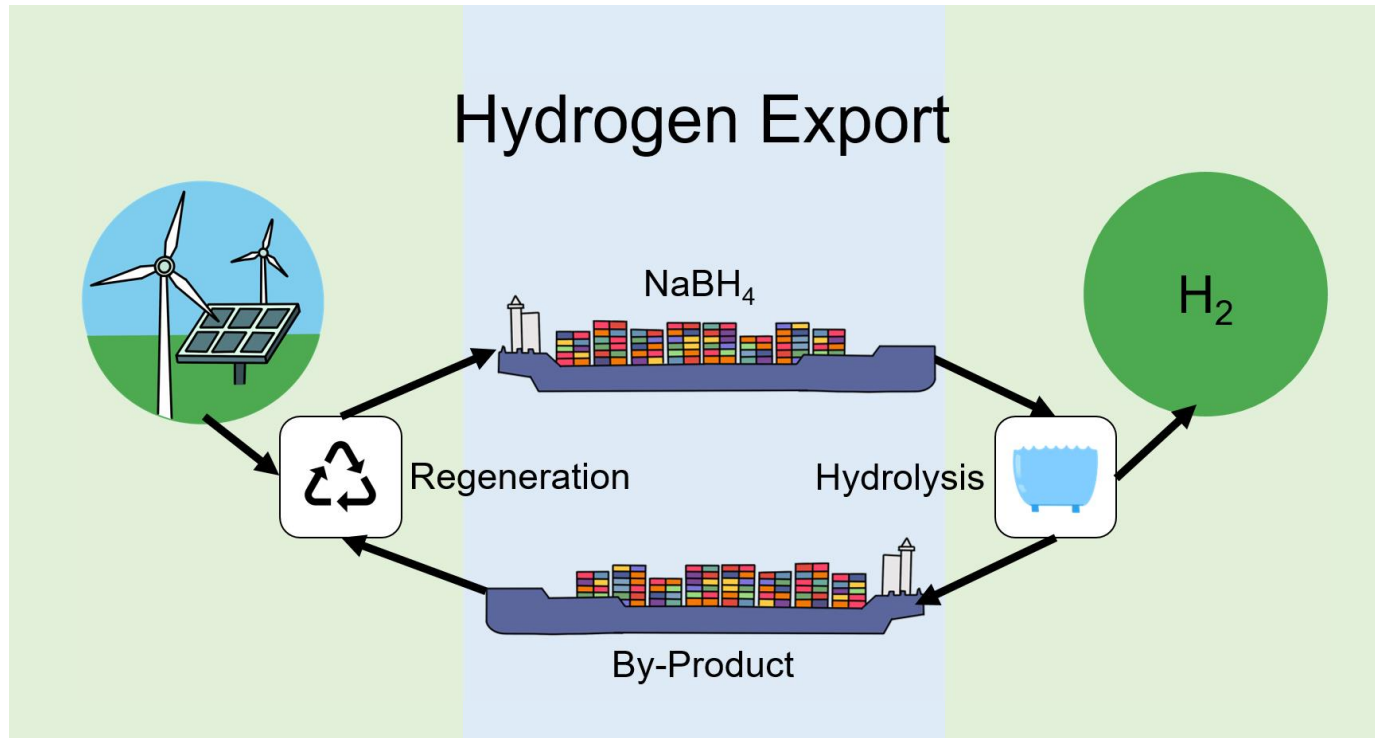
Reduction:



- Applying a potential to regenerate NaBH_4 from $\text{NaBO}_2 \cdot \text{H}_2\text{O}$
 - Parameters include: voltage, time, electrolyte, electrodes, cell configuration
 - Enhance electron efficiency for desired reaction



Conclusion



- New hydrogen export material
- Reducing cost of regeneration
- Enhance electrochemical efficiency for desired regeneration reaction
- Powered by renewable energy
- Closed loop solid-state green hydrogen export cycle
- Potential cost as low as **\$USD 4/kg H₂**
(Based on electricity cost of \$0.0685 USD/kWh)

Acknowledgements

- Professor Craig Buckley
- Associate Professor Mark Paskevicius
- Dr Terry Humphries
- Dr Peter Connolly
- HSRG
- ARC Linkage Grant
- Kotai Energy
- FEnEx CRC



References

- [1] Kojima, Y. and Haga, T. 'Recycling process of sodium metaborate to sodium borohydride. *International Journal of Hydrogen Energy*, 2003. **28**(9): p. 989-993.
- [2] Eom, K., et al., *Thermochemical production of sodium borohydride from sodium metaborate in a scaled-up reactor*. *International Journal of Hydrogen Energy*, 2013. **38**(6): p. 2804-2809.
- [3] Liu, B.H., Z.P. Li, and J.K. Zhu, *Sodium borohydride formation when Mg reacts with hydrous sodium borates under hydrogen*. *Journal of Alloys and Compounds*, 2009. **476**(1-2): p. L16-L20
- [4] Le, T.T., et al., *Efficient Synthesis of Alkali Borohydrides from Mechanochemical Reduction of Borates Using Magnesium–Aluminum-Based Waste*. *Metals*, 2019. **9**(10).
- [5] Ouyang, L., et al., *Enhancing the Regeneration Process of Consumed NaBH₄ for Hydrogen Storage*. *Advanced Energy Materials*, 2017. **7**(19).
- [6] Çakanyıldırım, Ç. and M. Gürü, *Processing of NaBH₄ from NaBO₂ with MgH₂ by ball milling and usage as hydrogen carrier*. *Renewable Energy*, 2010. **35**(9): p. 1895-1899.
- [7] Hsueh, C.-L., et al., *Regeneration of spent-NaBH₄ back to NaBH₄ by using high-energy ball milling*. *International Journal of Hydrogen Energy*, 2009. **34**(4): p. 1717-1725.
- [8] Sanli, A.E., et al., *Recovery of borohydride from metaborate solution using a silver catalyst for application of direct rechargeable borohydride/peroxide fuel cells*. *Journal of Power Sources*, 2010. **195**(9): p. 2604-2607.
- [9] Shu, C., et al., *Mild Process for Reductive Desulfurization of Diesel Fuel Using Sodium Borohydride in Situ Generated via Sodium Metaborate Electroreduction*. *Industrial & Engineering Chemistry Research*, 2013. **52**(23): p. 7660-7667.
- [10] Shu, C., et al., *A novel desulfurization process of gasoline via sodium metaborate electroreduction with pulse voltage using a boron-doped diamond thin film electrode*. *Fuel*, 2013. **113**: p. 187-195.
- [11] Shen, Y., T. Sun, and J. Jia, *A novel desulphurization process of coal water slurry via sodium metaborate electroreduction in the alkaline system*. *Fuel*, 2012. **96**: p. 250-256.
- [12] Shimin Zhang, et al., *Electrochemical reduction of NaBO₂ into NaBH₄ with pulse voltage using the Eu-Co-Ni-B coating electrode*. *Journal of Dispersion Science and Technology*. 2020.