Theme: Hydrogen Export

Exporting Green Hydrogen as a Powder

Aneeka Patel, Peter Ó Conghaile, Terry D. Humphries, Mark Paskevicius, Craig E. Buckley
Department of Physics and Astronomy, Institute for Energy Transition, Curtin University, Bentley, WA, 6102, Australia
Email: aneeka.patel@postgrad.curtin.edu.au

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Closed loop green hydrogen export cycle

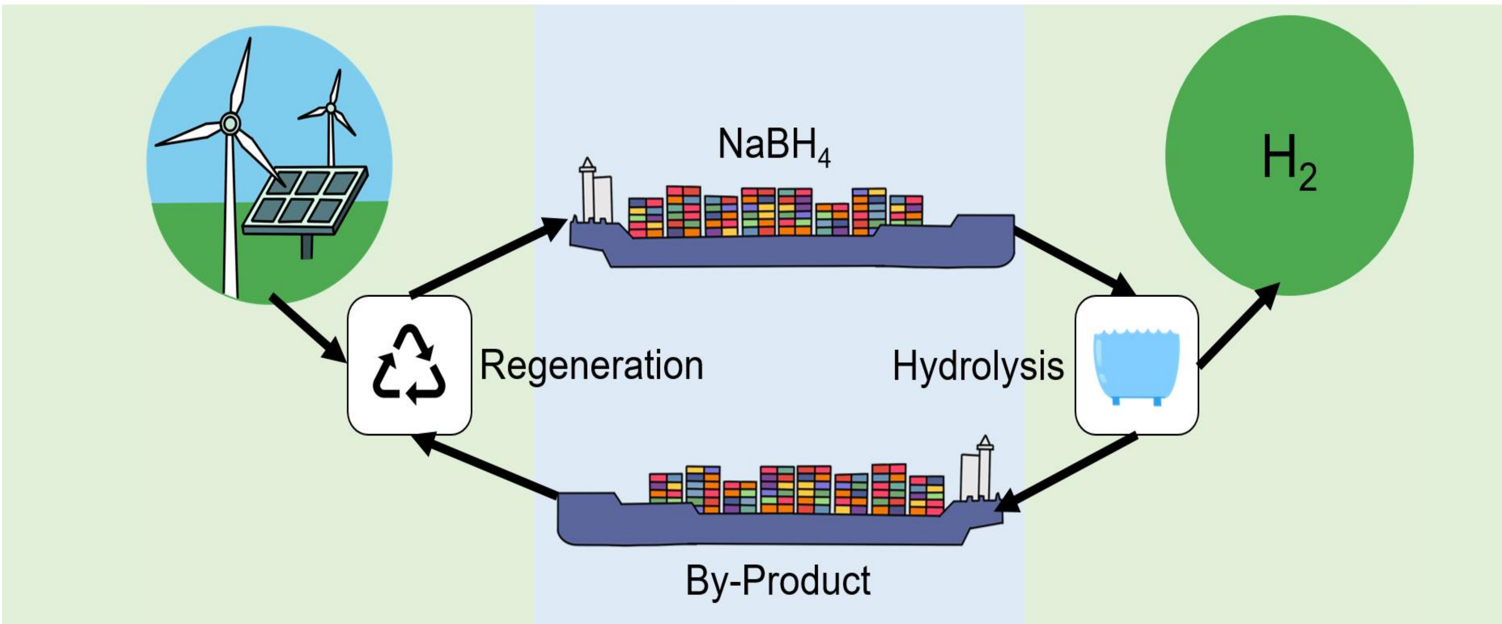


Figure 1: Schematic of proposed closed loop green hydrogen export cycle.

What is green hydrogen?

Green hydrogen is hydrogen which is produced from **renewable energy**, such as solar, wind or hydropower. Typically green hydrogen is made from the electrolysis of water, using only renewable energy sources to power the process.

Why export hydrogen energy?

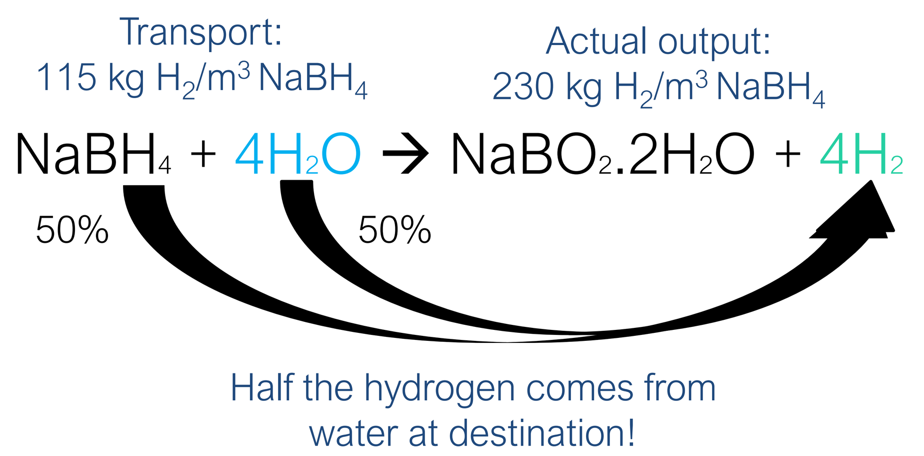
Globally the energy demands are rising and there is a shift away from fossil fuels towards **Net Zero carbon emissions by 2050**. As **hydrogen** is a **clean energy carrier** it can offer a **sustainable solution** to this problem. **Australia** is an **energy rich** country which can produce more energy than it can consume and has renewable sources in plentiful supply. Therefore, it can **produce and export green hydrogen** to countries who are unable to meet their own energy demands. **To use hydrogen** as an energy source it needs to be **stored after generation and released on demand** when required. However, **hydrogen** is extremely **light**, so it is vital to **increase** the **storage density of hydrogen to make export viable.**

Exporting hydrogen as a powder

Sodium borohydride ($NaBH_4$) is a metal hydride which can be used to store hydrogen. This non-toxic **white powder** has a **high hydrogen content** by weight (**≈ 10.7 wt.%**). As it is **solid-state at room temperature and pressure** it is a strong candidate for hydrogen export as it is **easy and safe to transport** on regular ships.

H_2…just add water!

To release the hydrogen, water is simply added in the presence of a metal catalyst, this is known as hydrolysis. During this reaction the **hydrogen molecules in the water** are also **liberated**, essentially **doubling the storage capacity** of this material (without having to ship the extra weight).



Project Aim:

Sodium borohydride could offer a solution to store and transport hydrogen. This **powder** could be **exported from Australia** to help countries **transition towards** a **hydrogen economy** to aid **decarbonisation**. At present, this powder is **too expensive** to be used commercially. To **reduce the costs, this project investigates the regeneration of sodium borohydride ($NaBH_4$) from its hydrolysis byproduct sodium metaborate ($NaBO_2.xH_2O$).** Current regeneration methods use thermal or mechanical energy, however these methods require high energy therefore they are not commercially sustainable.

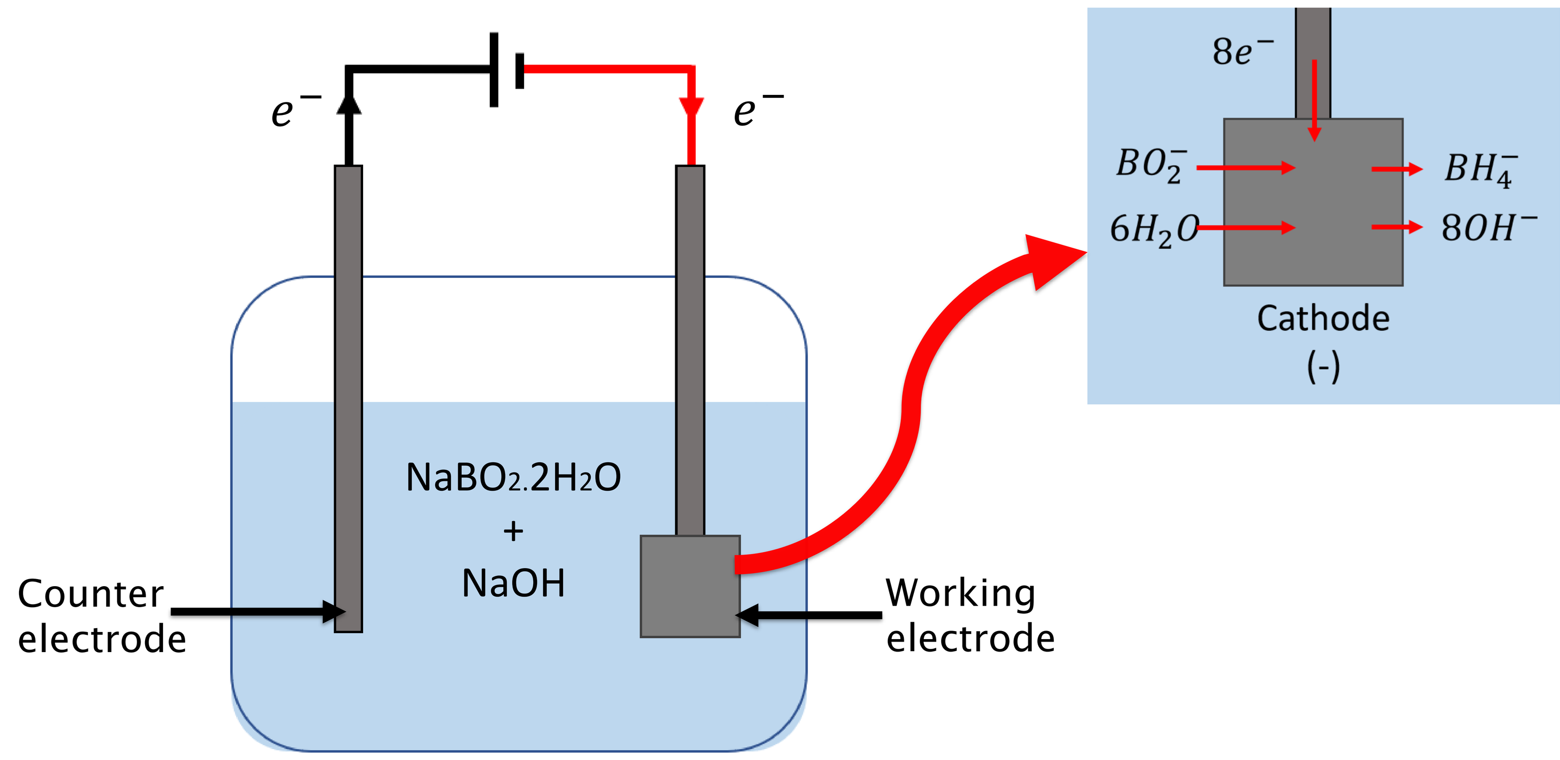
To overcome this, the storage material could be **regenerated using electrochemistry**. This can be done at **ambient conditions**, eliminates the need to de-hydrate the by-product and re-uses the electrodes so that the **only input is electricity.** By powering this system using **renewable energy sources** it will ensure **green hydrogen is exported**. By **enhancing the electrochemical efficiency for the desired reaction** this **project aims to develop a closed loop green hydrogen export cycle,** which has the potential to **reduce the costs of hydrogen to as low as $US 4.40/kg***.

*based on electricity cost of $US 0.0685/kWh)

Electrochemical Regeneration of $NaBH_4$

The **sodium metaborate by-product ($NaBO_2.xH_2O$)** is placed in an **aqueous solution** with **sodium hydroxide (NaOH).** As $NaBH_4$ hydrolyses in water, **NaOH increases** the **pH** of the solution to **stabilise any borohydride formed** from decomposing too quickly. It also acts as an electrolyte. There are **two electrodes**, a working and a counter electrode, which are placed in the solution and a **voltage applied** across them.

During this process, electrons may take part in other undesired reactions such as water splitting. This research looks into **optimising electrochemical parameters** such as **electrode materials, applied voltages** and **cell configurations** to **enhance the electron efficiency towards the desired reaction.**



Oxidation:

$$8OH^- \rightarrow 4H_2O + 2O_2 + 8e^-$$

Reduction:

$$BO_2^- + 6H_2O + 8e^- \rightarrow BH_4^- + 8OH^-$$

Figure 2: Electrochemical cell containing $NaBO_2.2H_2O$ and NaOH in an aqueous solution. A voltage is applied across electrodes to reduce the $[BO_2]^-$ to $[BH_4]^-$ at the working electrode (cathode).

How to detect $NaBH_4$ after regeneration

After attempting regeneration using electrochemistry, the solution needs to be **analysed to confirm if borohydride was successfully produced** – and **how much** was made. There are several ways in which this can be done.

Spectroscopy techniques such as **nuclear magnetic resonance (NMR), Fourier transform infrared (FTIR)** or **Raman** can be used to confirm the presence of borohydride. These techniques rely on the nuclei interacting with a magnetic source at specific frequency or B-H bonds interacting with the radiation source at a specific wavenumber to **produce a characteristic signal** for $[BH_4]^-$. The **intensity of the peak** can be used to **determine the amount of borohydride** in solution if **calibrated.**

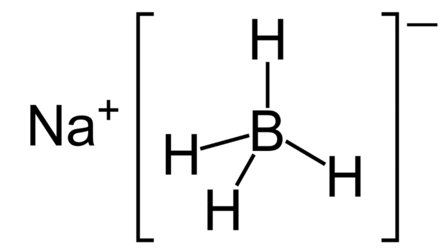


Figure 3: $NaBH_4$ molecule

Alternatively, the amount of borohydride can be determined by **hydrolysing the solution** in the presence of a metal catalyst or adding acid to reduce the pH. The **volume of gas** produced can then be **measured** using a **water displacement** apparatus (Figure 4). Using the **stoichiometry** of the **hydrolysis reaction** the **quantity of borohydride** in solution can be determined. To **confirm** that the **gas** is H_2, a gas sample is analysed using a **gas chromatograph.**

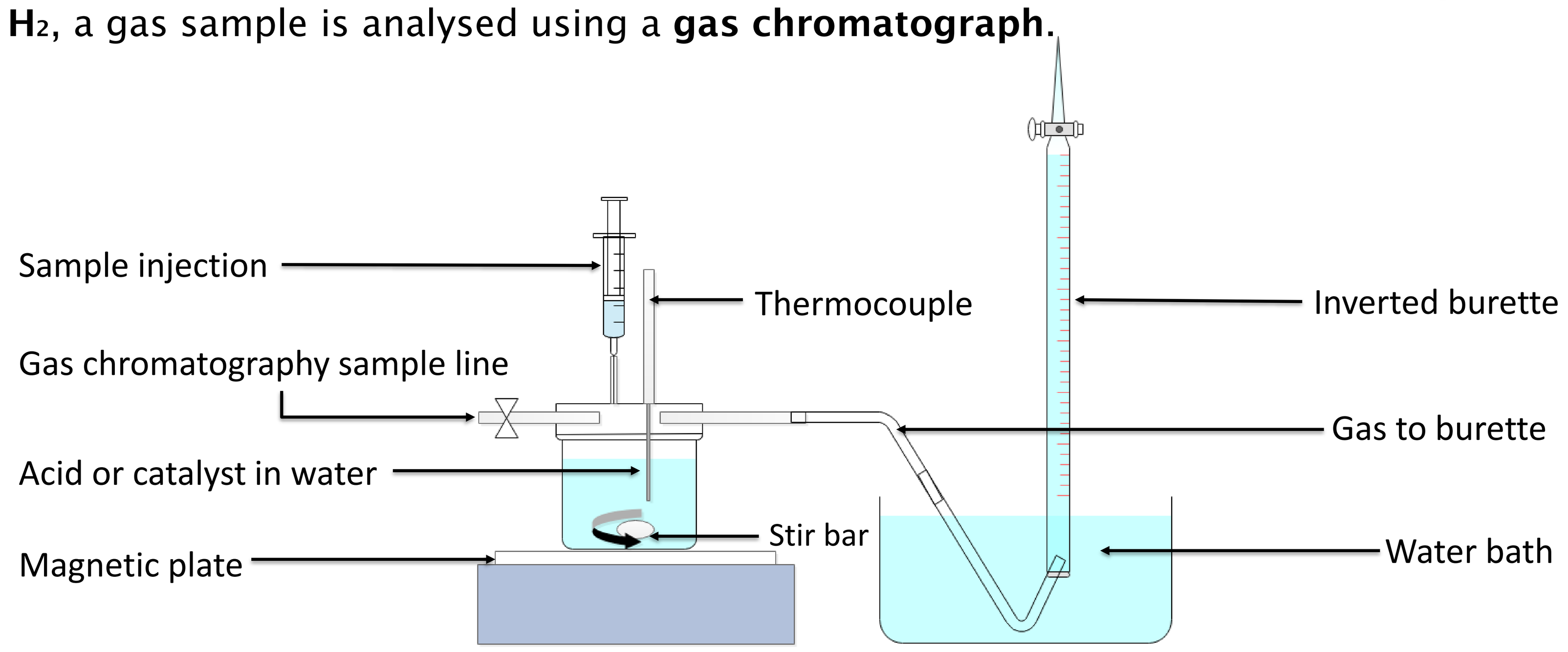


Figure 4: Hydrolysis and water displacement set up to determine amount of $NaBH_4$ regenerated

Another option is to use **electrochemistry** to detect borohydride. **This can detect the lowest concentration compared to the other techniques.** A **gold electrode** is used to **oxidise** the $[BH_4]^-$ in solution. A **cyclic voltammogram (CV)** is used to apply a changing voltage at a specific scan rate [V/s] between two voltages. The **response provides the current** during the oxidation and reduction process. When the $[BH_4]^-$ is **oxidised it produces a characteristic peak**, in this case at around **≈ -0.6 V vs the Ag/AgCl** reference electrode (Figure 5). The **intensity** of this **peak increases with concentration.** Therefore, this can be **calibrated** to **determine the amount of sodium borohydride** regenerated.

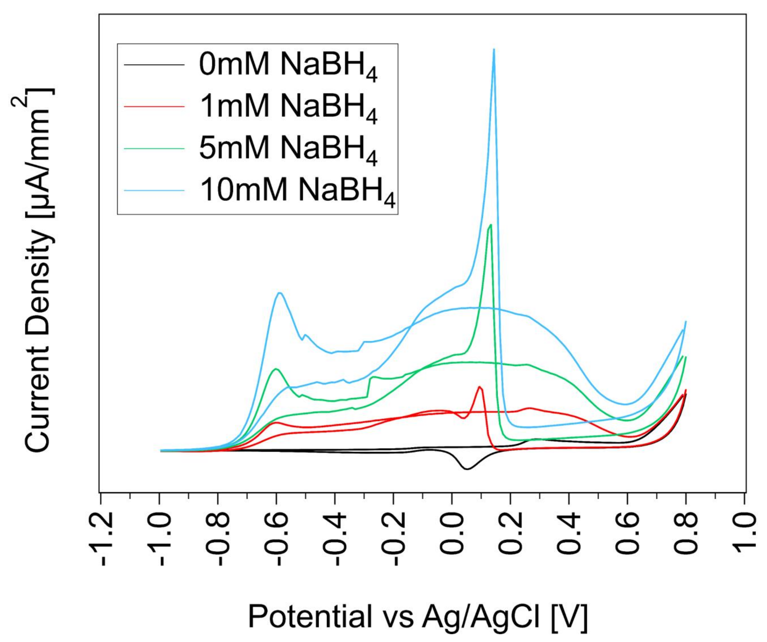


Figure 5: Cyclic voltammogram between 0.8 and -1.0 V vs. Ag/AgCl reference electrode, using gold working electrode and Pt counter electrode to oxidise $NaBH_4$ in 1M $NaBO_2$ and 1M NaOH.

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