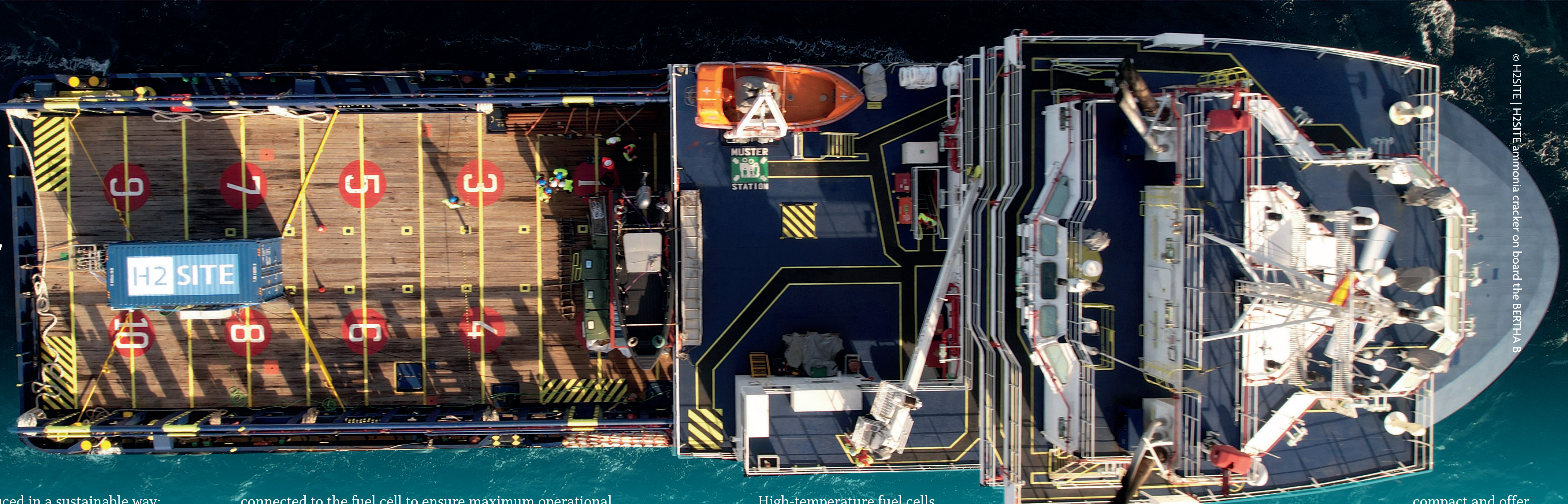
Hydrogen carriers for fuel cells

By Stephen B. Harrison, sbh4 consulting



© H2SITE | H2SITE ammonia cracker on board the BERTHA B

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

The benefit of converting hydrogen to 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 are incurred when converting hydrogen to derivatives, but the costs incurred through these molecular conversions can be saved through simplification of the storage and distribution supply chain.

The US company AMOGY Inc. is commercialising an ammonia cracker system that can generate pure hydrogen to feed 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. Methanol is also seen as a viable hydrogen carrier for similar applications.

Direct use of methanol on a fuel cell

The German company SFC Energy AG has commercialised the EFOY direct methanol fuel cell (DMFC). The feed to the DMFC is pure methanol from cartridges. As power is generated by the fuel cell, methanol is converted to 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.

Stephan Laistner, Business Development Manager at SFC, in Germany, added "Up to eight fuel tanks, each containing up to 60 litres of methanol fuel, can be connected to the fuel cell to ensure maximum operational duration." He continued to say, "The bestselling unit, the EFOY Pro 2800 can deliver up to 125W, weighs 7.8kg and is approximately the size of a briefcase. The operating temperature range is from -20°C to 50°C."

As with other fuel cell technologies, over the lifetime of the stack, its power output reduces from the maximum 125kW 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 87W. "The fuel cells are normally not 24/7 in operation and when the unit is used to backup wind or solar power," Laistner said. "The system life would be significantly longer than 6,000 hours due to intermittent operation of the fuel cell."

SFC is one of the few fuel cell producers worldwide operating profitably. In recent years, 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 500kW.

Methanol reforming for high temperature PEM fuel cells

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

The methanol reformate 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.

High-temperature fuel cells have the additional benefit of a very high current density, meaning that they can generate more power kg of fuel cell than a LT- PEM fuel cell. This lends them to application in aviation, where weight is a critically important factor.

Storing liquid green or blue methanol on board 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.

Ammonia as a hydrogen carrier for maritime fuel cells

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

Cracking ammonia must be energy efficient to avoid excessive losses in the full value chain. Beyond efficiency, there are additional criteria which must be met. Guillermo Garcia-Miguel, head of product at H2SITE in Spain, said, "Our ammonia cracker operates at around 90% efficiency. Also, for distributed applications, the cracker must be compact and offer a flexible operating range. And if the hydrogen from the cracker is to be used on a LT-PEM fuel cell, then it must be pure."

> "Other ammonia cracking technologies yield a mixture of hydrogen and nitrogen"

As part of the H2Ocean project, H2SITE demonstrated the performance of their ammonia cracker on board the oil field services vessel Bertha B, sailing from Bilbao in November 2023. The 30kW 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 reactor that contains the catalyst and the palladium membrane. The ammonia is cracked, and simultaneously, the hydrogen separated. The combination of both process steps enhances the efficiency of the reaction and makes sure no ammonia reaches the PEM fuel cell. Then, due to the selectively of the membrane only fuel cell purity hydrogen passes through.

Other 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 loss of power.

When filled with a different catalyst, the H2SITE cracker can break down methanol or a syngas to produce high purity hydrogen that can be fed to a HT-PEM fuel cell.

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"Beyond ammonia or methanol cracking, our membrane gas separation technology can be used to separate hydrogen from >>

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>> other mixed gas streams even in very low concentration blends," added Garcia-Miguel. "For example, our membrane units can be used for extracting pure hydrogen from a gas blend stored inside a salt cavern, as an enabler for hydrogen storage projects."

Centralised and decentralised ammonia cracking

Large scale ammonia crackers are being planned for several European ports to convert imported ammonia to high pressure hydrogen to be injected into pipelines for distribution to off takers. Cracking ammonia must be energy efficient to avoid excessive losses in the full value chain. 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," said Andreas Bachmeier, Head of Business Development & Energy Transition at Clariant. The amount of this precious metal in the catalyst is a very small percentage of the total weight, however annual production is less than 35 tonnes per year.

"Clariant rigorously supports the recovery precious metals from all our catalysts. Together with processing firms such as Umicore, we offer a fully 'circular' approach," Bachmeier said.

Ruthenium-based ammonia cracking catalysts operate at temperatures between 370 and 550°C at pressures in the range of 5-8 bar. This pressure is ideal to supply hydrogen to fuel cell applications or for injection into combustion engines. "We recommend the HyProGen 850 DCARB for this application", Bachmeier explained.

He continued, "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 power demand for hydrogen compression into transmission pipelines."

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In contrast to 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 hydrogen storage and transportation medium. The 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 hydrogenated and dehydrogenated on multiple occasions to transport further loads of hydrogen.

Their LOHC has chemical, environmental and safety attributes which are like diesel. This means they can be used in storage and distribution equipment that has previously been aligned to refined products. The capital costs of the transition from fossil fuels to clean hydrogen can be reduced through redeployment of existing infrastructure. LOHCs can thereby avoid the waste associated with stranded legacy hydrocarbon assets.

Platinum group metals are used to lock the hydrogen into the LOHC and when the hydrogen is liberated from the carrier. "Clariant supported liquid organic hydrogen carrier research team at the University of Erlangen-Nürnberg before some members of that team spun off to start up Hydrogenious," confirmed Bachmeier. "We have been at the cutting edge of LOHC catalyst technology for more than 10 years and we are proud to be the catalyst partner for Hydrogenious."