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Chemical Compression and Transport of Hydrogen using Sodium Borohydride

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As the need for renewable energy is heightened, energy storage and distribution solutions must be developed. Hydrogen is an abundant energy source with the highest gravimetric energy density of all materials. It can be utilised in fuel cells to generate electricity, with only a water vapour by-product. For hydrogen storage and re-fuelling stations for vehicles, hydrogen compression is required to improve the volumetric energy density in storage tanks. It is proposed that sodium borohydride ($NaBH_4$), a hydrogen carrier, could be utilised to transport and chemically compress hydrogen for refuelling stations. Chemical compression of hydrogen to over 1000 bar has been demonstrated in this study using either hydrolysis or methanolysis of $NaBH_4$. Interest has been growing to improve the cost of closed-cycle regeneration of this borohydride energy carrier. A cost and efficiency analysis of the $NaBH_4$ regeneration cycle using green energy demonstrates that it may be cost competitive with alternative methods of hydrogen transport, including using liquid hydrogen, ammonia, or liquid organic hydrogen carriers.

Introduction

To transition into a zero-carbon emission future, renewable energy systems are necessary. These sustainable sources of energy can provide environmental and economic benefits as opposed to the current dependence on, and depletion of, fossil fuels. To improve renewable energy use, energy storage solutions must be developed to level out fluctuations between the production and consumption of energy.

Hydrogen is an ideal energy carrier due to its abundance, high gravimetric energy density, and lack of adverse environmental impact.[1, 2] Hydrogen can be stored in molecular form within high-pressure gaseous or liquid hydrogen tanks. It can also be stored chemically within a diverse range of liquids and gases, including as ammonia, liquid organic hydrogen carriers, and traditional hydrocarbons, such as petroleum. Alternatively, atomic hydrogen can be stored in the solid-state, chemically bound within metal hydrides, including borohydrides (e.g. $NaBH_4$).[3-5] In 1838, the first fuel cell was developed to generate electricity from the reaction between hydrogen and oxygen, after the electrolysis of water was demonstrated in 1801.[6] The idea of a hydrogen economy can be dated back to 1972.[7] Despite these early roots, the hydrogen economy is only now becoming a widespread reality as our need for a renewable future manifests.

The global market for renewable hydrogen, or 'green' hydrogen, is predicted to expand significantly in the coming decades.[8] Australia, in particular, is suitable to hold a significant share of this hydrogen export market due to its proximity to Asia and its plentiful renewable energy sources. Japan has a goal to become the world's first "hydrogen society" with targets to have 800,000 hydrogen vehicles and 5.3 million residential fuel cells by 2030.[9] The International Energy Agency (IEA) estimates that hydrogen produced from solar photovoltaics in Australia and imported to Japan will cost less ($4.20 USD/kg H_2, $0.0315 USD/kWh) than producing it in Japan from renewables ($4.50 USD/kg H_2, $0.0833 USD/kWh) by 2030.[10] In the same time-span, Korea aims to become the world's largest producer of hydrogen vehicles and fuel cells with a hydrogen demand of 1.94 million tonnes by 2030 (5.26 million tonnes by 2040).[11] As Japan and Korea have a limited capacity for green hydrogen production, there is a market for Australia and other renewable-rich countries to export some of the required hydrogen to meet global energy demands. In fact, the demand for clean energy delivery also grows across Europe due to geopolitical concerns and a shift away from natural gas.[12]

Transportation of energy over long distances requires high volumetric energy densities.[13] For this reason, energy is more efficiently transported using molecules rather than electricity.[10] This is the backbone of today's world's energy network, where 40% of all maritime trade consists of fossil fuels.[14] In the case of natural gas, it is transported worldwide as liquefied natural gas (LNG) on ships or in large-scale pipelines.[10] LNG shipping usually involves cryogenic storage at −162 °C to increase energy storage densities and reduce the tank pressure requirements.[15] Hydrogen transport may also be undertaken in a similar fashion.

ARTICLE

Table 1. Hydrogen carriers and their properties, costs are from 'The Future of Hydrogen' report by the IEA which includes production ($0.0685 USD/kWh), conversion, shipping, and reconversion costs.

Hydrogen carrier	Export temperature (°C)	Export pressure (bar)	Volumetric density of H_2 (kg/m^3)	Cost (USD/kg H_2)
H_2 (gas)	20	700	39.7 [16]	-
H_2 (liquid)	-253	1	71.1 [16]	$7.10 [17]
NH_3 (liquid)	20	10	107 [16]	$5.50 [17]
LOHC - methylcyclohexane (liquid)	20	1	47.4 [16]	$5.90 [17]
$NaBH_4$ (solid)	20	N/A	69* - 137**	See discussion

* During transport considering a powder packing fraction of 60%

** During transport considering a powder packing fraction of 60% and noting the additional hydrogen generated from water in the hydrolysis reaction at the destination

At a local level, for short distances, hydrogen can be transported in storage tanks via trucks in the form of compressed gas, albeit at a low energy density, even at high pressure (Table 1). This is expensive and not particularly viable for long distance overseas transport, which requires higher energy densities on ships to be economical.[10] For seaborne transportation, a variety of hydrogen storage methods and hydrogen carriers are being considered in order to achieve reliable international hydrogen trading.[17]

The large-scale transportation of hydrogen remains a technical challenge, primarily due to the low volumetric density of hydrogen gas. This means that hydrogen is more efficiently transported long distances after transforming it into a higher density form. Typically, hydrogen export is considered to be viable in the form of liquid hydrogen (LH$_2$), liquid organic hydrogen carriers (LOHC), or ammonia (NH$_3$), but often solid-state hydrogen carriers such as NaBH$_4$ are overlooked (Table 1).[10, 17, 18] Some of these hydrogen storage methods involve significant energy penalties on conversion, including cooling, compression, chemical conversion, and chemical release.[10] The

entire hydrogen value chain must be assessed from a technological standpoint along with safety and feasibility, but achieving a low cost of hydrogen at the export destination is potentially the main driver. Figure 1 illustrates the different options for hydrogen export. LH$_2$ is significantly more energy dense than the gaseous form with a volumetric energy density of 71.1 kg H$_2$/m^3 as opposed to 39.7 kg H$_2$/m^3 (Table 1). However, the hydrogen liquefaction process is energy intensive, requiring a temperature of -253 °C, causing issues due to boil off losses and noting that liquefaction consumes a third of the energy contained in hydrogen.[19]

Chemically converting hydrogen into an alternative molecular form as a hydrogen carrier can achieve high volumetric hydrogen densities ideal for long distance transport. Transporting hydrogen as NH$_3$ is potentially advantageous to LH$_2$ as NH$_3$ is a liquid at -33 °C (at atmospheric pressure). Alternatively, it can be exported as a compressed gas at 10 bar at ambient temperature (107 kg H$_2$/m^3, Table 1). Since NH$_3$ is also already commercially traded on an international scale, its export is an established process with well-known infrastructure
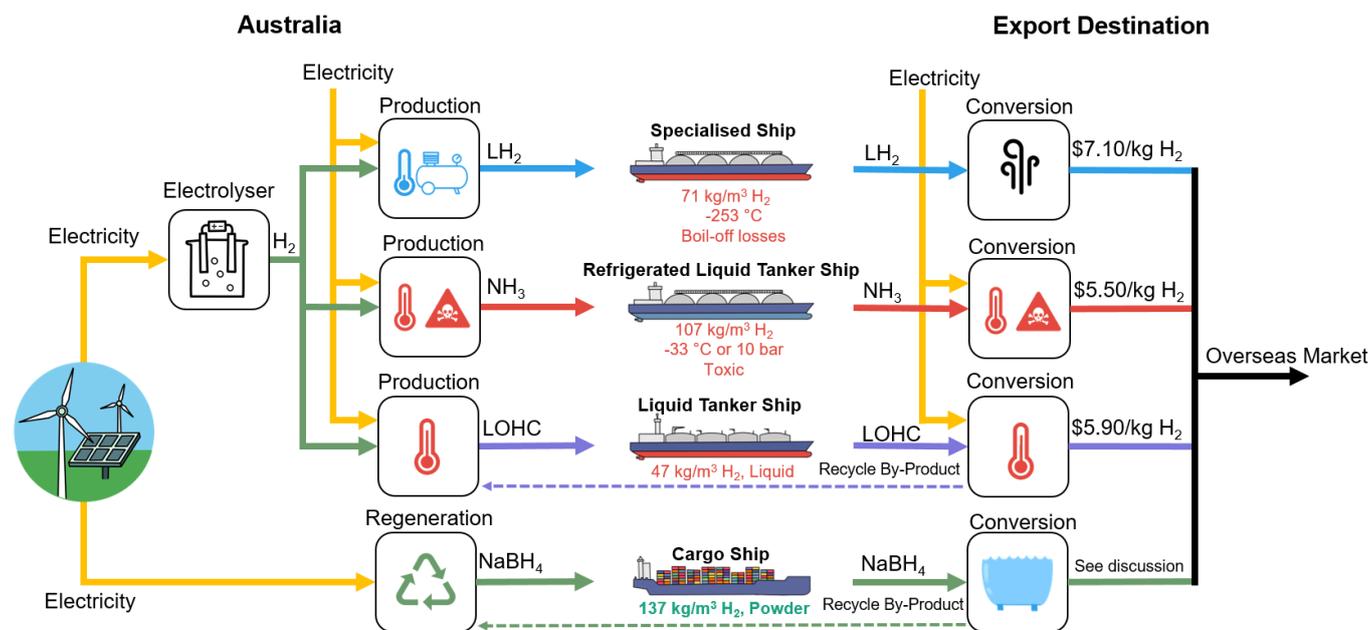
Figure 1. Comparison of different methods of hydrogen export, costs are in USD from 'The Future of Hydrogen' report prepared by the IEA. Production of hydrogen through electrolysis uses 54 kWh/kg H$_2$ at $0.0685 USD/kWh.

for production. However, the extreme toxicity of NH_3 makes it a less favourable option when considering potential safety issues, especially in populated ports and trade centres. Additionally, the conversion of H_2 into NH_3 and the reconversion back to H_2 at the export destination involves additional energy requirements, purification steps, and significant capital expenditure.

LOHCs can be transported at atmospheric conditions without the need for low temperatures in a manner similar to petroleum. However, unlike petroleum, LOHCs are a recyclable hydrogen carrier, which are not burnt but only processed to extract hydrogen before being recycled. A commonly considered LOHC is methylcyclohexane, which has a volumetric hydrogen density of 47.4 kg H_2/m^3 (Table 1). LOHCs are generally expensive, and the conversion and reconversion processes add to the cost. By design, the by-product left after H_2 extraction has the potential to be recycled back to the original LOHC. Despite having to ship the LOHC by-product back to the export location for reprocessing, this technology does have a promising cost of hydrogen for the user. Depending on the type of LOHC, the toxicity could also be an issue.[20]

Metal borohydrides are typically solids that have some of the highest gravimetric and volumetric densities for hydrogen, above that of liquid hydrogen.[4, 21] $NaBH_4$ has a gravimetric hydrogen storage capacity of 10.7 wt% and a volumetric hydrogen storage capacity of 115 kg m^{-3}.[4] Due to the high hydrogen storage capacity offered by $NaBH_4$, and its easily transportable form as a powder, it has interested researchers for many decades as a potential hydrogen energy carrier.[22-24]

When exposed to water, $NaBH_4$ releases hydrogen gas through hydrolysis, releasing not only its own hydrogen, but also splitting water to release twice the amount of hydrogen it contains. The hydrolysis process generates hydrogen gas, but also forms a water-soluble by-product: sodium metaborate dihydrate, $NaB(OH)_4$, which can be dried to sodium metaborate, $NaBO_2$:

$$NaBH_4 + 2H_2O \rightarrow 4H_2 + NaBO_2 \qquad (1)$$
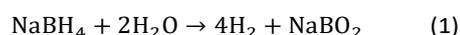
The formation of the metaborate by-product increases the pH of the water, inhibiting the hydrolysis reaction of $NaBH_4$.[25] The hydrogen release reaction can therefore be controlled by pH or by using a catalyst. In fact, $NaBH_4$ is relatively stable in highly alkaline solution, so could also be pumped as a solution.[25] In the 1950's, Schlesinger *et al.* demonstrated that $CoCl_2$ provided a catalytic improvement in the rate of $NaBH_4$ hydrolysis.[22] At present, the hydrolysis of $NaBH_4$ is a well-studied process and a plethora of catalysts have been established, including numerous cobalt-based catalysts.[3, 26, 27] Alternatively, an alcohol such as methanol can be added to the $NaBH_4$ to release hydrogen and produce a different by-product, sodium tetramethoxyborate:

$$NaBH_4 + 4CH_3OH \rightarrow 4H_2 + NaB(OCH_3)_4 \qquad (2)$$
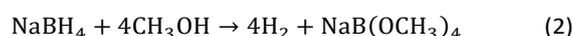
For these reactions, half of the produced hydrogen gas comes from the water or methanol used. This results in an effective gravimetric and volumetric hydrogen density of 21.4 wt% H_2 and 137 kg H_2 m^{-3} for each unit of shipped $NaBH_4$ (assuming a powder packing fraction of 60%). This means that the volumetric hydrogen density in $NaBH_4$ is 1.28 times greater than ammonia and 1.93 times greater than liquid hydrogen. Despite a 'no-go' recommendation for $NaBH_4$ hydrolysis for on-board vehicular application by the US Department of Energy in 2007, $NaBH_4$ stands as a promising hydrogen energy carrier for alternative applications, including stationary applications, heavy vehicle transport, and hydrogen export.[24, 28, 29] $NaBH_4$ powder can be stored as a powder at room temperature, making it ideal for export and transport in regular shipping vessels, e.g. in shipping containers. At the destination, hydrogen can be released from $NaBH_4$ by simply adding it to water in the presence of a hydrolysis catalyst with no additional energy input.

$NaBH_4$ could be synthesised where renewable energy is in excess (e.g. Australia) and then shipped to regions requiring green energy. The sodium borate by-products of the hydrolysis reaction can be exported back to the export location (e.g. Australia) to be reprocessed into $NaBH_4$ using renewable energy (Figure 1).[30-33]

Hydrogen is typically required to be gaseous for it to be stored in most hydrogen vehicles and/or converted to electricity, such as in a fuel cell. Although, it should be noted that direct borohydride fuel cells (DBFC) are an emerging technology that could bypass this requirement.[34] Hydrogen compression is required for most local hydrogen storage and distribution operations, including for hydrogen refuelling stations. Heavy vehicles are typically refuelled with hydrogen to 350 bar and lighter vehicles to 700 bar.[35] The hydrogen is typically compressed to 900 bar at refuelling stations for storage until dispensed.[36]

Most commonly, hydrogen is compressed using mechanical compressors (pistons, diaphragms, and current generation ionic liquid compressors).[37] However, these devices have issues with high energy consumption, mechanical maintenance, and potential hydrogen embrittlement.[37] Non-mechanical hydrogen compressors have also been explored including the use of metal hydrides, electrochemical methods, and absorption-desorption compressors.[37] Mechanical ionic liquid compressors have the highest energy efficiency, over 70%, and have the lowest energy consumption of 2.7 - 4.4 kWh/kg H_2 (5 to 900 bar).[18, 37] However, there remains potential problems such as leaks, cavitation, and corrosion.[12]

Sodium borohydride can be used to generate hydrogen above atmospheric pressure through hydrolysis as a form of chemical hydrogen compression.[38, 39] Thus, it should be considered that $NaBH_4$ could directly generate high hydrogen pressure suitable for use at refuelling stations by simply adding water, avoiding the use of mechanical compression. The thermodynamics for

hydrolysis and methanolysis of $NaBH_4$ suggest that extreme hydrogen pressure is possible,[40] but to date it has not been shown that hydrogen can be generated at pressures comparable to mechanical compression technology.

Results and Discussion

On a large scale, $NaBH_4$ could be used for energy transport, but potentially also be utilised for high pressure hydrogen compression for refuelling vehicles. For this application, a stable alkaline solution of $NaBH_4$ could be pumped into a hydrogen compression chamber that contains a catalyst, which would initiate hydrolysis. This would result in the production of H_2 gas in a closed volume leading to hydrogen compression. The compressed hydrogen gas could then be pumped into a hydrogen vehicle for refuelling, whilst the remaining by-product solution would be removed for reprocessing back to $NaBH_4$ (Figure 2a). This is a simplified concept, but could be reconfigured to include additional components such as hydrogen gas storage tanks, liquid reservoirs, cooling units, safety release valves, hydrogen sensors, piping, and dispensers.[41]

High pressure hydrolysis and methanolysis experiments were undertaken in closed-volumes within a laboratory setting, which demonstrated that hydrogen compression is viable using $NaBH_4$ to extreme pressures (Figure 2b, 2c). Hydrolysis was initiated by pumping water into a closed volume containing $NaBH_4$ and a Co-based catalyst to enable hydrogen release,

whereas methanolysis was performed by pumping methanol into a closed volume containing $NaBH_4$ powder. During hydrolysis, the $NaBH_4$ aqueous solution was observed to be clear initially, with black catalyst particles dispersed through the solution. Once pumping of the liquid had ceased, the hydrolysis reaction continued and the solution became opaque as less soluble white $NaB(OH)_4$ by-product was precipitated (Figure 2c). Both the hydrolysis and methanolysis reactions demonstrated the production of hydrogen at pressures exceeding 1000 bar (Figure 2b), demonstrating that this technology is suitable for high pressure hydrogen compression applications. The choice of solvent (water or methanol) dictates the by-product that is formed by either hydrolysis or methanolysis. A key factor in making chemical compression technology using $NaBH_4$ viable is the commercial feasibility of the regeneration of $NaBH_4$ from the reaction by-products.

To be a commercially viable hydrogen compressor, $NaBH_4$ must be able to be recycled in an energy efficient manner, using renewable energy, to compete with other hydrogen compression technologies. The energy cost of mechanical hydrogen compression is high, but insignificant compared to the energy required to first synthesise the hydrogen via electrolysis. The mechanical compression of hydrogen from 5 bar to 900 bar requires 2.7 - 4.4 kWh/kg H_2.[18, 37] Whereas, the energy cost of the electrolysis of water to hydrogen (and oxygen) requires 54 kWh/kg H_2.[42] Hydrogen compression via the hydrolysis or methanolysis of $NaBH_4$ is exothermic and therefore does not require any external energy for hydrogen compression.
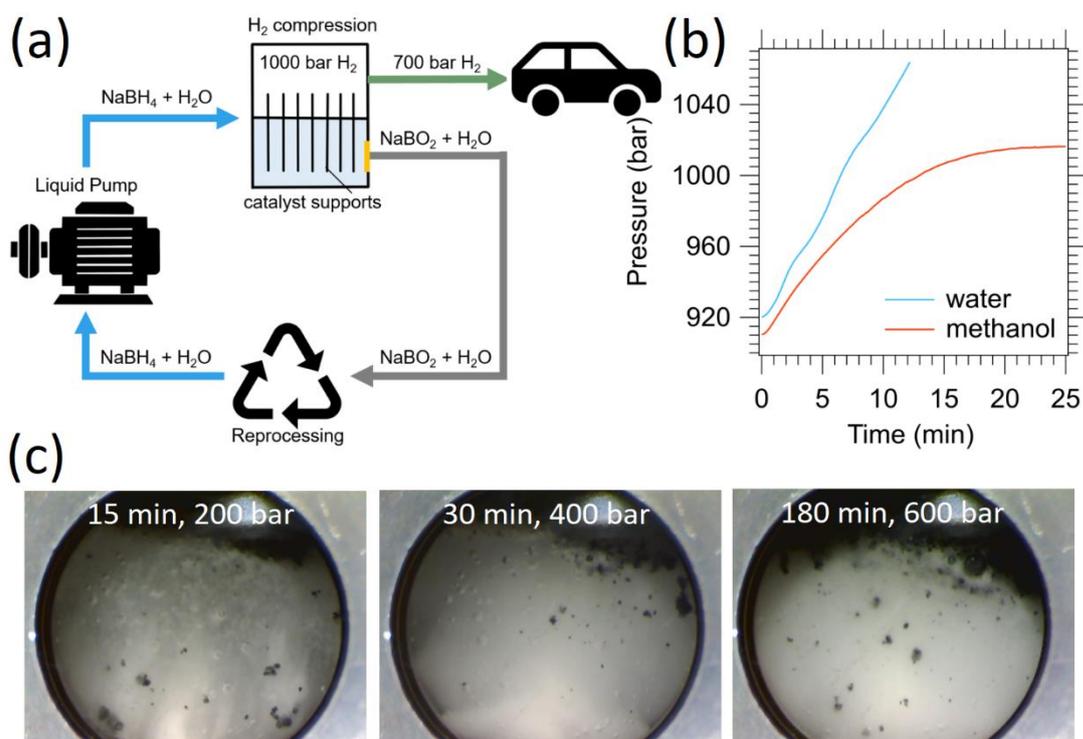
Figure 2. Hydrogen compression using $NaBH_4$: (a) Schematic of hydrogen compression for refuelling vehicles. (b) Pressure data from the hydrolysis (water) and methanolysis (methanol) of $NaBH_4$, demonstrating hydrogen compression to over 1000 bar. (c) Hydrolysis of $NaBH_4$ to 600 bar using a catalyst (black) pictured through a 20 mm diameter sapphire window.

ARTICLE

However, to make this technology renewable, the sodium borohydride must be recycled, which would account for the main energy cost. It is unlikely that $NaBH_4$ production, or recycling, could be made competitive with mechanical compression in a direct comparison on an energy basis. However, the production of $NaBH_4$ for export applications may be competitive, with an added bonus of 'energy-free' hydrogen compression at the export destination.

$NaBH_4$ is currently synthesised using either the Schlesinger or Bayer process, which results in a price of up to $260 USD/kg H_2.[43-45] Both of these processes are not fully closed-cycle, with the formation of waste products, such as Na_2SiO_3. A recyclable process for $NaBH_4$ formation is required, which must enable a lower cost to these existing methods. $NaBH_4$ can be recycled from its hydrolysis by-products in either metallothermic or ball milling processes using metals, metal hydrides, or metal alloys including magnesium, sodium, and aluminium,[46-49] for example:

$$NaBO_2 + 2H_2 + 2Mg \rightarrow NaBH_4 + 2MgO \qquad (3)$$
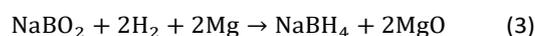
The greatest energy cost comes from recycling the resulting metal oxides back to the starting metal compound (Figure 3, e.g. MgO back to Mg). This is because most of the current regeneration methods for metals are energy intensive and include a significant carbon footprint.[50, 51] There are also some emerging green electrochemical methods for metal regeneration to consider, which could enable green $NaBH_4$ production.[52, 53] It should also be noted that both the metallothermic and ball milling regeneration processes often require a hydrogen gas input stream, which would need to be sourced, potentially through traditional electrolysis of water, at a further energy, and cost, penalty. However, there are studies where the hydrogen locked in $NaB(OH)_4$ can be utilised in the reformation of $NaBH_4$, albeit, at the expense of more metal being required during the regeneration step,[31] for example:

$$NaB(OH)_4 + 4Mg \rightarrow NaBH_4 + 4MgO \qquad (4)$$
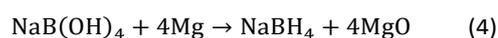
The energy cost for $NaBH_4$ regeneration using magnesium will be substantially determined by the regeneration energy of MgO back to Mg (Figure 3) which is reported to be 102 kWh/kg Mg,[40] corresponding to a hydrogen energy cost of 615 kWh/kg H_2.

Specifically, magnesium metal has shown to be effective in $NaBH_4$ regeneration, but currently has a great energy and carbon cost associated with its production using the Pidgeon process.[54] Magnesium metal production currently requires 102 kWh/kg Mg and has CO_2 emissions of 37 kg CO_2/kg Mg.[55, 56] Based on the 2030 cost of electricity (considering capacity factor by the IEA Future of Hydrogen report),[17] an energy cost of $0.0685 USD/kWh results in a Mg production cost of $7 USD/kg Mg. Based on the molar ratio of Mg required to produce H_2 using $NaBH_4$ using reactions (1) and (3), a cost for hydrogen at an export destination can be calculated as $42.10 USD/kg H_2. Considering electrolysis of the initial H_2 ($3.70 USD/kg H_2)[17] and shipping costs ($0.44 USD/kg H_2)[17], the total cost is $46.24
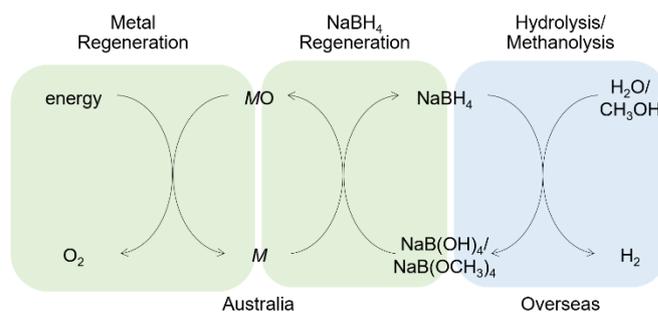
Figure 3. Reaction processes for H_2 production using $NaBH_4$, where M represents a metal.

USD/kg H_2. Similarly, using reactions (1) and (4), the cost for hydrogen is calculated to be $84.20 USD/kg H_2 ($88.34 USD/kg H_2 considering the electrolysis of initial H_2 and shipping costs).[17] This cost for hydrogen from $NaBH_4$ is significantly reduced from the hydrogen price using the current Schlesinger method of $NaBH_4$ production, however it is not competitive with alternative hydrogen export technologies (Figure 1). The DOW Chemical Company reported a production cost of $6 - 12 USD/kg H_2 using an aluminium-based reduction method for $NaBH_4$ regeneration from $NaBO_2$.[57] A less costly method is the carbothermal reduction method with a reported cost of $2 - 7 USD/kg H_2, however this method results in the production of large quantities of CO_2.[57]

Electrochemical regeneration methods for $NaBH_4$ from $NaBO_2$ are also reported in the literature, but are often inconsistent or even reported to be irreproducible.[58] It is noted that the electrochemical production of $NaBH_4$ would bypass the requirement of hydrogen gas in regenerating $NaBO_2$, as the hydrogen is split from water directly, in a single step process, during $NaBH_4$ formation:

$$NaBO_2 + 2H_2O \xrightarrow{electricity} NaBH_4 + 2O_2 \text{ (g)} \qquad (5)$$

Electrochemical regeneration studies for $NaBH_4$ report electrical current efficiencies up to 80%.[58] Using this value and the IEA 2030 energy cost of $0.0685 USD/kWh,[17] $NaBH_4$ could potentially be produced at $4.00 USD/kg H_2 ($4.44 USD/kg H_2 considering shipping). This low cost of production is promising and much lower than any of the 2030 predictions for competing hydrogen export technologies (> $5.50 USD/kg H_2 in Figure 1). A number of patents and research articles suggest that electrochemical synthesis of $NaBH_4$ is possible at low cost but they must be investigated further to ensure a reliable and cost-effective process for $NaBH_4$ synthesis at scale.[43, 59-62]

The energy available from the conversion of hydrogen back to water is dictated by the thermodynamics for the following reaction, for the higher heating value (HHV) of hydrogen:

$$4H_2 \text{ (g)} + 2O_2 \text{ (g)} \rightarrow 4H_2O \text{ (l)} \qquad (6)$$
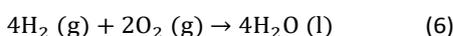
The maximum theoretical energy efficiency of the $NaBH_4$ cycle can be calculated by comparing the energy required for the

endothermic reactions required to make $NaBH_4$ (Eq 5) to the exothermic energy produced by the hydrogen oxidation reaction (Eq 6).[63, 64] For example, the maximum theoretical energy efficiency for the hydrolysis and regeneration of $NaBH_4$ from $NaBO_2$ using MgH_2 has been reported to be 49.9%.[63] Although this maximum theoretical energy efficiency was deemed feasible, a much higher efficiency is possible from electrochemical regeneration of $NaBH_4$. The standard enthalpy of reaction for the electrochemical regeneration of $NaBH_4$ (Eq 5) is 1355.5 kJ/mol $NaBH_4$, which is the minimum theoretical energy input needed.[40] The standard Gibbs free energy of the hydrogen oxidation reaction is the maximum theoretical energy output of the system, 948.6 kJ/mol $NaBH_4$ (Eq 6) considering the hydrolysis of $NaBH_4$ produces 4 moles of hydrogen gas according to Eq 1.[40] Therefore, the theoretical maximum efficiency of the $NaBH_4$ system is 70.0% when electrochemical regeneration is used. This potential efficiency is remarkably close to the maximum theoretical limit of 83.0% for a typical electrolyser-fuel cell combination,[65] but the $NaBH_4$ scenario also includes convenient hydrogen storage within a powder.

Conclusions

The potential of $NaBH_4$ as a hydrogen carrier opens up new avenues for the production, storage and compression of green hydrogen. The ability to compress hydrogen using the hydrolysis and methanolysis of $NaBH_4$ to over 1000 bar can be utilised at hydrogen refuelling stations to compress hydrogen on-site. Cost predictions for the electrochemical production of $NaBH_4$ could enable hydrogen to be exported at a cost of $4.44 USD/kg H_2, at costs much lower than competing technologies. However, to make $NaBH_4$ competitive for hydrogen storage and export, green methods of regeneration must be proven at scale and optimised. This could ultimately change the future of the global hydrogen economy.

Methods

Catalyst Preparation

A catalyst is required for rapid hydrogen evolution during the alkaline aqueous hydrolysis of sodium borohydride. To prepare the Co_3O_4 catalyst, sodium borohydride (powder, 98.0%, Sigma-Aldrich) and cobalt chloride (97%, Sigma-Aldrich) were used as raw materials, using a similar method to Wu *et al*.[66] A 10 mL aqueous solution of $NaBH_4$ (0.225 mol/L) was added dropwise to a 50 mL aqueous solution of $CoCl_2$ (0.3 mol/L) in an ice bath to slow the reaction. The mixture was left to stir for 30 minutes, then filtered to separate the solids and washed with H_2O (~8 times) and ethanol (~5 times). The resulting black powder was then dried at room temperature in air.

High Pressure Equipment

A gas manifold was constructed from Autoclave Engineers and Sitec components rated to above 1378 bar. A Maximator pressure relief valve (MT25RV), rated to 1723 bar, was used to prevent over-pressurisation and control pressure release from the system after the completion of experiments. Pressure was logged using an Additel ADT686 GP20K-DL, rated to 1378 bar, with gas/liquid capability, and an accuracy of 0.7 bar. Liquids were injected into a closed volume using an ultra-high-pressure liquid chromatography (UHPLC) pump from Simadzu (LC-40D X3), rated to 1300 bar using solutions with pH from 1 - 14, operated at 3 mL/min (± 0.03 mL/min). A Rayotek Scientific 20 mm diameter sapphire window was used for pressures up to 600 bar.

Hydrogen Compression using Hydrolysis

For hydrolysis, two different methods were used for the lower pressure (i, 600 bar) and higher pressure (ii, 1000 bar) experiments:

i. 10 g of sodium borohydride (powder, ≥ 98.0%, Sigma-Aldrich) and 10 g of sodium hydroxide (pellets, ≥ 98%, Sigma-Aldrich) were combined in a 58 mL of Milli-Q water to produce an alkaline solution. 0.1 g of the Co_3O_4 catalyst was placed in a closed volume of approximately 95 mL. 58 mL of the alkaline $NaBH_4$ aqueous solution was pumped into the gas manifold.

ii. 15 g of sodium borohydride (≥ 98.0%, Sigma-Aldrich) and 0.2 g of the Co_3O_4 catalyst were placed in a closed volume of approximately 50 mL. 45 mL of Milli-Q water was pumped into the high pressure gas manifold.

Some of the water was consumed in the hydrolysis reaction, and the rest occupied the volume. The gas manifold was under hydrogen pressure before the liquid pumping was ceased (370 bar for the low pressure experiment, 930 bar for the high pressure experiment). From this point onwards, the pressure was allowed to be generated to over 600 bar (low pressure experiment) and to over 1000 bar (high pressure experiment) from hydrolysis alone.

Hydrogen Compression using Methanolysis

4 g of sodium borohydride (≥ 98.0%, Sigma-Aldrich) was placed in a closed volume of approximately 50 mL. 54 mL of methanol (≥ 99.8%, Sigma-Aldrich) was pumped into the system using the UHPLC pump. Some of the methanol was consumed in the hydrolysis reaction, and the rest occupied the volume. The gas manifold was under 910 bar of hydrogen pressure before the liquid pumping was ceased. From this point onwards, the pressure was allowed to be generated to over 1000 bar from methanolysis alone.

Author Contributions

Ainee Ibrahim was involved in formal analysis, investigation, methodology, visualisation and writing. Mark Paskevicius was involved in conceptualisation, funding acquisition, investigation, methodology, supervision and writing. Craig Buckley was involved in funding acquisition, supervision and writing.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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