

High-energy-density hydrogen carriers for fuel cells

Fuel cells generate power from hydrogen or other chemicals. In an electrified future, green hydrogen can be produced, stored, and then used to generate electricity on demand. This is a Power-to-X-to-Power cycle. Key questions surrounding this pathway include: Which 'X' should be used to achieve the best results? Which technologies are best suited for preparing the chemical to feed the fuel cell? And, which type of fuel cell is optimal for the application?


By Stephen B. Harrison, sbh4 consulting

Green hydrogen can be produced in a sustainable way, but it has the disadvantage of being difficult to store and transport. A hydrogen road tanker using steel tube compressed gas cylinders will transport less than 0.5% of the total vehicle weight as usable hydrogen.

Hydrogen is a building block from which many chemicals can be made. These are referred to as hydrogen derivatives. The benefit of converting

hydrogen into hydrogen carriers or derivatives, such as ammonia or methanol, is that these molecules are readily liquefied. This ensures they have a high volumetric energy density, which enables cost-effective storage and transportation.

Energy losses occur when locking hydrogen into carriers and derivatives. However, these costs can be saved through the simplification of the overall hydrogen storage and distribution supply chain.

Hydrogen, hydrogen derivatives and e-fuels						
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	Hydrogen Gas	Liquid Hydrogen	Liquid Ammonia	Liquid Methanol	Liquefied Natural Gas (LNG)	Synthetic Aviation Kerosene (SAF)
Ideal universal reaction	Compressed H ₂	Liquefied H ₂	3H ₂ + N ₂ → 2NH ₃	3H ₂ + CO ₂ → CH ₃ OH + H ₂ O	4H ₂ + CO ₂ → CH ₄ + 2H ₂ O	10CO ₂ + 31H ₂ → C ₁₀ H ₂₂ + 20H ₂ O
Hydrogen yield	100 %	100 %	100 %	4/6 = 67 %	4/8 = 50 %	22/62 = 35.5 %
Volumetric energy density, LHV (MJ/L)	2.43 - 6.8	8.52	12.7	15.7	22.2	35
Gravimetric energy density, LHV (MJ/kg)	120	120	18.6	19.9	48.6	42.2
Infrastructure readiness for large scale deployment in mid-term	Low	Low	High	High	High	High
Transportation and storage temperature	Ambient	-253 °C	-33.3 °C	Liquid at ambient temperature	-162 °C	Ambient
Transportation and storage phase and pressure	Compressed gas at 250 to 700 bar	Liquid at atmospheric pressure	Liquid at atmospheric pressure	Liquid at atmospheric pressure	Liquid at atmospheric pressure	Liquid at atmospheric pressure
Density	0.017 kg/L	0.071 kg/L	0.68 kg/L	0.79 kg/L	0.46 kg/L	0.83 kg/L
Toxicity	Non toxic	Non toxic	TWA 25 ppm	TWA 200 ppm	TWA 1,000 ppm	TWA 30 ppm
Flammability (% in air)		4 - 74 %	14.8 - 33.5 %	6.0 - 36.5 %	4 - 15 %	0.7 - 4.8 %

E-methanol steam reforming for LT PEM fuel cells

E-methanol is easy to handle as a pure liquid or as a mixture with water. It can be stored and transported in plastic containers. The freezing point of pure methanol is -97.6°C , so, unlike diesel, it will not freeze in harsh winters, even in the coldest climates.

Methanol steam reforming can further boost the hydrogen supplied by methanol since the steam introduces hydrogen to the system, which means the overall volumetric density ($\text{kg of H}_2/\text{m}^3$) is 40–50% higher than what can be achieved by methanol decomposition.

Element 1 has developed a methanol steam reforming-based hydrogen generator using Clariant's HyProGen[®] 251 and Element 1's hydrogen purification module to supply high-purity hydrogen for low-temperature (LT) PEM fuel cell applications. The HyProGen[®] 251 catalyst is based on a zinc-alumina formulation, which comfortably operates up to 500°C . This temperature allows heat integration with a thin-foil gas separation membrane that can deliver high-purity hydrogen to the fuel cell.

Distributed methanol steam reforming is common in remote areas, where houses and flats use can fuel cells of around 1 kW capacity to power a battery that supplies electricity to lighting and domestic appliances. Heat from the fuel cell can also be used to warm the building, if required.



HyProGen[®] 251 Methanol reforming catalyst. Image © Clariant Catalysts



EFOY Pro 2800 direct methanol fuel cell (DMFC). Image © SFC Energy AG

The upper end of distributed methanol steam reforming is at around 250 kW per fuel cell module. With a modular design, the power generation from several fuel cells can reach multi-MW capacity. This is attractive for maritime applications, where ships require significant amounts of power for auxiliary systems and propulsion.

Direct methanol fuel cells

The German company SFC Energy AG has commercialised the EFOY direct methanol fuel cell (DMFC). The EFOY Pro 2800 can deliver up to 125 W, weighs 7.8 kg, and is approximately the size of a briefcase. As power is generated by the fuel cell, methanol is converted into carbon dioxide, which is vented to the atmosphere. Water is also produced, and this is condensed to dilute the methanol as it is fed to the fuel cell.

The feed to the DMFC is pure methanol from tanks. Up to eight fuel tanks, each holding up to 60 litres of methanol fuel, can be connected to the fuel cell to ensure maximum operational duration.

As with other fuel cell technologies, over the lifetime of the stack, its power output reduces from the maximum 125 kW to the point at which it requires replacement. After the warranty of 6,000 hours of operation (250 days), the power from the EFOY Pro 2800 would be 87 W. The fuel cells

are normally not in operation 24/7 when the unit is used to back up wind or solar power, so the system life would be significantly longer than 6,000 hours due to intermittent operation of the fuel cell.

SFC Energy is one of the few fuel cell producers worldwide operating profitably. In recent years, its fuel cell production and sales have grown to up to 10,000 units per year. SFC offers a wide portfolio of fuel cell modules and systems based on methanol or hydrogen fuels, with power levels to up to 500 kW.

DMFC as backup power for offshore windfarms

Getting electricity to remote locations can be challenging. Diesel generators have been used for such applications for several decades, but they need regular fuel deliveries, and their noise and exhaust emissions are not attractive environmental features. Furthermore, they cannot operate at extremely cold temperatures due to diesel fuel freezing.

The combined use of renewable solar and wind power generation is a clean alternative to a diesel gen-set for remote power generation. When a methanol-fed fuel cell is integrated with these renewable power generation modes, electricity will continue to flow during calm days and dark nights.

UK-based firm Leading Edge Power has been active in the provision of remote power for many years. They offer bespoke remote power supply systems which integrate wind and solar with batteries and fuel cells.

In many locations, cloudy, windless moments can stretch to durations beyond the storage capacity of batteries. Additionally, battery life at low temperatures is reduced. For these harshest conditions, Leading Edge Power has integrated an EFOY DMFC into their PowerBox™ to ensure backup power is available beyond the duration that a battery alone could offer.



EFOY fuel cell methanol cartridge. Image © SFC Energy AG

In 2023, Leading Edge Power installed two off-grid systems on offshore wind turbine rigs to provide power for satellite communications from the wind farms to the shore. Each unit uses two EFOY Pro 2800 DMFC fuel cells. Since their installation, these PowerBox™ units have been powering up the DC equipment at a continuous power load of 150 W.

E-methanol reformat for HT PEM fuel cells

The German company SIQENS GmbH has commercialised the Ecoport system that reforms pure methanol into a hydrogen-rich reformat, which is fed to a high-temperature PEM (HT PEM) fuel cell. A single 25-litre container of methanol can yield around 45 kWh of power through the Ecoport.

The methanol reformat contains carbon monoxide (CO), which would poison a low-temperature PEM (LT PEM) fuel cell. However, the HT PEM fuel cell used by SIQENS is tolerant of CO. The Ecoport stack is designed for 3,000 hours (125 days) of use over 500 cycles.



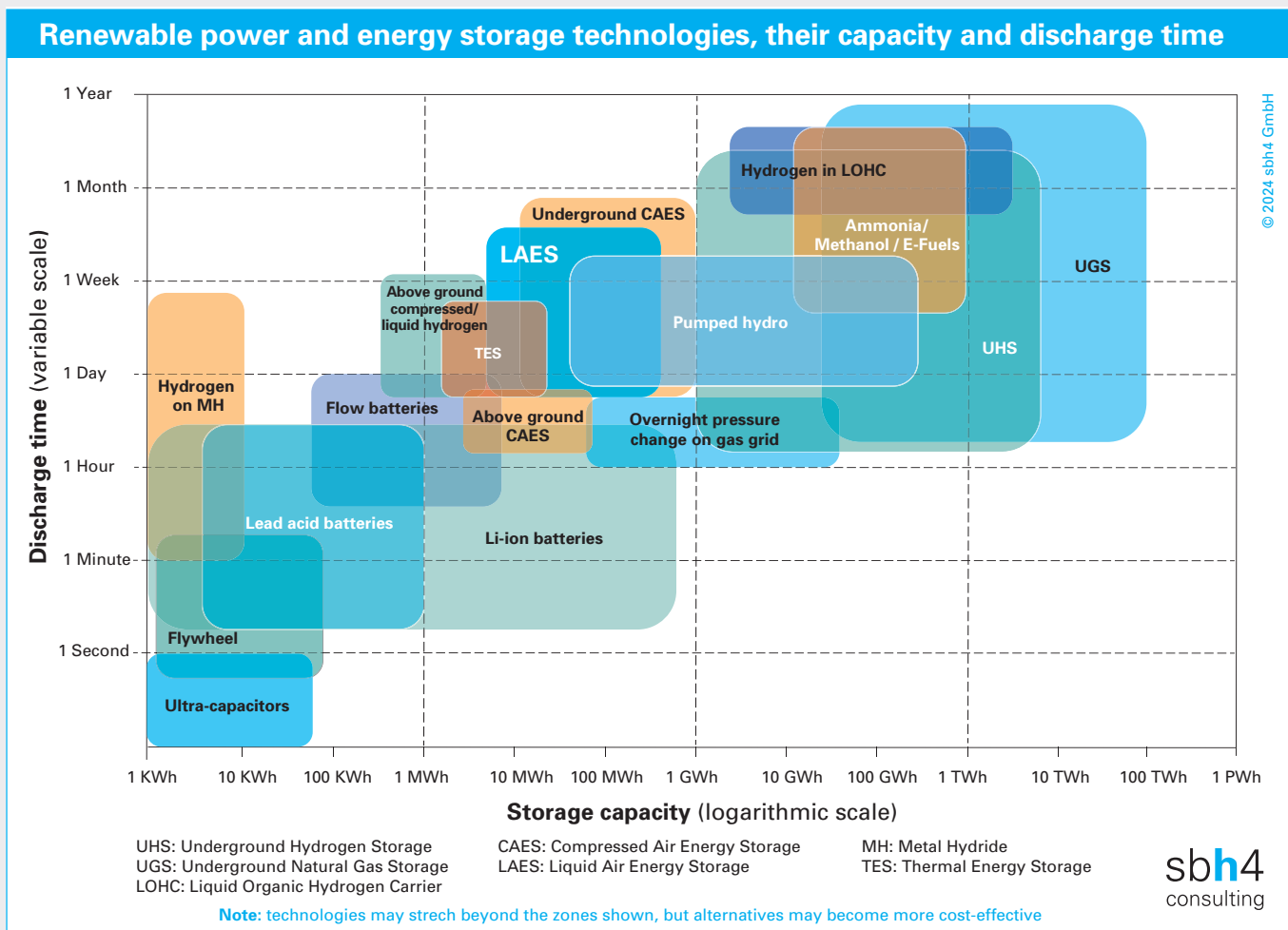
Advent Technologies also uses methanol reformat as the feed for their HT PEM fuel cells. They are actively targeting aviation applications. HT PEM fuel cells can achieve a higher power density than LT PEM fuel cells. This means that the HT PEM fuel cell can be lighter to achieve the same power output. In aviation applications, weight is often the overriding factor in technology and materials selection. This is especially true for vertical take-off and landing (VTOL) aircraft such as drones and helicopters.

Storing liquid green or blue methanol onboard the aircraft as a compact, low-carbon fuel could be achieved in a similar way to storing aviation kerosene today. Running that methanol through a reformer and HT PEM to provide electrical power for turbo-prop flight may be a winning technology combination for short-haul aviation in the future.

Hydrogen from cracked ammonia

Ammonia is a highly effective hydrogen carrier, with 17.6% of its molar mass being hydrogen. This is slightly more than methanol, which contains 12.5% hydrogen by mass. Cracking ammonia back to hydrogen and using the hydrogen in a fuel cell has been proposed for several applications in heavy-duty mobility.

The US company AMOGY Inc. is commercialising an ammonia cracker system that can feed pure hydrogen to a fuel cell to generate power. The target applications are powerful maritime



engines and heavy-duty mobility on land, such as agricultural machinery and long-range trucks.

H2SITE in Spain has developed an ammonia cracker which operates at around 90% efficiency. For distributed applications, the cracker must be compact and offer a flexible operating profile. And if the hydrogen from the cracker is to be used on a low-temperature PEM fuel cell, it must be extremely pure.

As part of the H2Ocean project, H2SITE demonstrated the performance of their ammonia cracker onboard the oil field services vessel Bertha B, sailing from the Port of Bilbao in November 2023. A 30 kW PEM fuel cell from Ajusa in Spain was used to power the ship's auxiliaries.

The ammonia cracker that H2SITE has commercialised uses a low-temperature cracking catalyst contained within palladium membrane tubes. Once the ammonia is cracked, hydrogen selectively passes through the membrane.

Many ammonia cracking technologies yield a mixture of hydrogen and nitrogen, the two atoms that are contained in the ammonia molecule. From these crackers, the hydrogen must be purified to fuel-cell grade to avoid the inert nitrogen gas suffocating the performance of the fuel cell, resulting in a loss of power.

When filled with a different catalyst, the H2SITE cracker can break down methanol into a syngas

reformate. This reformate can be fed to a high-temperature PEM fuel cell or upgraded with water gas shift reactors and purified to yield hydrogen.

Beyond ammonia or methanol cracking, the H2SITE's membrane gas separation technology can be used to separate hydrogen from other mixed gas streams. For example, it can extract pure hydrogen from a natural gas and hydrogen blend that may be used for pipeline transmission.

Ammonia cracking at import terminals

Large scale ammonia crackers are being planned for several European ports to convert imported ammonia into high-pressure hydrogen to be injected into pipelines for distribution to off takers. To avoid excessive energy losses in the full value chain, cracking ammonia must be energy-efficient. Catalysts reduce the amount of energy required to convert the ammonia to hydrogen.

For decentralised ammonia cracking, a ruthenium-based catalyst can be used. Ruthenium is a highly active catalyst, which means the cracker can be compact.

Ruthenium-based ammonia cracking catalysts operate at temperatures between 370 and 550°C and at pressures ranging from 5 to 8 bar. This pressure is ideal for supplying hydrogen to fuel cell applications or for injection into combustion engines. Clariant offers the HyProGen 850 DCARB for this application.

The amount of precious metal ruthenium in the catalyst constitutes only a very small percentage of the total weight. However, with annual ruthenium production being less than 35 tonnes, other catalysts are preferable for larger systems.

Large-scale centralised ammonia cracking can operate at high temperatures, using sophisticated materials. And there is a benefit of operating the reformer at high pressure to avoid the cost and



HyProGen 850 DCARB ammonia cracking catalyst. Image © Clariant Catalysts



Hydrogenious benzyltoluol LOHC supplied to the HRS Erlangen. Image © HyPlus

power demand of hydrogen compression into transmission pipelines. Unlike the selection of a ruthenium catalyst for use at low pressures, high-pressure operation favours the use of a nickel-based catalyst such as Clariant's HyProGen 821 DCARB.

Liquid organic hydrogen carriers

Liquid organic hydrogen carriers (LOHCs) are gaining momentum as a medium for hydrogen storage and transportation. An LOHC is generally an aromatic organic chemical, such as toluene. The German company Hydrogenious LOHC Technologies GmbH uses benzyltoluene as the LOHC molecule.

Through a catalytic hydrogenation reaction, hydrogen reacts with the LOHC. The LOHC loaded with hydrogen can then be shipped as a liquid. At the point of use, a catalytic dehydrogenation reaction is used to release hydrogen gas from the LOHC. The regenerated LOHC can be repeatedly hydrogenated and dehydrogenated to transport further loads of hydrogen. Platinum group metals are used both to lock the hydrogen into the LOHC and to liberate hydrogen from it.

Their LOHC has chemical, environmental, and safety attributes similar to diesel. This means it can be used in storage and distribution equipment previously aligned with refined products. The capital costs transitioning from fossil fuels to clean hydrogen can be reduced through the redeployment of existing infrastructure. LOHCs can thus help avoid the waste associated with stranded legacy hydrocarbon assets.

About the author

Stephen B. Harrison is the founder and managing director of sbh4 GmbH in Germany. He focuses on decarbonisation technologies and strategies. Hydrogen and Power-to-X are fundamental pillars of his consulting practice. With a background including 27 years at BOC Gases, BOC Group, and Linde Gas, Stephen possesses an intimate knowledge of hydrogen from commercial, technical, operational, and safety perspectives. His expertise extends across the full length of the value chain, from production, purification, distribution and storage through to utilisation.

