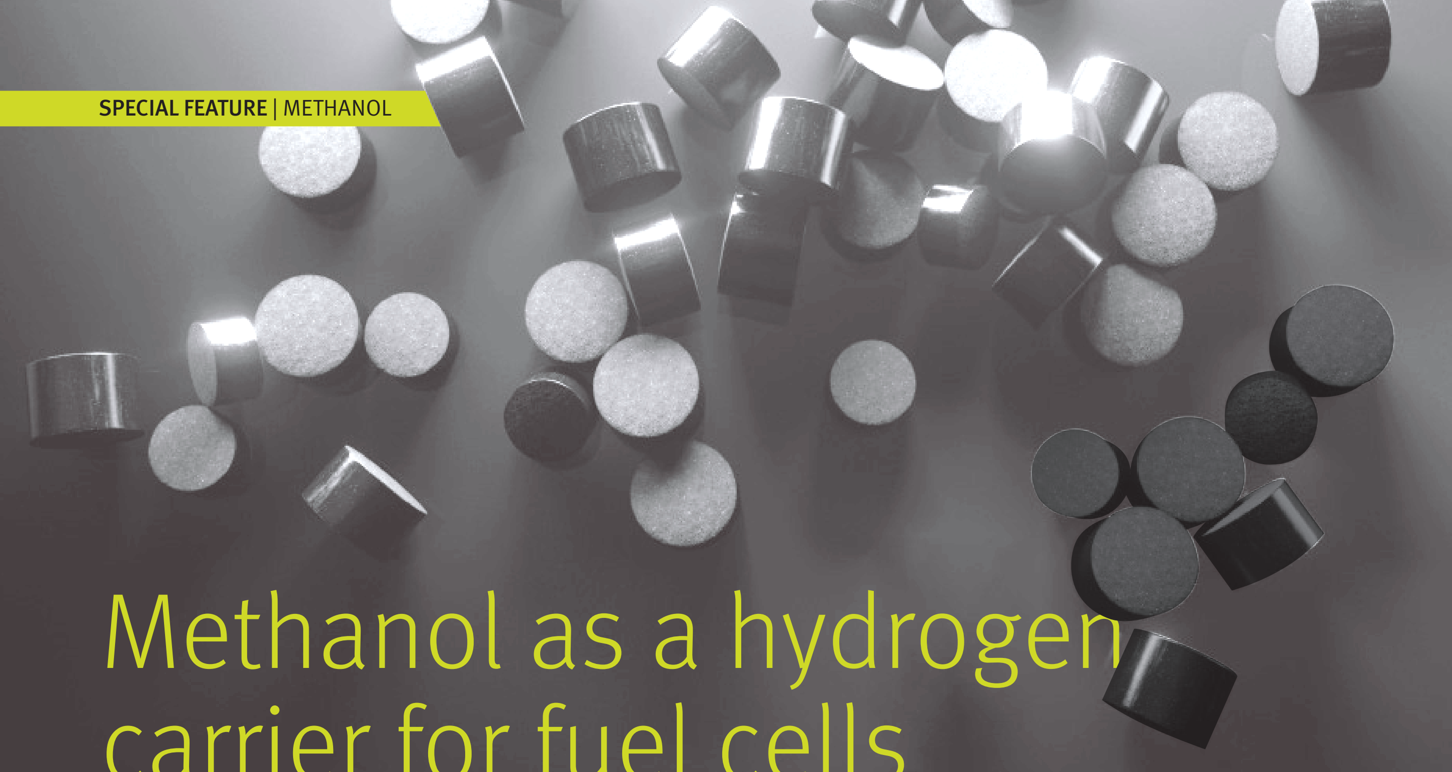

Methanol as a hydrogen carrier for fuel cells

By Stephen B. Harrison, sbh4 consulting

Crude oil has been the starting point for plastics and refined products for decades. Whilst crude itself is never used by consumers, it is the precursor to many fuels and materials in daily use. Hydrogen can play a similar role to crude oil since it is a building block from which many chemicals can be made. These are referred to as hydrogen derivatives.

Whilst hydrogen has the advantage over crude oil that it can be produced in a sustainable way, it has the disadvantage that 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 methanol is that methanol is readily liquefied. This ensures a high volumetric energy density which enables cost effective storage and transportation. Energy losses are incurred when converting hydrogen to methanol, but the costs incurred through this molecular conversion can be saved through simplification of the storage and distribution supply chain.

Methanol as a hydrogen carrier for fuel cells

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.

Jason Spencer, Sales and Global Product Manager for Fuel Cells at Clariant Catalysts said,

"We are seeing a high level of interest in methanol steam reforming since the steam introduces hydrogen to the system and means the overall volumetric density (kg H_2/m3) is 40 – 50% higher than ammonia cracking or methanol decomposition."

Clariant has developed and commercialised the novel HyProGen 251 catalyst for methanol steam reforming.

It is based on a zinc-alumina formulation that is comfortable operating up to 500 °C. "At 400–500 °C, the reactor temperature is perfect for heat integration with a thin-foil gas separation membrane that can deliver high purity hydrogen to the fuel cell", adds Spencer.

Clariant has partnered with Element 1, which has developed a methanol steam reforming-based hydrogen generator using HyProGen 251 and Element 1's hydrogen purification module to supply high purity hydrogen for low temperature (LT) PEM applications.

Distributed methanol reforming is more common in remote areas, where houses and flats use fuel cells at 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.

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 hit multi-MW capacity. This is especially attractive for marine applications where large ships require significant amounts of energy for auxiliary power and propulsion", said Spencer.

Direct use of methanol on a fuel cell

The German company SFC Energy 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 that "up to 8 fuel tanks, each containing up to 60 litres of methanol fuel, can be connected to the fuel cell to ensure maximum operational duration." He said that "the bestselling unit, the EFOY Pro 2800 can deliver up to 125 W, weighs 7.8 kg 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 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 87W. "The fuel cells are normally not 24/7 in operation and when the unit is used to backup wind or solar power", said Laistner, "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 500 kW.

Fuel cell power enables satellite communications

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 the 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 the renewables, power will continue to flow during calm days and dark nights.

UK-based firm Leading Edge Power has been active in the provision of remote environmental monitoring instrumentation for many years. David Sully, Managing Director, explained their 'belt and braces' approach to remote power generation. "We 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 longer durations stretching the storage capacity of batteries. Furthermore, battery life at low temperatures is reduced. For these harshest conditions, we have integrated an EFOY DMFC into our PowerBox™ to ensure backup power is available beyond the duration that a battery could offer."

"The EFOY Pro 2800 can deliver up to 125W, weighs 7.8 kg and is approximately the size of a briefcase"

© SFC Energy

Sully added, "This year, we installed bespoke Off Grid systems on two offshore wind turbine rigs to provide power for off-grid satellite comms from the wind farms to the shore. Each unit uses two EFOY 2800Pro DMFC fuel cells. Since their installation these PowerBox™ units have been powering up the DC equipment at a continuous power load of 150W without breaking into a sweat."

Methanol reforming for high temperature PEM fuel cells

German company SIQENS 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 45 kWh of power through the Ecoport.

The methanol reformate contains carbon monoxide (CO) which would poison a low temperature PEM (LT-PEM) fuel cell. However,


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Hyprogen 250-51 methanol reforming catalyst

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Siqens HT PEMFC Stack assembly

> "If the hydrogen from the cracker is to be used on a low temperature PEM fuel cell, then it must be extremely pure"

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 an alternative hydrogen carrier for 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.

Guillermo Garcia-Miguel, head of product at H_2SITE in Spain says that "our ammonia cracker 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, then it must be extremely pure."

As part of the H_2Ocean project, H_2SITE demonstrated the performance of their ammonia cracker on board the oil field services vessel Bertha B, sailing from the Port of Bilbao in November 2023. The 30 kW PEM fuel cell from Ajusa in Spain was used to power the ship's auxiliaries.

The ammonia cracker that H_2SITE 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 loss of power.

When filled with a different catalyst, the H_2SITE cracker can break down methanol into a syngas reformate. This reformate can be fed to a high temperature PEM fuel cell or can be upgraded with water gas shift t reactors and purified to yield hydrogen.

"Beyond ammonia or methanol cracking, our membrane gas separation technology can be used to separate hydrogen from other mixed gas streams", adds Garcia-Miguel. "For example, extracting pure hydrogen from a natural gas and hydrogen blend that may be used for pipeline transmission." gw

Liquid methanol