HYDROGEN STORAGE IN FUTURE WARSHIPS

BY

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ABSTRACT

Fuel cells, offering high electrical efficiency and power density, low emissions and reduced acoustic
and infra red signatures, are now being incorporated into the U214 class of submarines in Germany,
and are being investi Ultimately, all fuel cell types either require, or work most effectively with, hydrogen. Storage of hydrogen poses difficulties in terms of mass and volume footprint and in dormancy for cryogenic storage, while generation of hydrogen at sea from logistic fuels, such as F-76, poses challenges in terms of system complexity, cost and heat signature. Improvements to both approaches are needed to bring systems to market and to maximize the benefits that fuel cells systems pose. Based on a recent extensive review for the Defence Procurement Agency, this article presents a brief overview of the state-of-the-art in these areas and considers potential future developments to the year 2015.

Introduction

The world now faces tremendous challenges associated with greenhouse gas emissions, climatic change and the need for sustainable development. Deposits of oil in the world are very unevenly distributed, over 70% of reserves being found in OPEC countries. Moreover, oil reserves are finite. Within two decades, consumption is anticipated to exceed supply. By five decades, many are seeing hydrogen as replacing petroleum as the primary energy vector with benefits of increased energy diversity, low emissions and enhanced integration with biomass and renewables. The interest in hydrogen within the UK MoD is motivated by the potential cost and operational advantages conferred by fuel cells and the need to be ready for a time when hydrogen is the dominant energy vector. In the military arena, fuel cells offer a number of distinct benefits, some of which are less important in civil markets:

High efficiency.

Improved fuel economy.

• High power density.

Improved tractive power.

Modularity.

Flexibility in placement and redundancy.

- Low noise.
- Reduced IR signature.

No moving parts – reduced maintenance cost.

While fuel cells offer many potential benefits, they must compete with a host of existing and emerging alternative power generation and transportation prime mover technologies. In particular, extensive deployment of fuel cells, within the Navy and beyond, is predicated on overcoming three major obstacles:

- A move to a full hydrogen economy would certainly entail significant costs, a replacement hydrogen distribution infrastructure for the US alone being estimated as \$570 billion.¹
- Once the hydrogen has been obtained, there is a need for the development of mass and volume efficient hydrogen storage means, most particularly for vehicular applications.
- In the absence of optimized technology for hydrogen storage without compromise to range, a parallel development track requires the development of low cost, efficient, small footprint, responsive reformers, taking infrastructure (or logistic) fuels and converting these to hydrogen on-board the platform.

The first of these bullets lies outside the scope of this article, the latter two are explored further.

Fuel Cells

While hydrogen can be used directly as a fuel, this makes limited sense, as the reactivity and lightness of hydrogen precludes its availability in large quantities terrestrially and the gas needs to be extracted from other vectors, such as water (by electrolysis) or hydrocarbons (by chemical reforming processes). The energy requirement to extract the hydrogen, and then distribute and supply the gas, means it is generally more efficient to use the electricity or hydrocarbon source directly. The key to unlocking the potential of hydrogen lies mainly with the fuel cell, since the electrochemical conversion does not suffer the limitations of the Carnot cycle seen with heat engines. While some fuel cells (particularly high temperature fuel cells, where internal reforming is possible) can utilize fuels other than hydrogen, all work most efficiently with hydrogen. The various fuel cell types are distinguished by the electrolyte and operating temperature. Fuel cells also traverse a wide variety of applications by size (FIG.1).

Early adoption of the fuel cell within the Royal Navy is most likely to be for auxiliary power for idling or harbour load, alongside gas turbines for primary propulsion, in lieu of longer-term improvements in power density and reductions in stack costs being sought by developers. The Royal Netherlands Navy has been working with De Nora (now Nuvera) and TNO in support of the All-Electric Ship (AES). The Polymer Electrolyte Membrane (PEM) fuel cell has been selected as most appropriate for the duty.

While fuel cells have clear application to surface warships and the AES concept in particular, perhaps the greatest benefit is extending Air Independent Propulsion (AIP) in submarines, offering a credible alternative to nuclear generation, with demonstrable safety benefits, reduced maintenance and extended range over batteries. In 1994, the German Navy decided to build four new 212 submarines to replace their existing diesel-electric 206/206A submarines. These are hybrids with nine 30-50 kW PEM fuel cells and a diesel motor. A high performance lead-acid battery can be run in parallel with the fuel cell for higher speeds when in stealth mode. HDW of Kiel is now working with Ballard to build a 214 submarine, an AIP vessel based solely on PEM fuel cells and H_2/O_2 . The Greek Navy has ordered four vessels and South Korea has ordered a further three. The larger 120 kW stacks used in these vessels will permit two weeks underwater endurance.

The Russians have been developing Alkaline Fuel Cell (AFC) technology for submarines for many years. SKBK (formerly the Special Boiler Design Bureau) has developed an improved matrix electrolyte, delivering 20-25% higher efficiency than the PEM alternative with the same overall dimensions and service life, for use in the Amur-class submarines, with an increase in dived endurance from 15 to 45 days, at the same time recharging the main lead acid batteries.

FIG.1 – FUEL CELL TYPES AND ASSOCIATED POWER GENERATION CAPACITY

Following the loss of the *Thresher* in 1963, the US Navy has maintained two AFC-powered boats on stand-by for rescue operations. The hydrogen-oxygen fuel cell system was chosen because the system is not affected by depth, it is compact, does not release poisonous waste gases and supplies 30 kW. The AFC pack has been in operation at greater depths than 1,500 meters, the gases being stored in pressurized tanks. Fuel cells are also being deployed in Autonomous Underwater Vehicles (AUVs). The HUGIN II AUV uses a 35 kWh $Al/O₂$ fuel cell in missions up to 45 hours. Other operational AUVs using $Al/O₂$ fuel cells include the XP-21, ARCS 3 and ALTEX.

Hydrogen Storage Technology

As can be seen from the foregoing paragraphs, the need for hydrogen storage for fuel cell operation is most acute in subsea applications where space is often at a greater premium than for surface vessels. While hydrogen has three times the energy content of logistic distillate fuels, such as F-76, on a mass basis, as a gas it has only $1/25$ th of the energy content of F-76 in volumetric terms even when compressed to 2,400 psi. This makes physical storage of H_2 bulky, translating to shorter times between refills for transportation applications and shorter useful periods for portable applications. Other challenging issues include energy

efficiency, cost and safety. (FIG.2) compares the energy content of hydrogen, stored by a number of means, with road transport infrastructure and alternative fuels. The situation gets worse when the volume occupied by the storage vessel is factored in. The need for more volumetrically efficient storage is a key requirement for most practical applications and has stimulated significant interest, and investment, in hydrogen storage research and development.

FIG.2 – ENERGY CONTENT OF STORED HYDROGEN AND LIQUID TRNSPORT FUELS³

Table 1 gives an overview of the hydrogen storage methods that are presently being deployed in fuel cell demonstrations, together with longer-term storage methods that are being investigated.

TABLE 1 – *Summary of hydrogen stowage approaches*

Storage System	Characteristics	
Hydrogen storage methods currently being applied to fuel cell applications		
Gaseous Hydrogen	Simplest storage method but poor weight efficiency at 172 bar (1 wt%, assuming steel cylinder). Can increase wt% by an order of magnitude by use of composite carbon wound cylinder with an Al or polymeric inner liner and use of higher pressures (700 bar).	
Liquid Hydrogen	Requires low temperature, well-insulated container and vent for boil off; complex and dormancy issues. Efficient on weight and volume basis, inefficient in terms of energy consumption on liquefaction.	

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In general, the current methods have drawbacks in weight, volume or complexity that are inherent; the future solutions which are being investigated address some (but not all) of these drawbacks. It is immediately apparent from Table 1 that there are a very wide range of technologies that have been investigated or are in active commercial development for storage of hydrogen, at varying degrees of maturity. Of these, the most mature are compressed and liquid hydrogen storage. Compressed hydrogen, even at high pressures, is voluminous, while liquid hydrogen, although denser, requires cryogenic (20 K) storage, with dormancy and efficiency drawbacks. These limitations have led to the chemical or These limitations have led to the chemical or physicochemical incorporation of hydrogen in various solid and liquid compounds (glass microspheres, zeolites, carbons, metal hydrides, alanates, chemical hydrides and borohydrides, methanol and light hydrocarbons, amongst others). Storage in solid media is generally safer and potentially more efficient than compression or liquefaction, due to leak-proof status, higher charging efficiency and lower selfdischarge. Conversely, liquid flows are generally more controllable for stop-start applications in terms of ease of processing.

Table 2 gives an overview of the more viable hydrogen storage technologies, together with an assessment of how they may develop to the year 2015 in the absence of funding by the UK Ministry of Defence or other sources. The data in the table is restricted to areas of naval application; hydrolysis of chemical hydrides and borohydrides, and ammonia borane, clearly have potential both to commercial and military (infantry) operations, but these are one-off supply systems, implying unrealistically frequent changeout at sea or return to base. Direct methanol fuel cells are the subject of considerable development effort but portable uses aside, methanol crossover and the relatively poor efficiency limit wider application.

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TABLE 2 – *Current and projected (year 2015) status of the more viable hydrogen storage technologies*

$H2$ storage technology	Overview of technolog	Anticipated state of development by 2015 in the absence of funding by the MoD
Compressed hydrogen gas $(CH2)$	Compressed gas storage systems offer simplicity of design and use, moderate H_2 fraction, rapid refuelling capability, excellent dormancy characteristics, limited infrastructure impact (assuming refuelling facilities are reachable), proven high safety, and little development risk. With advanced tanks, the major disadvantage is the system volume, even at high $(10,000 \text{ psi})$ pressure.	This technology, subject to active commercial development, is close to maturity and is likely to develop further even in the absence of MoD funding. The of development extent <i>is</i> dependent on pressure limitations of materials and the energetics of ever-increasing pressurisation.
Liquefied hydrogen (LH ₂)	LH_2 systems have one of the highest H_2 mass fractions and one of the lowest system volumes, along with low development risk, good fast-fill capability and acceptable safety characteristics. LH_2 would be a good hydrogen medium were it not for two significant drawbacks that appear insurmountable: 1. Dormancy (boil-off) limits mission/application time and lowers efficiency. 2. The liquefaction process is costly and unsuited to localized generation or distribution, which has implications for supply chains. Even though LH_2 is currently being used in some submersibles, the limited storage capacity of LH_2 is prompting development of reforming technology for future vessel	BMW is actively partnering with Linde in the development of LH_2 storage, with GM showing some interest. Dormancy is likely to be reduced with materials & design improvements. It is quite possible that LH_2 will not be bettered in of hydrogen terms capacity (hydrocarbon reforming excepted).
Interstitial metal hydrides	Metal hydrides proven are technology, delivering H_2 at low, controllable pressure, permitting conformable packaging. However, alloy cost is an issue and no metal hydride system of today meets all the demands of a practical H_2 storage medium, most particularly for light duty vehicle application. A future metal hydride material has to show volumetric and gravimetric efficiencies at least as Mg-class hydrides, fast kinetics at low temperatures as TiFe- and La- class hydrides, and ideally make use of elements, which are common in nature. Although the lightweight Mg-class hydrides show high H_2 storage capacities even after extensive cycling, slow kinetics at lower temperatures precludes practical use.	Significant funds are being expended on interstitial metal hydride storage, however, progress in increasing capacity at low release temperatures is likely to be limited.

In examining the alternatives, now and projected, it appears that no technology has repeatedly greater volume density than liquid hydrogen, or greater stability and simplicity than compressed hydrogen. Metal hydrides are best used where weight is not a serious limitation, for example in submarines where the buoyancy must be matched with the weight of the vessel. In the latest German class 212A submarines utilizing 300 kW Siemens PEM stacks, hydrogen is stored as a low temperature metal hydride outside the pressure hull. For extended AIP range,

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however, on-board reforming of hydrocarbons to hydrogen is considered essential, by HDW, utilizing methanol for the next generation of submarines, and by SKBK, utilizing diesel. The limitations of hydrogen storage technology have also led the US Navy to fund demonstrations of on-board reforming of diesel for surface ships.

Hydrogen Safety

Lack of familiarity in handling hydrogen, together with images of the HINDENBURG airship incident, raise questions as to the safety of hydrogen as a fuel. In this context, it is worth noting that it was the skin of the airship, which ignited, rather than the hydrogen, and that most deaths from the incident were caused from people jumping to their deaths, rather than from the combustion of the gas. All of the survivors rode the airship down to the ground and safety. Today, procedures currently in place for handling nitrogen and oxygen (liquid and gaseous) are much the same as those that would be required for handling hydrogen. Handling hydrogen is less hazardous than handling oxygen, since the need to keep the oxygen totally separated from any grease or oil would not be a requirement for hydrogen.

Hydrogen is a colourless, odourless gas with no harmful physiological effects. A potential for asphyxiation would exist in a closed room if sufficient hydrogen were released to displace oxygen to below 18%, the risk of which is minimized by the rapid dispersal of hydrogen. To avoid accumulation of the gas, well-engineered containment and safety systems are needed, including the use of commercially available hydrogen gas detectors. The ignition and detonation properties of hydrogen-air mixtures are particularly important from a safety point of view. One of the main risks of many hydrocarbon gases is that they pool, thereby remaining unnoticed as a potential explosive risk. The diffusion coefficient of hydrogen in air is more than an order of magnitude greater than that for hydrocarbon gases; consequently, hydrogen does not pool, but disperses rapidly by turbulent convection, drift and buoyancy, thus shortening the duration of any hazard. Prompt dispersion, however, favours the formation of gas mixtures with wider flammability and detonation limits; the lower limit is the critical one in most applications and is comparable to that of other fuels. When an air/gas mixture does explode, the energy of explosion determines the damage or injury that occurs. The energy of explosion of hydrogen is many times lower than methane, propane or gasoline.

In conclusion, compared to other flammable gases, hydrogen is less hazardous than many of the common vapours that personnel are exposed to, such as gasoline, propane or natural gas. Leaked hydrogen is self-dispersing and unlike hydrocarbons, a hydrogen fire can be fought with water.

Reforming

Hydrocarbon liquid fuels, such as methanol and diesel, contain more hydrogen by volume than even liquid H_2 . By reforming hydrocarbons, the hydrogen within the feedstock can be liberated, yielding a H_2 -rich reformate, together with CO, CO₂ and water. A number of reforming methods can be used, steam reforming being considered the most efficient, however, the endothermic nature of this process and the common use of packed-bed catalytic reactors is generally characterized by poor kinetics, translating to slow start-up and sluggish load-following characteristics. Further, while steam reforming is well-suited to light hydrocarbons, heavier feedstocks, in particular logistic fuels such as F-76, are liable to generate carbon as an unwanted by-product during reforming. For such heavier feeds, alternative approaches include partial oxidation, in which air is added to the feedstock to give rise to an exothermic, fast reaction; or autothermal processing, effectively a mixture of partial oxidation and steam reforming in

which the two reactions are in heat balance. This approach forms the basis for many of the reformers being developed today.

Dependent on the stack type, the reformate may need some clean-up prior to use by the fuel cell. In general, the clean-up requirements are more exacting the lower the stack temperature. For example, the PEM requires a stream substantially free $\left(\langle 20 \rangle$ ppm) of CO, while the AFC, with its alkaline electrolyte, requires the reformate to be free of $CO₂$. Sulphur acts as a poison both for reforming catalysts and high temperature stacks, where internal reforming is possible (the heat to drive the reforming process coming from the stack rather than from combustion of some of the fuel). This again poses difficulties when reforming F-76, which can contain up to 1 wt% sulphur. The need to maximize H_2 productivity and minimize contaminants yields a complex fuel processing train, with attendant issues of cost, control and integration. On a vehicle platform, the advantage of a high energy density store is offset to a small degree by the size and weight of the fuel processor.

Two major "Ship Service Fuel Cell" demonstration projects are being funded by the US Office of Naval Research. MTI, alongside Ballard and Gibbs & Cox, are developing a PEM fuel cell generator for navy ship electrical power. Phase 1, now complete, produced a system conceptual design of a 2.5 MW ship service fuel cell and proved critical components under military marine conditions, including salt air, shock and vibration of the PEM stacks and operation of a logistics fuel processor on F-76. With a minimum system efficiency of 40% at 50% of rated load, it is believed that production costs will equate to around \$1500/kWe, comparable to marine diesels. Phase 2 of the work aims to demonstrate an integrated 500 kW generator operating on naval distillate on land and then at sea. In a parallel ONR programme, Fuel Cell Energy is developing a 625 kW fuel cell power plant for marine applications based on its Direct Carbonate Fuel Cell (DFC) technology. The power plant is also designed for operation on F-76. Work began in 1997, with delivery of a larger (0.5 MW) system expected at the time of writing (2003).

Methanol reforming is less complex than diesel reforming and the methanol has 2.7 times the weight-related energy density of $LH₂$. Steam reforming of methanol was chosen by HDW because it yields a higher level of hydrogen, no added oxygen demand, and lower $CO₂$ generation than diesel partial oxidation, all important requirements for submarine use. $CO₂$ produced during reforming must be stored on board of the submarine or discharged into the ambient seawater in a signature-free manner. Development of the methanol reformer began with a study in 1995, with construction in 1999 and testing in 2000. Once proven, HDW plan to replace the low temperature metal hydride store currently deployed in the 212 and 214 with reformers, with significant range and cost benefits.

Application to Commercial Shipping

Commercial shipping is characterized by an incredible diversity of vessels, with bespoke propulsion systems for a given design. The major (95%) share of the marine propulsion market is taken by diesel engines, with slow speed diesels taking the lion's share (80%) and growing compared to medium and high speed diesel engines.⁵ Fuel cells offer only marginal benefits in efficiencies compared to slow diesels, except when operating at part load. In contrast to commercial shipping, Naval vessels have embraced gas turbines for primary propulsion due to their high gravimetric and volumetric power density. Fuel cells have difficulty here, the PEM delivering up to 180 kW_e/m³ power density (projected), against gas typical test than to 4000 kW $/m^3$ fo turbines with up to $4000 \text{ kW} \text{m}^3$.

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Fuel cells do offer clear benefits in retaining high efficiency conversion at part load and in low emissions, hence the prospect for Naval fuel cells for hotel load and for harbour manoeuvring in view of impending MARPOL regulations. For commercial markets, dominated by diesel engines, the best fit for fuel cells is conventional ferries, intercontinental cargo vessels, and cruise liners in particular, where low noise and image are important.⁶ Despite the conservatism of commercial shipping operators, a recent study by the US Coast Guard⁷ suggested a potential market of tens of thousands of modular $250-500$ kW_e fuel cell systems to satisfy the majority rating of sub-2 MW_e engine replacement. Small trials have taken place in Italy, the US and Germany (the *Hydra*, a 22 passenger carrying excursion boat fitted with a 5 kW_e AFC and a 32 Nm³ hydrogen capacity metal hydride tank), and there are long-term plans to covert the Icelandic fishing fleet to hydrogen generated geothermally. If a significant market for fuel cells in commercial shipping is to emerge, however, in the absence of adequate hydrogen storage means, fuel processing becomes the key enabling technology, and the bunker fuel is likely to be residual with up to 3.5 wt% sulphur rather than more benign naval distillates.

Conclusions

- 1. Fuel cells are finding niche applications on board naval vessels, however, hydrocarbons aside, an energy dense hydrogen storage medium has yet to emerge. While improvements, particularly in compressed gas storage for road transport are likely to be seen by 2015, these are unlikely to satisfy the needs of naval or commercial shipping applications.
- 2. The lack of any credible hydrogen storage means outside hydrocarbons implies a need for continued investment in, and development of, logistic fuel reforming processes and the catalysts on which they depend. Reforming has the twin advantage of making use of logistic fuels and dealing with the issue of energy density but does not deal directly with the longer-term issue of energy security. Ultimately, this can only be addressed through the use of renewables and biomass, with synthetic fuels as a vector.
- 3. Significant advances are needed to fuel cell system durability, design, performance and cost. Shipping operations are most likely to be a fast follower rather than an early adopter, however, even with support from navies, the fuel processing requirements of residual fuels is demanding.

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