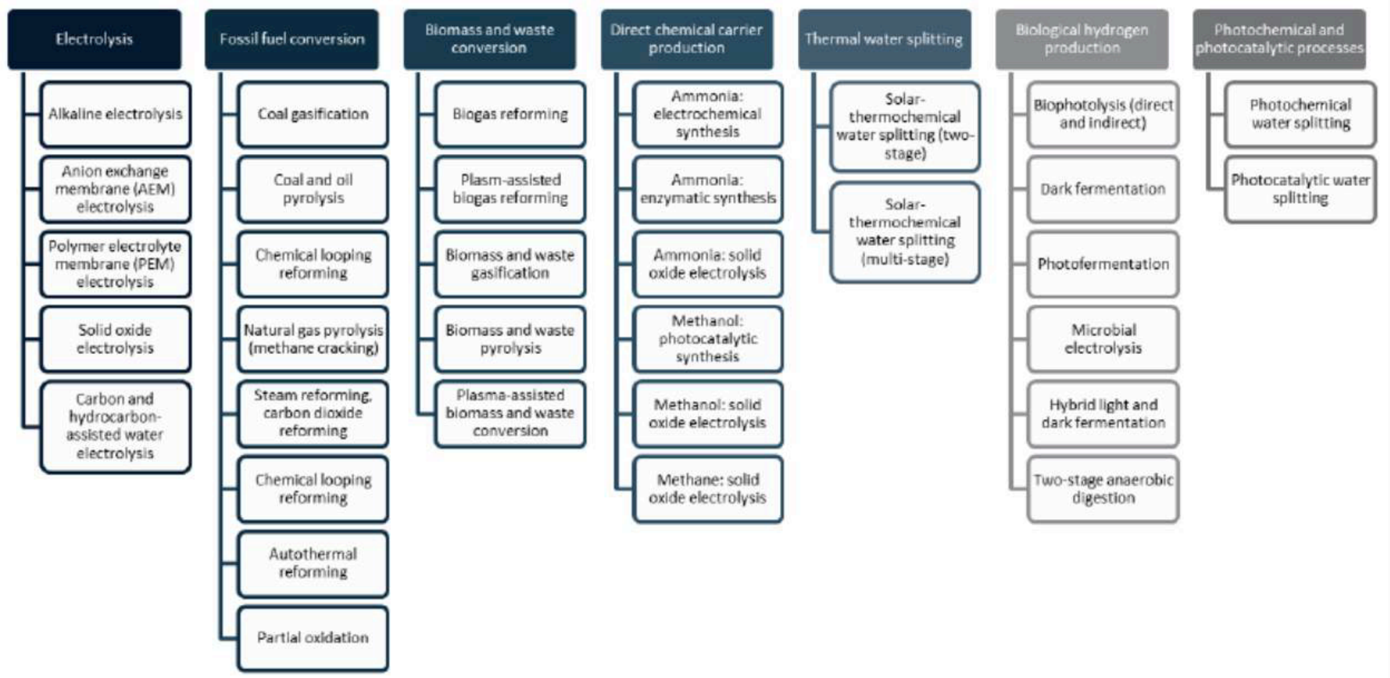
Production

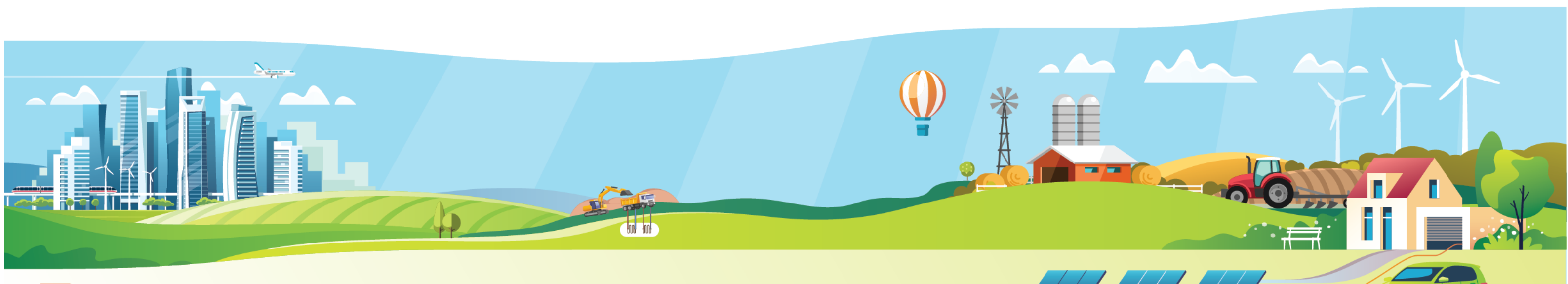
Hydrogen is the most abundant element on Earth, but it is rarely found as a diatomic gas H2. Hydrogen gas needs to be produced from other hydrogen containing compounds using a primary source of energy. Many different primary energy sources can be used to produced hydrogen, fossil fuels, such as natural gas and coal, biomass, non-food crops, nuclear energy, or renewable energy sources such as wind, solar, geothermal and hydroelectric power.

Hydrogen can be produced by many different processes, however not all these processes are technologically and commercially viable at the present time.



From Charnock, S., Temminghoff, M., Srinivasan, V., Burke, N., Munnings, C. & Hartley, P. (2019) Hydrogen Research, Development and Demonstration: Technical Repository, CSIRO. Page 25.

The more established and mature hydrogen production processes are steam methane reforming, gasification, methane pyrolysis and water electrolysis.



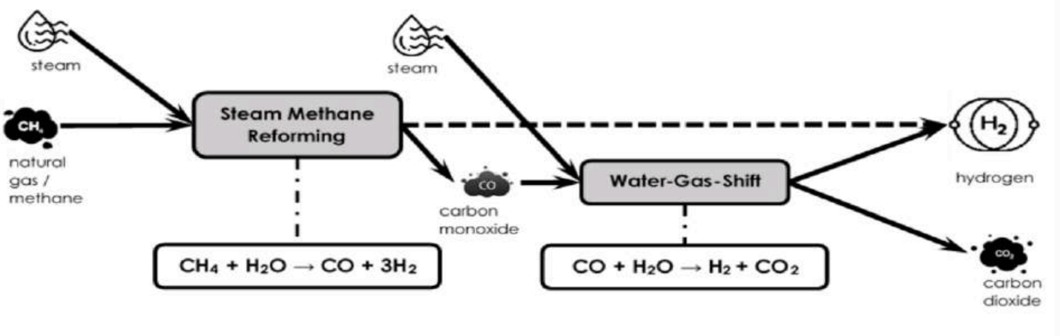
Comparison of different production methods

Property	Steam Methane Reforming	Coal Gasification	Biomass Gasification	Methane Pyrolysis	Alkaline Electrolysis
Inputs	- water - heat - natural gas	- coal - water - heat	- biomass - air - oxygen - steam	- natural gas (methane) - heat	- water - electricity
By-products	- carbon dioxide	- carbon dioxide - carbon - other hydrocarbons (temperature dependent)	- carbon dioxide	- high purity carbon (dependent on catalyst type)	- oxygen
Operating Temperatures	-750°C	>500°C	500 - 1400°C	>500°C	<100°C
Energy Efficiency	74 – 85%	~63%	~52%	~55%	~69%

Steam Methane Reforming

Steam Methane Reforming is an endothermic process where high-temperature steam (700°C–1,000°C) is used as the oxidant to produce hydrogen from a methane source, usually natural gas or biogas. Steam reforming can also be used to produce hydrogen from other fuels, such as ethanol, propane, or even gasoline.

In the presence of a catalyst, the methane reacts with steam under 3–25 bar pressure to produce hydrogen, carbon monoxide, and a relatively small amount of carbon dioxide. Then, in what is called the 'water-gas shift reaction', the carbon monoxide and steam are reacted using a second catalyst to produce carbon dioxide and more hydrogen. Finally, carbon dioxide and other impurities are removed from the gas stream, leaving essentially pure hydrogen.



Animation video clip about the process inside HyGear's Hydrogen Generation System (HGS). HyGear's HGS uses the process of Steam Methane Reforming to generate hydrogen on a small-scale. Steam Methane Reforming Comparison of different production methods
https://www.youtube.com/watch?v=eoF2EoFhIJw

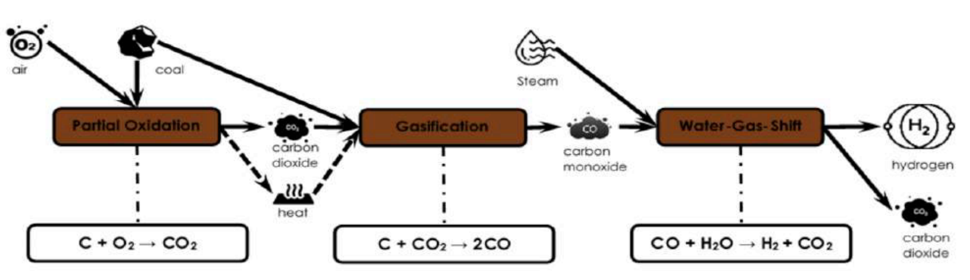
Gasification

Gasification of coal, or biomass, is a three-step process in which the dry feedstock is partially oxidised before the gasification and water gas shift reaction produce hydrogen.

The initial partial oxidation reacts the hydrocarbons or biomass with limited amounts of oxygen, so they are not completely oxidized. This is an exothermic reaction, so it produces some heat as well as some carbon dioxide.

The carbon dioxide is a gasification agent and when it is hot it reacts with the rest of the carbon in the feedstock to form carbon monoxide. The gasification reaction is endothermic, so it requires the input of heat for the carbon dioxide and the carbon to react.

The carbon monoxide is then reacted with steam in the presence of a catalyst, in what is called the 'water-gas shift reaction' to produce carbon dioxide and hydrogen. The hydrogen is then separated from the carbon dioxide and purified.



Methane Pyrolysis

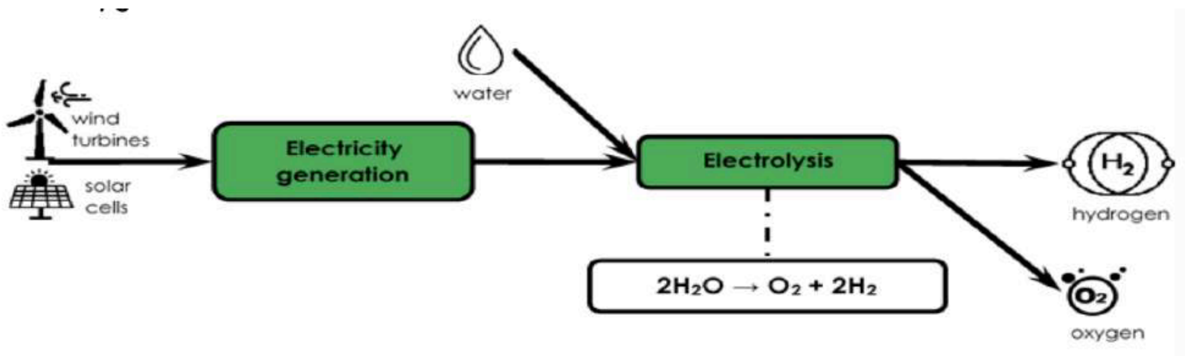
Methane Pyrolysis involves decomposing methane at high temperatures, >500°C, in the absence of oxygen but typically in the presence of a catalyst. The methane decomposition is an endothermic reaction which uses heat and natural gas to produce low-CO2 hydrogen and high purity carbon powder. The hydrogen gas produced can easily be separated from the carbon powder. The carbon is a marketable by-product that can be used as carbon black in tyres and inks, for activated carbon in water purification and for graphene and nanotubes for use in electronics and composites.

The HAZER® Process https://hazergroup.com.au/about/

Video https://www.youtube.com/watch?v=7C4QUqynGAc&t=165s

Electrolysis of Water

Electrolysis of water is a process that uses an electrical current in an electrolytic cell to induce the non-spontaneous chemical reaction that splits water into hydrogen and oxygen.



An electrolytic cell consists of a DC power supply connected to two noble metal coated electrodes, a cathode and an anode, that are separated by an ionically conducting electrolyte.

The electric current sent through the electrolytic cell flows in the form of electrons in the electrodes and as ions in the electrolyte causing two sets of reactions to take place at the separate electrodes. The electric current splits the water molecules (H2O) into hydrogen (H2) and oxygen (O2) molecules via two half reactions at the electrodes with the overall reaction:

$$2\,H_2O_{(l)} \rightarrow 2\,H_{2\,(g)} + O_{2\,(g)}$$

Electrolysers are used for the commercial production of hydrogen gas and can range in size from small, appliance-size equipment to large-scale production facilities. In their most basic form, electrolysers contain a stack of electrolytic cells within a system that also contains pumps, vents, storage tanks, a power supply, a separator and other components.

The three main types of electrolyser cells used to produce hydrogen by electrolysis of water alkaline electrolysers, proton exchange membrane (PEM) electrolysers and solid oxide electrolysers. The different electrolysers function in slightly different ways because of the different electrolytes involved.

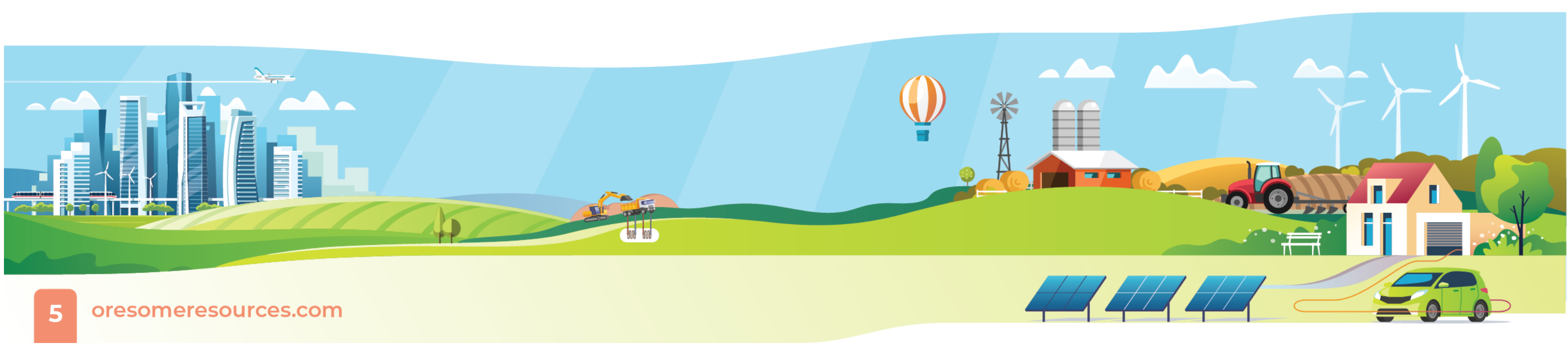
Properties of the three main water electrolysers:

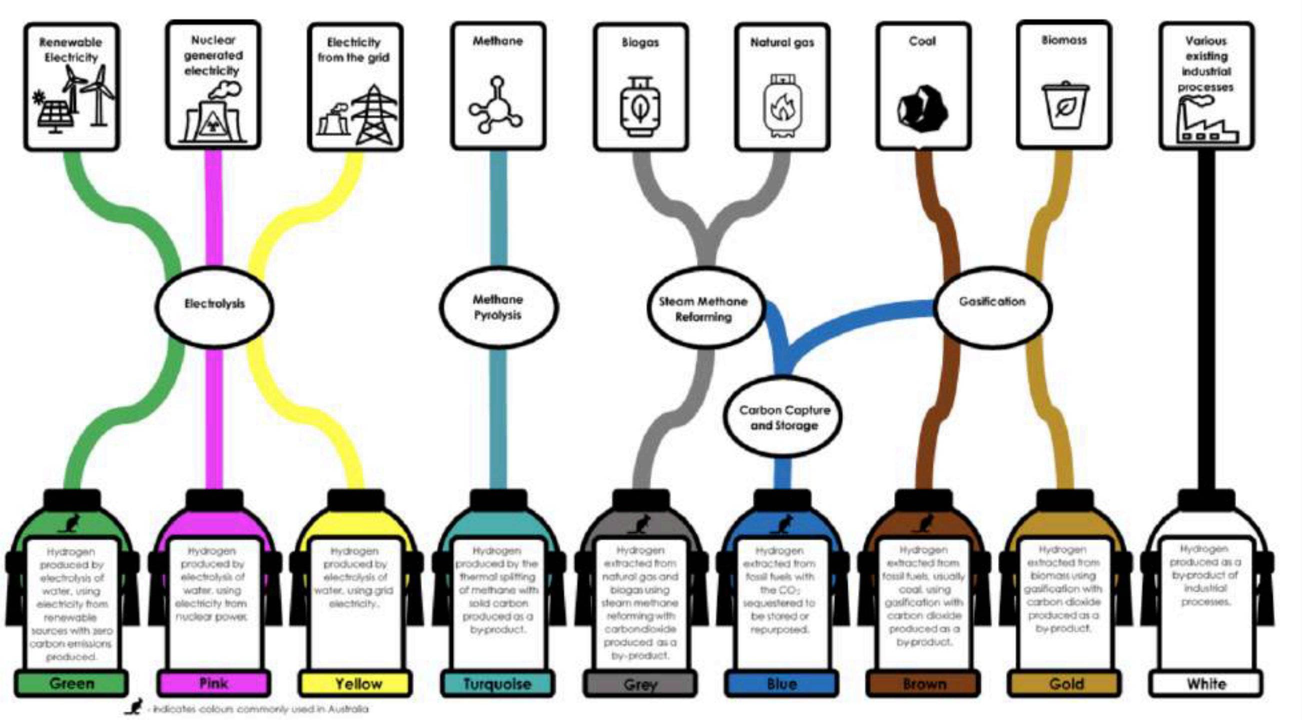
Property	Alkaline Electrolyser (AE)	Polymer Electrolyte Membrane Electrolyser (PEM)	Solid Oxide Electrolyser (SOE)
Electrolyte	30% potassium hydroxide	specialty solid plastic material	solid ceramic material
Electrode/ Catalyst	nickel	platinum	platinum
Electrical Efficiency (kWh to produce 1kg H2)	48 -52kWh	56 – 60kWh	41 – 45k
Operating Temperature	100□- 150□C	70 - 90□C	700 - 800□C
Anode Half Reaction	$4OH^- \text{ -> } O_2 + 2H_2O + 4e^-$	$2H_2O \text{ -> } O_2 + 4H^+ + 4e^-$	$2O^{2-} \text{ -> } O_2 + 4e^-$
Cathode Half Reaction	$2H_2O + 2e \text{ -> } H_2 + 2OH^-$	$2H^+ + 2e \text{ -> } H_2$	$H_2O + 2e^- \text{ -> } H_2 + o^{2-}$

(Charnock, et al., 2019)

Hydrogen Colour Coding

The use of hydrogen does not produce any harmful emissions, so the production process employed determines the carbon footprint of the hydrogen produced. The hydrogen produced from renewable or nuclear energy is carbon free. However, currently most of the world's hydrogen production is through more CO2 intensive processes. Industry has proposed the use of colours to reflect the environmental friendliness of the different production methods. Green, pink, yellow, turquoise, grey, blue, brown, gold and, white, used around the world, however only green, grey, blue and brown are commonly used in Australia.



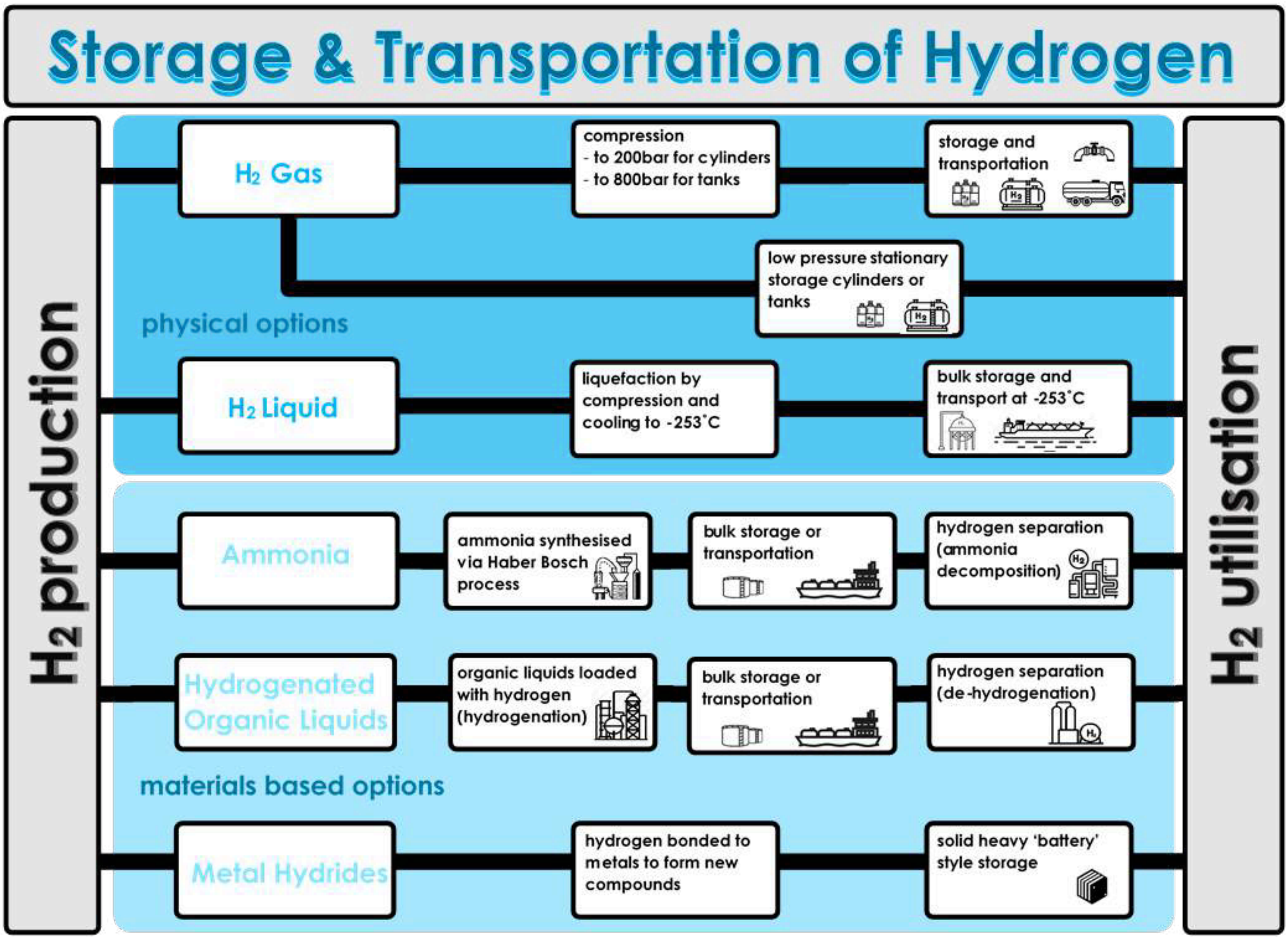


Colours as described in The Alchemist, Issue 39 - Hydrogen: Applications in Mining and Metals. (RFC Ambrian Limited, 2021)

Storage and Transportation

Hydrogen's low density means it is a bulky gas which is difficult to store and transport. How it is stored and transported is a crucial component to the advancement of hydrogen applications and utilisations.

The hydrogen storage and transportation technologies can be broadly classified as physical based or material based. The different types of hydrogen storage options each have their own advantages and limitations, and some methods are more established than others. More research and development is required to improve the energy efficiency of the storage and transportation options for hydrogen.



Physical Storage and Transportation Options

Physical storage options are based around hydrogen's state of matter. Hydrogen can be compressed in a gaseous state then stored and transported under pressure or it can be liquefied like natural gas to increase its energy density.

The most mature options for physical storage are compression via ionic liquids and cryogenic tanks for liquid hydrogen.

Properties of mature physical hydrogen storage options

Property	Hydrogen Gas Compression via Ionic Liquids	Liquid Hydrogen in Cryogenic Tanks
Description	Ionic compressors make use of ionic liquids instead of a piston to compress hydrogen gas. Ionic compressors are currently in use in several hydrogen refuelling stations to reach the required pressures for hydrogen FCEVs.	Hydrogen is liquefied and stored at -253°C, at ambient-moderate pressures, in cryogenic tanks through a multi-stage process of compression and cooling.
Importance	Potentially lower-cost compression. As with other mechanical compressors, could be effective for large scale compression of hydrogen.	More financially viable where high density hydrogen storage is required under limited space, or where a larger roundtrip distance is involved.
Benefits	• Potential to yield energy saving of 40% over standard mechanical compressors. • Do not require bearing and seals, which are the most common sources of failure in mechanical compressors	• Higher volumetric storage capacity than compressed gas • Fewer evaporation losses than typical compression mechanisms
Limitations	• Low volumetric energy density • Energy intensive process • High cost of Ionic liquids	• Requires advanced and more expensive storage material. • Liquefication requires complex technical plant. • Liquefied hydrogen incurs boil-off losses. • To be liquefied, up to 40% of energy content of hydrogen is required
Characteristics	• Storage conditions: Up to 1000 bar pressure demonstrated	• Volumetric hydrogen density: 70.85 kg H_2/m^3 at 1 bar • Storage conditions: 2 – 10 bar, 20K • Well-to-tank efficiency range: 20-25%. The energy required to ;liquify the hydrogen is 6 – 8 kW/kg H_2. Well-to-tank efficiency includes from the feedstock natural gas consumed to the low heating value of H_2 delivered to tank

(Charnock, et al., 2019)

Technical concerns over using existing gas tanks and pipes to store and distribute hydrogen include:

- The potential for hydrogen to embrittle the steel and welds used.
- The need to control hydrogen permeation and leaks.
- The need for more reliable and more durable hydrogen compression technology.

Therefore, new specialised fibre reinforced polymer (FRP) delivery infrastructure is required to store and transport gaseous and liquefied hydrogen.

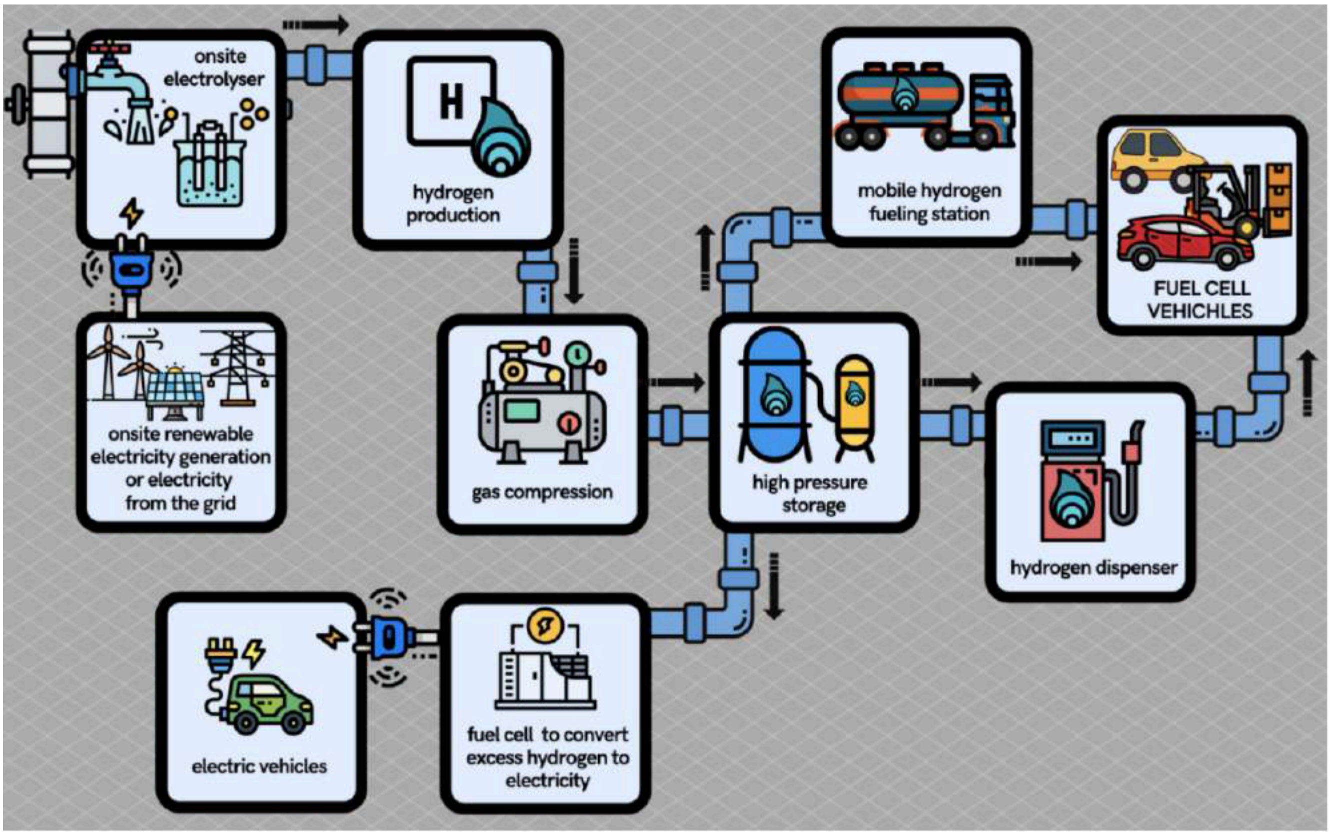
The onsite hydrogen production and delivery design systems are one option to avoid some of the technical issues, reduce costs and improve the energy efficiency of the storage and transport of hydrogen. Localise hydrogen refuelling stations are being developed and trialled at various locations in Australia and around the world to produce and deliver hydrogen for use in hydrogen fuel cell vehicles.

A typical hydrogen refuelling station design includes 5 main components on site:

- renewable electricity generation, wind or solar
- an electrolyser
- compressors,
- storage tanks
- hydrogen dispensers

Compressors are necessary as the hydrogen gas must be compressed for storage and subsequent fuelling of vehicles. The hydrogen can be dispensed direct to vehicles on-site or it can be distributed via trucks as mobile refuelling stations.

To compliment the renewable energy sources some stations may have back up connection to the electrical grid or batteries. Some stations will also have an onsite fuel cell that can convert excess hydrogen produced back to electricity to the power the station or to charge electric vehicles.



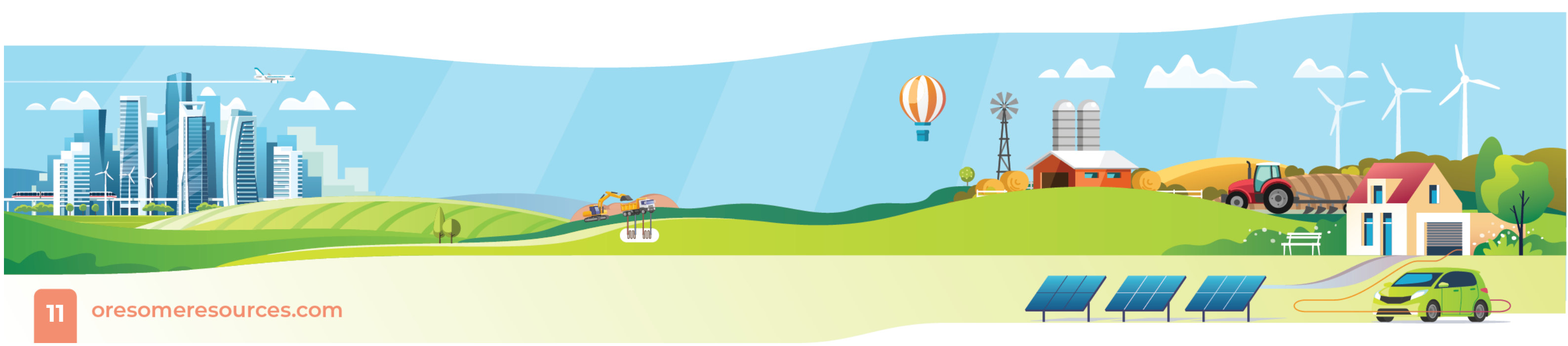
Material Based Storage and Transportation Options

Material based options require hydrogen to be incorporated into other chemical compounds that can more easily be stored and transported. These can use existing supertankers to transport at normal temperature and pressures. However, they require processing on delivery before hydrogen can be utilised.

The most mature options for physical storage are ammonia via Haber-Bosch synthesis, liquid organic hydrogen carrier: toluene/methylcyclohexane and hydrides: metal (room temperature).

Properties of mature materials-based hydrogen storage options

Property	Ammonia: Haber-Bosch synthesis	Liquid organic hydrogen carrier: Toluene/ methylcyclohexane	Hydrides: metal (room temperature)
Description	Ammonia is synthesised by reacting hydrogen with nitrogen gas at high temperatures and pressures	Hydrogen is reacted with toluene to form methylcyclohexane (MCH), a compound that can be transported at ambient temperature and pressure. The hydrogen can be extracted after transport via the application of heat or catalysis.	Metals, such as magnesium, chemically bond with hydrogen gas to be transported as a metal hydride. When the hydrogen is required, heat is applied to release it from the metal. Intermetallic hydrides are a variation in which transition metals are present instead of main group metals.
Importance	Haber-Bosch synthesis is a well-established industrial process that has been optimised for hydrogen production.	Hydrogenated toluene can carry hydrogen in liquid form at ambient temperature and pressure.	Metal hydrides offer storage at moderate pressure, retrieval at safe temperatures, and a higher hydrogen storage density than pressurised or liquefied hydrogen
Benefits	- Established industrial process	- Stays in liquid state under ambient temperature and pressure. - Minor loss over long-term storage and transport - Can utilise existing oil and chemical infrastructure for storage and transportation	- H_2 release is endothermic and self-regulated, reducing risk of accidental explosion. - Higher hydrogen-storage density than pressurised or liquefied hydrogen - Increased safety due to near-ambient operating pressure and temperature - Extremely long cycle life, up to 20,000 cycles in some cases - Negligible self-discharge - 90% round trip efficiency for room temperature hydrides - Can be readily scaled to very large capacities for grid storage. - Suitable for hydrogen transport to fuelling stations.



Limitations	• High operating temperature and pressures, highly • Energy-intensive • Generates large amounts of carbon dioxide. • Diminishing returns expected from improvements to this synthesis method	• Both toluene and MCH are toxic substances • Purification requirements • Need to return carrier if exported. • High temperature required for both hydrogenation and dehydrogenation	• Low gravimetric hydrogen density for current generation of low temperature metal hydrides • Many intermetallics with favourable thermodynamics have low gravimetric capacities and/or poor cycling capacity • Sensitive to air and humidity
Characteristics	• Volumetric hydrogen density: High (107 kg H_2/m^3 at 10 bar and 25°C) • Gravimetric hydrogen density: High (17.8% by mass) • Storage conditions: Liquid at ambient temperature, 10-11 bar pressure. • Synthesis energy efficiency: Production of hydrogen via SMR paired with Haber-Bosch synthesis has an overall energy efficiency of approximately 61-66%	• Volumetric hydrogen density: 47 kg H_2/m^3 • Gravimetric hydrogen density: 6.1% by mass • Storage conditions: Ambient storage, should be kept below 30°C. Container should be carefully sealed to prevent exposure to sunlight, heat and humidity. • Roundtrip Energy efficiency: <50% heating value of H_2 delivered to tank	• Volumetric hydrogen density: >100 kg H_2/m^3 • Gravimetric hydrogen density: Low (<2% by mass) • Hydrogenation and extraction conditions: -10 to 50°C • Storage conditions: Reversible at room temperature and reasonable hydrogen pressure conditions (e.g. TiFe and LaNi5 can absorb hydrogen at 30 bar and 25°C) • Hydrogenation/ dehydrogenation energy efficiency: 90%

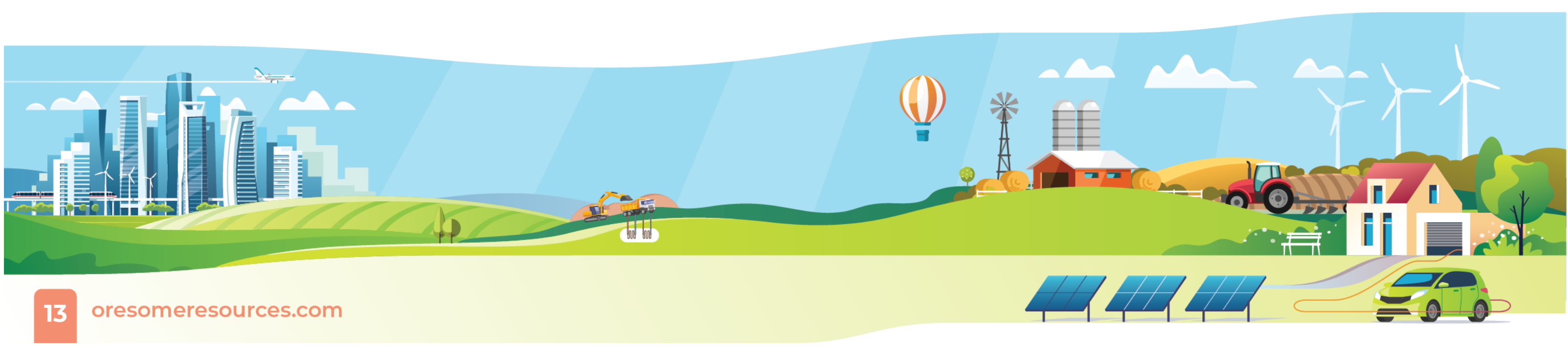
(Charnock, et al., 2019)

Utilisation

There are several possible ways that hydrogen can be used in and by Australia, including hydrogen fuelled transport, remote area power systems (RAPS), industrial feedstocks, export, electricity grid firming, heat or as synthetic fuels. They all have positive potential but also barriers to their successful application:

Utilisation	Positive Potential	Barriers
Hydrogen Fuelled Transport (FCEV)	• Travel Longer distances without refuelling (400 – 600km) • Shorter refuelling times • The relative lighter weight of hydrogen compared with batteries	• Current capital cost of FCEVs • Lack of infrastructure supporting use. • Deployment of hydrogen refuelling stations
Remote Area Power Systems (RAPS)	• Hydrogen based RAPS (using dedicated renewable energy inputs) could replace diesel generator RAPS.	• The cost of hydrogen production via electrolysis • Fuel cell technology and cost
Industrial Feedstocks	• Clean hydrogen as an industrial feedstock to replace hydrogen derived from steam methane reforming. • Reduce Australia's dependence on liquid fuel imports. • Decarbonise the transport sector	• The cost of hydrogen production via electrolysis
Export	• High worldwide demand for clean hydrogen	• Dependent on the production, storage and transport technologies • Target hydrogen production price of $2-3/kg (excluding storage and transport)
Electricity Grid Firming	• Provide both electricity grid stability (i.e. seconds to hourly storage) and grid reliability (i.e. seasonal storage) services.	• Need for a hydrogen price of less than $2/kg to compete with batteries, pumped hydro and gas turbines
Heat	• Direct combustion of hydrogen for the purpose of generating heat. • Decarbonisation of the gas networks • Hydrogen enrichment of the natural gas network	• A move to 100% displacement of natural gas with hydrogen will require an upgrade to existing appliances and possibly pipelines
Synthetic Fuels	• Complete with crude derived fuels on a purely commercial basis. • Provide a localised fuel supply. • Combination if hydrogen with a waste stream of CO_2 could be used to synthesise lower emissions fuels for heavier forms of transport such as aviation and shipping	• A significant emissions profile

(Bruce, et al., 2018)



Energy Efficiency

An important consideration for the use of hydrogen is the total energy efficiency of the whole process, combining the energy efficiency of each step from production, storage, transportation and utilisation. For example, hydrogen use in existing technology fuel cell electric vehicles could have an overall efficiency rate of around 30%.

(From Volkswagen AG. (2019). Hydrogen or battery? A clear case, until further notice. https://www.volkswagenag.com/en/news/stories/2019/08/hydrogen-or-battery--that-is-the-question.html#)

Useful Links

- This TEDx Talk ‘So, what is all this hot air about Hydrogen?’ by Andrew Clennett from 2018 provides a good overview of hydrogen, its history of use and development on technology.
  https://youtu.be/jFYbmTV-itI

- Information about energy efficiency of water electrolysis and hydrogen fuel cells can be found in Hydrogen Production: Fundamentals and Cas Study Summaries
  https://www.nrel.gov/docs/fy10osti/47302.pdf

- Australia’s pathway to $2/kg hydrogen, ARENA.
  https://arena.gov.au/blog/australias-pathway-to-2-per-kg-hydrogen/

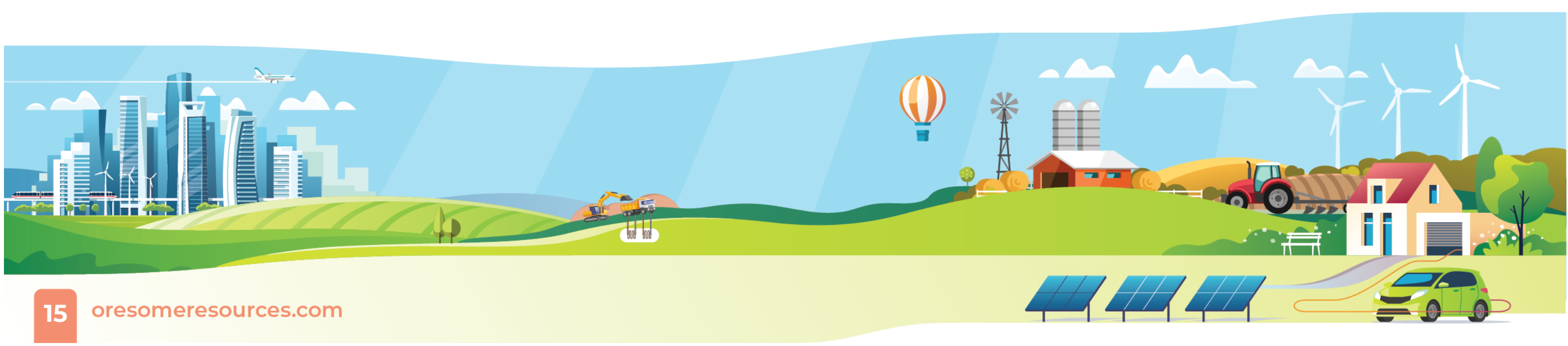
- “What is renewable 'green' hydrogen gas?” (video)
  https://www.youtube.com/watch?v=fFGT2z82tOM&t=34s
- Hydrogen Park - South Australia, is an example of an innovative energy project that produces renewable hydrogen gas, blends it with natural gas and supplies to nearby homes via the existing gas network.
  https://www.agig.com.au/hydrogen-park-south-australia

- Australian Hydrogen Generation, a subsidiary of Amtronics, is an Australian company which specialises in providing hydrogen equipment and installation needs with turnkey solutions – Hydrogen Generation, purification, compression, storage and dispensing/refuelling – plus full life-cycle maintenance for the hydrogen industry.
  https://h2gen.com.au/

- LAVO™ hydrogen battery system is an Australian innovation that stores hydrogen as metal hydride
  https://lavo.com.au/

- The Australia Hydrogen Opportunities Tool (AusH2) provides free access to geoscience data and tools for mapping and understanding the potential for hydrogen production in Australia
  https://portal.ga.gov.au/persona/hydrogen

- Embracing clean hydrogen for Australia: How the journey towards decarbonisation can be fuelled by Hydrogen
  https://www.pwc.com.au/infrastructure/embracing-clean-hydrogen-for-australia-270320.pdf



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