

FUEL CELLS

BY

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ABSTRACT

Fuel cells have recently attracted the attention of the maritime industry because of their non-polluting nature together with high thermodynamic efficiency and low noise levels. The Solid Polymer Fuel Cell (SPFC) is generally accepted as the most appropriate cell for marine applications. Practical marine systems will use a fuel processor to produce a hydrogen rich gas from diesel or another liquid fuel. The gas produced requires processing to meet the high standards of purity necessary in the fuel cell. The cell generates DC electricity, directly from an electrochemical reaction between the hydrogen and oxygen; the only waste product being water.

This article looks at the history of the development of the fuel cell and the basic thermodynamics behind their operation. It then looks briefly at why the SPFC is the most appropriate fuel cell and at methods for reforming the fuel.

Introduction

The fuel cell was first invented in the 1800's by Sir William GROVE. Since the early 1900's, enthusiasts have been predicting that the fuel cell will replace the Internal Combustion Engine (ICE). The apparent failure of the fuel cell is due in part to the relative simplicity of the thermodynamics of the ICE. This allowed scientists and engineers to understand what was happening in the engine and rapidly improve its performance. The thermodynamics of the fuel cell are not so easily modelled and it has taken the development of ion diffusion theory for fuel cells to be fully understood.

Enthusiasts still state that the fuel cell will replace the ICE. The only difference today is that all the major car and utility manufactures are actively developing fuel cells.

This article presents a brief review of the development of fuel cells and the current state of the art. It then looks at the underlying thermodynamics of the fuel cell before considering the requirements of a maritime fuel cell power system.

History of fuel cell development (FIG.1)

1800's

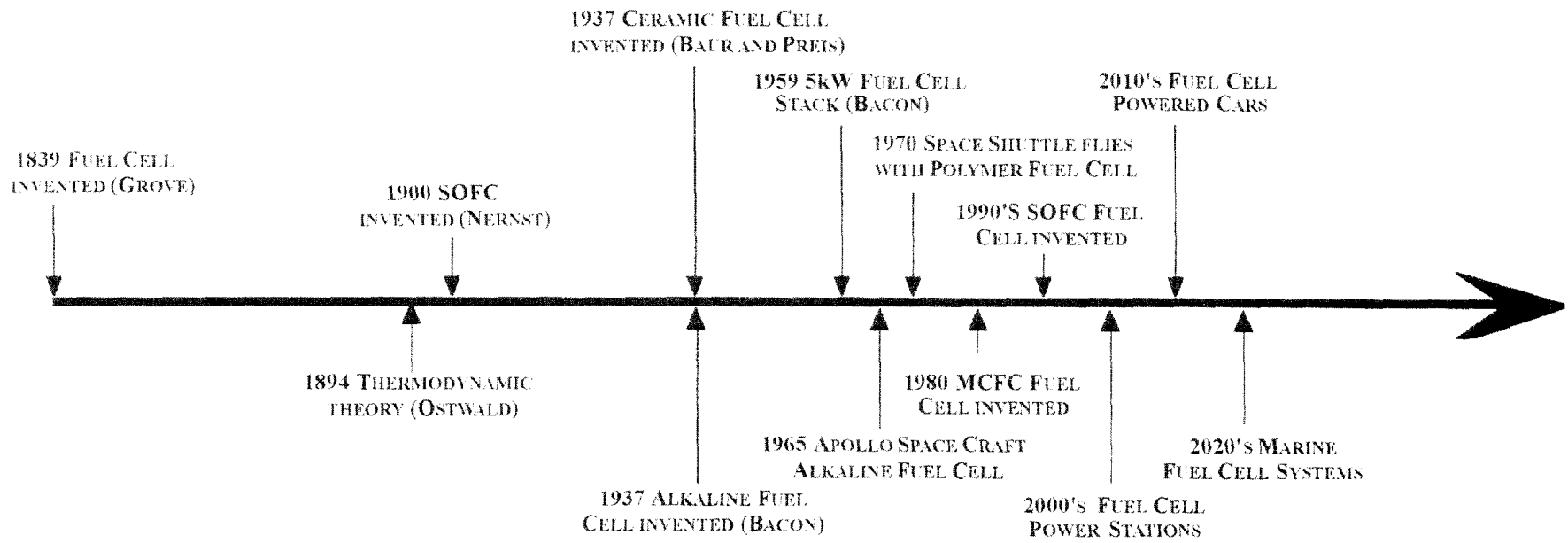
Sir William GROVE, a barrister from Swansea, is generally credited with the invention of the fuel cell. During his lifetime GROVE was famous for work on the galvanic *Grove Cell*, but the significance of his work on fuel cells was not appreciated for a number of years. The first hydrogen-oxygen, very dilute sulphuric acid fuel cell was reported in January 1839.⁷ This cell was able to generate a small amount of electricity by reacting hydrogen and oxygen. Within three years of his classic experiment GROVE showed that he was well aware of the fact that three-phase contact is essential:⁸

‘As the action could only be supposed to take place with ordinary platina foil, at the line or water-mark where the liquid, gas and platina met.’

GROVE sought to extend the area of contact by coating the electrodes with *spongy platina* this method was not able to extend the surface area available for reaction significantly and the cell could not compete with powers generated by more conventional galvanic cells. GROVE soon abandoned his research noting that,

‘A notable surface of action was required.’

FIG. 1 – KEY EVENTS IN FUEL CELL DEVELOPMENT



He also noted that the cell was a possible source of commercial electricity, particularly if the cell could be fuelled by coal, wood or other combustibles.

In 1855, A.C. BECQUEREL attempted to develop a direct carbon fuelled cell. The cell consisted of a carbon electrode and a platinum electrode immersed in a fused nitrate electrolyte. It was later pointed out that this was actually a nitrate-nitrate concentration cell.³

The fuel cell was shown to be, theoretically, an excellent solution for electrical generation, by the renowned physical chemist W. OSTWALD in 1894. He showed that direct conversion of the free energy of the fuel combustion reaction in a galvanic cell, was more efficient than conventional methods. OSTWALD also mentioned the advantages of no smoke, soot or fire.⁶

In 1896, W.W. JACQUES published data on a direct carbon and air fuel cell with a reported efficiency of 82%. JACQUES believed that his invention would make the dynamo obsolete. It was later found that much of the performance could be attributed to a chemical reaction rather than an electrochemical reaction and the efficiency was in fact much lower.³

The next significant step in the development of the fuel cell was in 1899 when Ludwig MOND and Charles LANGER repeated and improved GROVE's earlier work. The oxygen and hydrogen used by GROVE were replaced with air and industrial gas obtained from coal by the 'Mond-gas process'. MOND and LANGER realised that the platinum black catalyst was soon lost if it became wet, its loss meant a significant reduction in the area of triple contact. They avoided this by using the electrolyte in a quasi-solid form. They soaked up the acid electrolyte in a non-conducting material such as Plaster of Paris. This was the first use of a matrix electrode. The fuel cell they produced was capable of producing 1.5 W at 50% efficiency. Unfortunately, they decided not to continue their work since the cell experienced high polarisation, excessive voltage drop due to concentration gradients in the matrix. It was also found that the platinum electrodes, which were expensive, were easily poisoned by carbon monoxide.⁶

W. NERNST is well known for his contributions in the field of physical chemistry. In 1899 he discovered the solid-oxide electrolyte and he became the first to make a Solid Oxide Fuel Cell (SOFC) in 1900.⁹

1900's

The first half of the twentieth century saw many attempts to develop a successful fuel cell. All attempts failed, primarily due to a lack of understanding of electrode kinetics. One of the first men to realize the importance of kinetics was BAUR and he built a number of high temperature fuel cells. The first ceramic fuel cell was built by BAUR and PREIS in 1937 and operated at 1000°C.⁹ BAUR was unable to overcome the corrosion and material problems inherent with molten carbon fuel cells and these problems eventually led to the end of his work. This period also saw the rapid development of thermodynamics and the development of the internal combustion engine. The fact that electrode kinetics were poorly understood, whilst thermodynamic principles were easily explained, goes some way to explain why the fuel cell has developed far more slowly than the internal combustion engine.³

The first development that led to a successful fuel cell began in 1937 with F.T. BACON an English engineer working for C.A. Parsons and Co. Ltd. in conjunction with Cambridge University. To avoid the excessive costs associated with platinum electrodes, BACON switched from the acid based electrolyte used by GROVE, MOND and LANGER, to an alkaline electrolyte which operated at increased pressure and temperature (40 Atm and 200°C) with a nickel electrode. The less

corrosive alkaline environment allowed nickel to be used successfully with an increase in temperature and pressure necessary to make the electrode sufficiently active. He found that with increased pressure fuel cell performance increased.⁶

1950's

BACON developed porous electrodes made with two layers of material with different porosity to achieve large, stable, active surface areas of three-phase contact (triple contact). This innovation led to the successful construction, in 1959, of a 40-cell 5 kW system, capable of powering a welding machine, a circular saw and a 2-ton capacity fork lift truck. Later in the same year Harry IHRIG of the Allis-Chalmers Manufacturing Company in the United States demonstrated a tractor driven by a 15 kW fuel cell stack. The fuel cell stack operated at low pressure and temperature and used 1008 cells.^{3,6}

In 1964, Allis-Chalmers produced a 750 kW fuel cell system for the Electric Boat division of General Dynamics. The system powered a one-man underwater research vessel and is the first application of a fuel cell as a motive power source (excluding novelty items such as the fuel cell tractor and the forklift truck).³

In 1961, BACON's company, 'Energy Conversion', joined forces with Pratt and Whitney to form the United Technologies Company (UTC). It was clear to the U.S. National Aeronautics and Space Administration (NASA) that fuel cells had a number of advantages when applied to aerospace flight. They have high operational efficiency (low specific fuel consumption), low heat rejection, produce potable water as a by-product of the reaction between hydrogen and oxygen stored as a cryogenic liquid. Mission times of 7 to 10 days, expected in the build up to a manned mission to the moon, were too long for non-rechargeable primary batteries. The fuel cells developed by 1965 were capable of a power density of 1.6 kWh/kg for a 200-hour mission; the most effective battery could only achieve 0.2 kWh/kg.³

NASA decided that fuel cells would be used in the space program and funded extensive research awarding over 200 contracts to industry and universities. The GEMINI spacecraft was the first to include fuel cells, developed by General Electric. These fuel cells employed an ion-exchange membrane. The fuel cells used in the APOLLO missions, developed by UTC, were based upon BACON's design. The two main competitors, UTC and General Electric joined forces to develop higher power, lighter weight fuel cells for the Space Shuttle.

The success of the fuel cell as the primary electrical power supply for the U.S. space program led to many claims that the fuel cell was the answer to the world's energy problems. The expected revolution did not materialise. Four major problems caused the failure of the fuel cell:

1. High-pressure hydrogen was the only effective fuel. The cost of this fuel and its pressure vessels was prohibitive for ordinary applications.
2. The alkaline system required very high purity hydrogen. Carbon dioxide reacts with the electrolyte making it inadequate to sustain reaction rates. Any carbon monoxide produced will poison the electrodes, preventing the reaction occurring at all. In addition, the requirement for pure hydrogen makes the fuel production very expensive.
3. The cell lifetimes were short, again making the system expensive.

4. Fuel cell developers tended to oversell the merits of the system and play down the technical difficulties in developing commercial systems and consequently deadlines were not met.

The net result was that the alkaline fuel cell, whilst fully developed for the aerospace, industry could not make the transition to terrestrial power production. This was because the very high production and running costs could not be significantly reduced.³

1970's

The early 1970's saw a dramatic reduction in fuel cell funding by the U.S. government and fuel cell development slowed. The gap in funding was met in part by the American Gas Association (AGA). The aim of the AGA was to develop small domestic natural gas fuel cells operating on reformed natural gas. The mid-1970s saw a change in direction away from alkaline fuel cells to phosphoric acid cells, which were believed to be better suited to large power stations. In parallel to the development of phosphoric acid cells was the development of reformers for hydrocarbon fuels. It was soon realized by UTC that economies of scale associated with larger plants might be capable of reducing the per kW cost of the Phosphoric Acid Fuel Cell (PAFC) and make it economic in the production of primary utility power. Prototype power plants of up to 10 MW achieved acceptable lifetimes. This trend to larger scale power plants was continued worldwide but particularly in Japan.⁶

High temperature plants offer better efficiency and the 1980's saw the development of Molten Carbon Fuel Cells (MCFC) and in the 1990's the SOFC. The 1990's have also seen the resurgence of the membrane fuel cell as better membranes and catalysts are developed. The high temperature systems may also led to internal reformation of hydrocarbon fuels.⁹

After the development of the alkaline fuel cell for the U.S. space program it was generally expected that commercialization would start with small power plants of several kW's. Because of economies of scale, it appears that the first plants will be in the multi-MW class costing hundreds of millions of pounds to develop. Smaller units for special applications and the automotive industry are then likely. There is increasing pressure for low environmental impact and high efficiency power sources and the fuel cell seems set to meet this requirement.⁶

State of the art

The papers listed in the bibliography, together with the references, constitute a comprehensive review of the current state of fuel cell technology. A full discussion of the information acquired is beyond the scope of this article. However, the major findings of this research are presented below.

There are five main types of fuel cell:

- Alkaline.
- Phosphoric Acid.
- Solid oxide.
- Molten Carbon.
- Solid Polymer.

The solid polymer has a variant that is fuelled directly with methanol. The Solid Polymer fuel cell is close to commercial maturity. Its cost per kWh is approaching that of an internal combustion engine. Table 1 is a brief summary of the cell characteristics, DIRCKS.^{10, 3,4,6}

TABLE 1 – Fuel Cell Characteristics

	Electrolyte	Operating Temp °C	Carbon Monoxide Tolerance	Sulphur Tolerance	Maturity
Alkaline	Potassium Hydroxide	40 – 70	Poison no tolerance	Poison no tolerance	Fully Developed
Phosphoric Acid	Concentrated Phosphoric Acid	150 – 220	Poison > 5%	Poison > 50 ppm	11 MW prototype plants
Solid Oxide	Non-porous metal oxide	600 – 1000	Fuel	Poison > 1 ppm	Small Scale Research < 10 kW
Molten Carbon	Alkaline carbonate	600 – 700	Fuel	Poison > 0.5 ppm	Research plants up to 120 kW
Solid Polymer	Fluorinated and sulfonic acid polymer	-20 – 120	Poison > 10 ppm	Poison - no data	40 kW prototype

Fuel cell research and development is aimed at three main market areas. These are:

Power Generation

AGA together with the US-Department of Energy (DOE) has funded extensive research into the development of the phosphoric acid fuel cell. It was initially intended to develop small domestic fuel cell units fuelled with reformed natural gas. It soon became clear that economies of scale make it economical to use fuel cells for the production of primary electrical utility power. Pilot plant demonstrators up to 11 MW have been constructed in the US. Molten Carbon units have been tested at 120 kW and a 2 MW plant is under construction.⁵ The Japanese have also been active in this area with an 11 MW PAFC plant operating in Goi.⁶ The Japanese and the US Company Westinghouse are collaborating in the development of SOFC's and a 100 MW plant is planned.⁶ High temperature fuel cells are very effective in co-generation systems. The unused fuel from the cell powers a boiler and steam turbine plant. The net efficiency of the plant can exceed 80%.³

A Dutch team has proposed the use of the Heron gas turbine, an advanced cycle machine, together with a fuel cell to increase generation efficiency, HENDRIKS et al.¹¹

In addition to utility power generation, fuel cells are being developed for use as on site generators, use both co-generation, as for utility and direct power generation. The on site generators can be used as 'back up' power or as the primary electricity supply. The SPFC is a likely contender in this area and a 250 kW plant is under development by the Canadian company Ballard, Ballard.¹²

The fuel cells used in the power generation industry tend to be fuelled with reformed natural gas. In the long term, it is generally accepted that renewable sources such as solar, wind and biomass will be used to generate hydrogen.¹³

Automotive Industry

Initially the development of fuel cells for the automotive industry concentrated on hydrogen powered SPFC's, leading to a vehicle with zero emissions. Concern about the infrastructure and time necessary to fuel a fleet of cars running on hydrogen has led to the development of Direct Methanol Fuel Cells (DMFC) and methanol reformers. The main disadvantages of using DMFCs are that they have a lower thermodynamic cell voltage and are slower to respond to changes in power demand, SCOTT et al¹⁴. It is possible to operate a cell directly on methanol and it is simple to reform methanol to produce hydrogen and carbon dioxide. Methanol reformers produce a hydrogen rich gas from liquid methanol.

Marine Industry

Fuel cell systems have been used on submarines, where the ability to operate independent of the atmosphere is of primary concern, RITTERHOFF.¹⁵ The cost of supplying oxygen and hydrogen to a fuel cell plant is acceptable when compared with the cost of nuclear power. Only recently have fuel cells been proposed for surface vessels.⁴ The marine industry is generally conservative and is not investing large sums in fuel cell research. It is likely that the cells developed for automotive use will be the first generation of cell to go to sea. In the long term, the MCFC and the SOFC are likely to be used at sea as the primary method of electrical generation. Again, it is likely that the marine industry will wait for the other industries to develop the power plants. This will reduce the cost and technological risk to the ship owners.

Fuel reformation is one area where the marine Industry is likely to have to take the lead. Gasoline reformers have been investigated by the automotive industry but it is concentrating on development of methanol reformers.^{10,11} The automotive and power generation industries look set to use natural gas to produce methanol and reform it to hydrogen which will then power the cells.¹⁰ The development of reformers that can produce a hydrogen rich gas from diesel will have to be developed by the marine industry.⁴ Table 2 presents some of the fuel issues being considered by the automotive industry.¹⁰

TABLE 2 – *Fuel Issues*

	Manufacturing	Distribution	On-Board System
Hydrogen	<ul style="list-style-type: none"> • Infrastructure required • Steam methane reforming known 	<ul style="list-style-type: none"> • Infrastructure required • Time to refill vehicle a concern 	<ul style="list-style-type: none"> • Lowest cost System • Good load response
Methanol	<ul style="list-style-type: none"> • Infrastructure required • Made from natural gas 	<ul style="list-style-type: none"> • Some of infrastructure in place 	<ul style="list-style-type: none"> • Additional complexity
Higher Liquid Hydrocarbons	<ul style="list-style-type: none"> • Infrastructure in place 	<ul style="list-style-type: none"> • Infrastructure in place 	<ul style="list-style-type: none"> • Technically challenging • Many unknowns

Fuel cell principles of operation

A fuel cell is a device that converts the chemical energy of a fuel gas and an oxidant gas directly into electrical energy, without combustion as an intermediate step. The operating principles of a fuel cell are similar to those of a battery; the electrochemical combination of the reactants generates electricity. However, unlike a battery the fuel cell does not require recharging with electricity produced in some other manner. The fuel cell employs gases, from external sources, as reactants and they will continue to operate as long as both fuel and oxidant are supplied to the electrodes.

In hydrogen fuel cells, the gas is fed to an anode where it is oxidized and electrons are released to the external circuit. The oxidant gas is normally oxygen or air and is reduced at the cathode by the electrons from the external circuit. The external electron flow produces DC electricity. The reaction will only proceed in areas of the fuel cell where the reactant gas, the external current and the electrolyte meet. This area is known as the area of triple or three-phase contact. Maximizing this area is necessary for a successful fuel cell and led to the development of porous electrodes and quasi-solid electrolyte.³

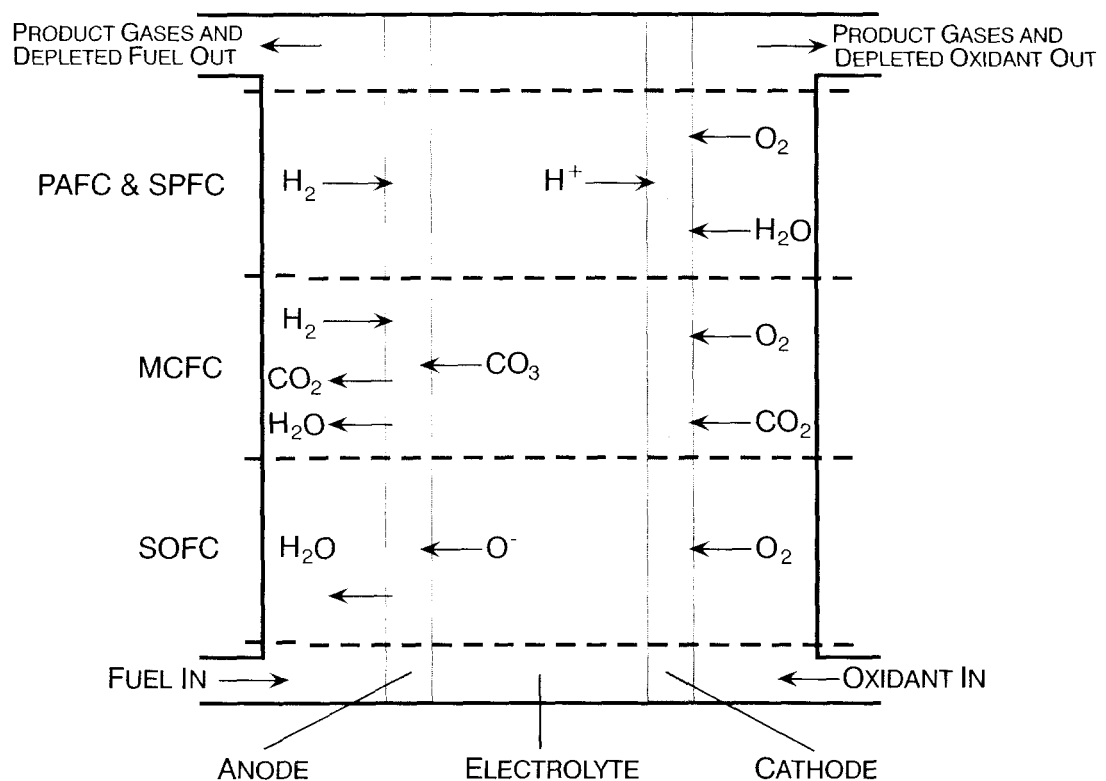


FIG.2 – FUEL CELL OPERATION

A schematic diagram of a fuel cell⁴ is shown in (FIG.2). The chemical reactions that occur depend on the type of fuel cell. Figure 2 shows the ion conduction between the reaction and product gasses for Phosphoric Acid fuel Cells (PAFC), Solid Polymer Fuel Cells (SPFC, also known as Proton Exchange and Proton Exchange Membrane fuel cells:– PEFC and PEMFC respectively), MCFC and SOFC. Alkaline fuel cells are limited to the aerospace industry, due to their sensitivity to their high cost and sensitivity to poisons.³ They are not shown in Figure 1.

Maritime Fuel Cells

Over the last decade, there has been a growing awareness of environmental issues and a realisation that unless action is taken now, the damage to the environment will be significant and lasting.

The International Maritime Organisation (IMO) issued new maritime exhaust regulations as part of Annex VI of the MARPOL convention in January 1998. The new exhaust regulations apply to new engines immediately and all engines after major overhaul. The MARPOL Annex limits the levels of sulphides (SO_x) and oxides of nitrogen (NO_x) discharged from a vessel.

It is expected that local, national and regional authorities will defer setting emission regulations to the IMO, provided that they are stringent enough to satisfy an increasingly environmentally conscious public.¹ Failure by the IMO to keep up with requirements of member nations will lead to a proliferation of confusing local regulations. In order to keep IMO deferral it will be necessary to revise the regulations regularly.

Diesels are currently used to generate and provide electrical power in most ships. It is likely that many future naval and merchant vessels will use electrical propulsion plant for economical reasons. If diesel engines are to be used it will be necessary to reduce emissions. Although several methods are proposed to reduce diesel emissions, all lead to either higher capital cost, a higher operational cost, or both.

A fuel cell is an electrochemical device that converts hydrogen and oxygen directly to DC electrical power without combustion, with clean water being the only waste product. The non-polluting nature of a fuel cell system makes it an attractive alternative for electrical generation in ships.

In addition to low emissions, the fuel cell has a number of other advantages that favour their use in ships, KOSEKI:²

- (a) High thermodynamic efficiency at approximately 50% (system efficiency is around about 40% including fuel treatment and power conditioning).
- (b) Very low levels of noise: 50~70 dB in engine room.
- (c) No vibration leading to improved signature reduction and increased onboard comfort.
- (d) A range of fuels can be reformed to produce the hydrogen required by the fuel cell.
- (e) Little maintenance, due to a small number of moving parts.
- (f) The system can be distributed throughout the ship, allowing a reduction in ship volume.

Fuel Cell selection

Selection between the various types of fuel cell, for the most suitable one for marine applications, is primarily dependent on the power density. Higher power density allows for lower system volume and weight.

(FIG.3) shows the rated current densities for the various fuel cells currently available.² The SPFC has by far the highest power density and is consequently the cell of choice. In addition to its high power density, the SPFC has the following advantages:²

- (a) The fixed solid electrolyte leads to very long cell life. SPFC used in the space industry have been operated for 40,000 hours, MAELROY.¹⁷
- (b) Good shock and vibration characteristics result from the solid structure.
- (c) There is no performance degradation from repeated start-up and shutdown.
- (d) The low operating temperature facilitates short start-up times.
- (e) The low temperature makes maintenance and operation easier.
- (f) Potential for cost reduction as the low temperature will allow cheaper materials to be used.

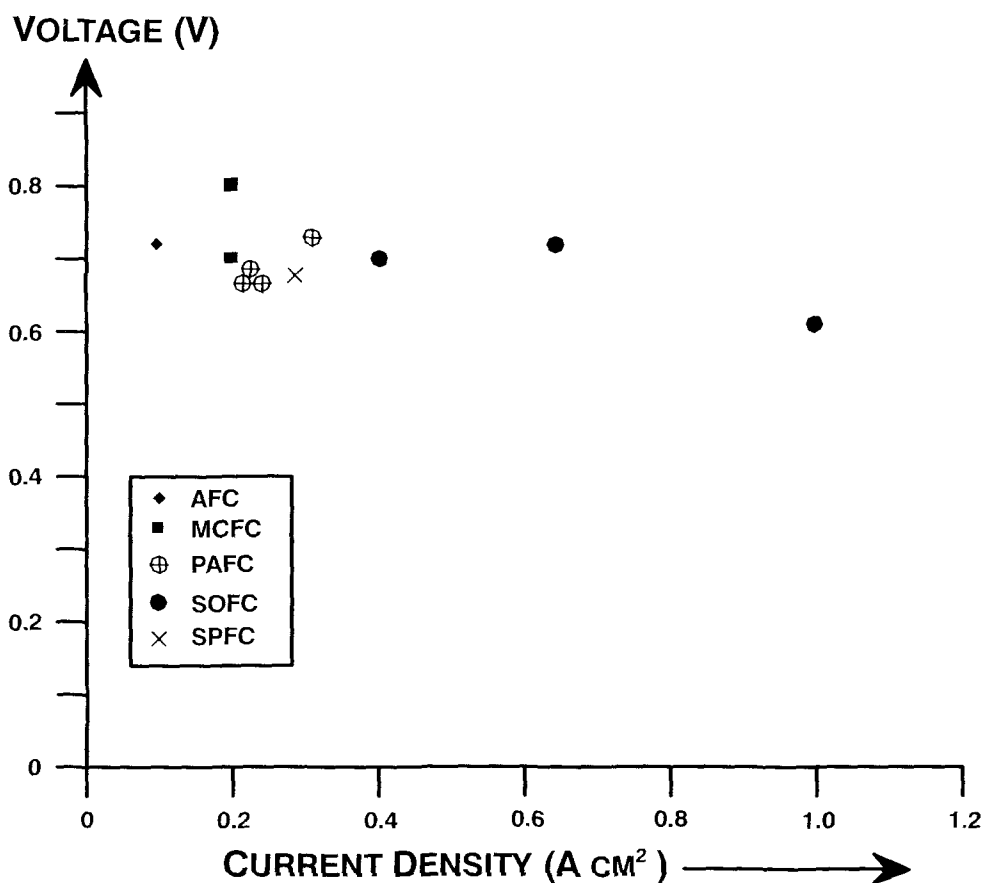


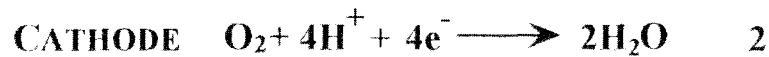
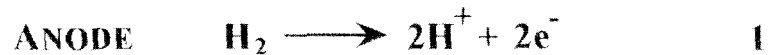
FIG.3 – RATED CURRENT DENSITY AND VOLTAGE OF VARIOUS FUEL CELLS

SPFC technology is technically commercial, able to equal or beat diesel efficiencies. However, it is currently more expensive per kW than a diesel.⁴ It is believed that the SPFC will be commercially economic in the near future.

In the long term, SOFC and MCFC will afford better efficiencies, higher power densities and higher contamination tolerance, with the added advantage of internal reformation of hydrocarbon fuels.⁹ Internal reformation is made possible by their high operating temperatures. The high operating temperature will not be a long-term engineering problem as they operate at temperatures below that used by gas turbines. The current problems are mainly due to the highly corrosive nature of the electrolytes.

The SOFC and MCFC may well be the second generation of fuel cell to go to sea.⁴ The time scale expected for this is likely to be greater than 20 years.

Solid Polymer Fuel Cell reactions



As discussed earlier the SPFC will be the next generation of fuel cell to reach maturity. The chemical reaction in a SPFC is based on proton transfer and is inherently faster than MCFC, SOFC and alkaline fuel cells, all of which require ion transfer.

The electrochemical reaction is isothermal; the fuel cell uses the available free energy in the fuel at the operating temperature. Detailed descriptions of the principles, operation and construction of the various types of cell is given by KORDESCH et al.⁶

Thermodynamic principles

Direct conversion of chemical energy to electrical energy is a main feature of the fuel cell. In conventional power generation, a heat engine is used to convert the thermal energy released by a chemical reaction into mechanical energy. The maximum efficiency of a heat pump is limited by the Carnot efficiency:

$$\epsilon_{\text{CARNOT}} = 1 - \frac{T_l}{T_h} \quad 3$$

Where T_h and T_l are the high and low temperatures of a heat engine.

Other energy systems, such as magnetohydrodynamic generators and thermionic converters, involve the conversion of chemical energy to thermal energy and then to electricity. These methods of electrical generation are also subject to the Carnot limitation. The energy conversion efficiency of a real system will be even lower as losses will be incurred during each stage of energy conversion.

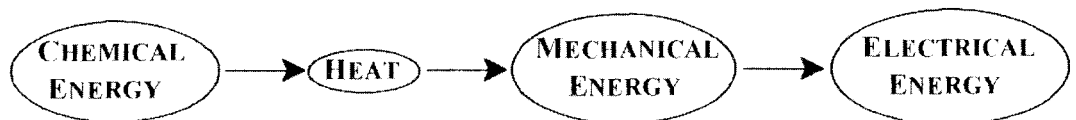


FIG.4 – CONVERSION EFFICIENCIES

The change in thermal energy, between reactants and products of a combustion reaction, is given by the change in enthalpy ΔH . When comparing the efficiencies of conversion devices, it is usual to look at the energy produced relative to the enthalpy change for that process

$$\epsilon = \frac{\text{ENERGY OUT}}{\Delta H} \quad 4$$

In a fuel cell, the enthalpy change is not all given out as heat. The maximum total electrical energy is given by the change in Gibb's free energy (ΔG), for the combustion reaction. In an ideal electrochemical cell all free energy would be converted to electrical energy. The maximum theoretical efficiency is given by:

$$\epsilon_t = \frac{\Delta G_T}{\Delta H_O} \quad 5$$

Where ΔG_T is the Gibb's free energy, at the reaction temperature and ΔH_O is the heat of combustion of the fuel, at standard conditions. The values used will depend on whether the product water is liquid or vapour. The corresponding values of ΔH_O are known as the Higher-Heating Value (HHV) and the Lower-Heating Value (LHV).

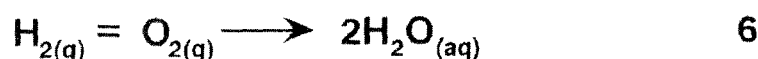
A practical fuel cell must use a commercially available fuel and produce either AC or constant voltage DC. This leads to the addition of a fuel processor and power conditioner which in turn reduce the system efficiency.



FIG.5 – FUEL CELL SYSTEM EFFICIENCY

The Thermodynamic Equilibrium Potential

The operation of a SPFC involves the oxidation of the fuel at the anode and the reduction of the oxidant at the cathode. The overall reaction can be written as:



The Nernst Equation defines the reversible thermodynamic potential of this reaction:⁶

$$E_r = E^\circ - \frac{RT}{nF} \ln[p_{\text{H}_2}^* (p_{\text{O}_2}^*)^{0.5}] \quad 7$$

Where E° , reference potential, is the thermodynamic potential produced by the electrochemical reaction at unit activity. At the standard state E_r equals E° , the following equation holds:

$$E^\circ = - \frac{\Delta G^\circ}{nF} = \frac{\Delta H^\circ - T\Delta S^\circ}{nF} \quad 8$$

This equation can be rewritten using a standard state reference potential E_0° :

$$E^\circ = E_0^\circ = (T - T_0) \left(\frac{\Delta S^\circ}{nF} \right) \quad 9$$

Fuel Cell Voltage Losses

The losses within a fuel cell are separated into activation, ohmic and diffusion polarisation (overvoltage). Each type of polarisation is influenced by many factors, including the type of electrolyte used, the electrode catalysts, the fuel, the materials used to construct the cell and the manner in which the cell is operated.

Activation Polarisation

All chemical reactions involve an energy barrier that must be overcome by the reacting species for a reaction to proceed. This energy barrier is called the activation energy and results in activation or charge transfer polarisation, η_{act} . At

the anode, hydrogen molecules react with the catalyst surface breaking the molecule bond. New bonds are formed between the hydrogen atoms and the catalyst surface releasing, an electron. Electron transfer and disorption of protons follows. A similar process occurs at the cathode catalyst with the oxygen atom being absorbed, with hydrogen ions and electrons discharged. After transfer of four protons and electrons, together with the breaking of an oxygen molecule bond, two water molecules are formed.

Breaking and reforming chemical bonds requires irreversible energy. The fuel used in the cell supplies the energy. The result of this is that the amount of energy available as electrical power is reduced.

The amount of activation polarisation is a function of the rate of reaction. An increase in the rate of reaction requires a greater gas flow rate, which in turn increases the kinetic energy of the gas. The increased kinetic energy reduces the amount of energy that needs to be supplied by the fuel to reach the reaction energy barrier, LEE et al.¹⁶

Other ways of reducing activation polarisation include increasing the active area of three-phase contact, increasing temperature and increasing fuel utilisation by using a more active catalyst.

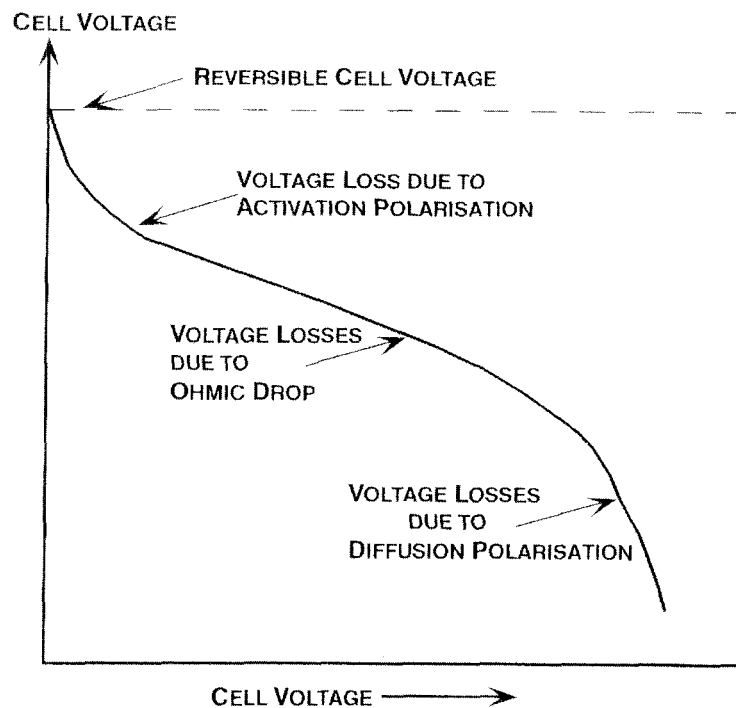


FIG.6 – TYPICAL FUEL CELL POLARISATION CURVE

Ohmic polarisation

Ohmic polarisation, η_{Ω} , is caused by resistance to conduction of ions through the electrolyte, the electrical resistance of the electrodes and contact resistance between cell components. Ohmic polarisation can be reduced by using highly conducting components, reducing the polymer electrolyte membrane thickness and reducing membrane electrical resistance.

Diffusion polarisation

Diffusion or concentration polarisation, η_{diff} , appears when the electrode reaction is hindered by mass transport effects. This is where the feeding velocity of the reactant and/or the removing velocity of product is slower than that corresponding to the discharge current. Lower than ideal quantities of process gases, at the reaction sites, decrease the number of chemical reactions at the electrodes. This results in a loss of voltage. Similarly, a build up of product water, at the reaction sites, dilutes the process gases. This again reduces the cell voltage. Increasing the operating pressure and area of three-phase contact together with using thinner electrodes, so the diffusion path is shorter, reduce diffusion polarisation.

A combination of these three types of polarisation results in a voltage/current relationship similar to that shown in (FIG.6). It is clear that each of the polarisation mechanisms is dominant in a particular current region. The steep slope at low current is indicative of activation polarisation. As the current increases, the slope becomes less steep. This is due to the activation polarisation becoming less significant and the ohmic effects increasing. The initial point of inflection on the polarisation curve marks the change between the activation and ohmic regions of fuel cell operation. The second inflection is the demarcation between the ohmic and diffusion regions of cell operation. The steep decline of the polarisation curve at high currents is consistent with the relationship between concentration gradient and diffusion rates.¹⁶

Power Generation

The power generated by the fuel cell is the product of voltage and current:

$$P = EI$$

10

(FIG.7) shows the typical power output of a fuel cell and the ideal power output if there was no polarisation.¹⁶

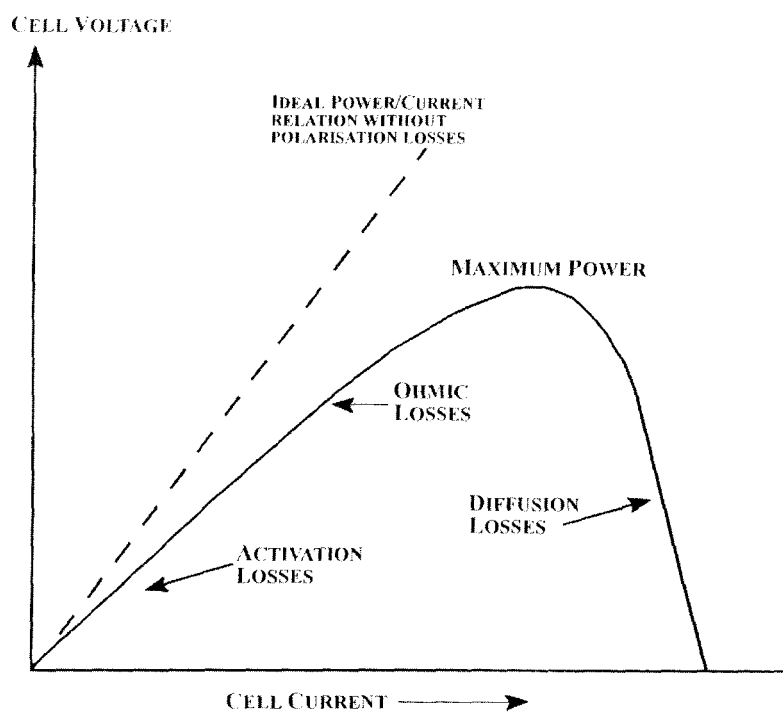


FIG.7 – TYPICAL POWER CURVE

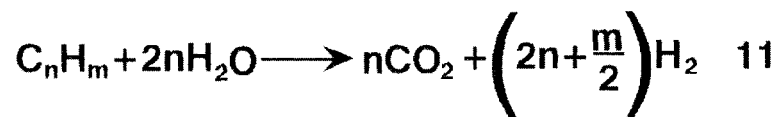
Fuel reformation

Currently the only practical fuel cell fuels are hydrogen and methanol. The use of methanol is inherently slower than hydrogen and requires more active, hence expensive, electrocatalysts. At present, Direct Methanol Fuel Cells (DMFC) cannot match the performance of hydrogen cells. The main advantage of methanol is that it can utilize the current liquid fuel infrastructure and Methanol can be easily reformed to produce hydrogen. DMFC are being actively pursued by the automotive industry.^{10,14} However, it would be preferable, for the marine industry, to be able to use diesel. The ability to produce a hydrogen rich gas from hydrocarbon fuel is necessary if fuel cells are going to be a viable alternative marine power source. There are three main methods of hydrocarbon reformation: steam reforming, partial oxidation and pyrolysis.

Steam reformation

Steam reforming is a highly endothermic reaction that involves the reduction of the fuel by steam, followed by a steam shift reaction, which reduces the carbon monoxide, produced by incomplete reformation of the fuel. A number of shift reactors are used to increase the amount of hydrogen produced.

(a) *Steam reforming:*



(b) *Steam-gas shift:*

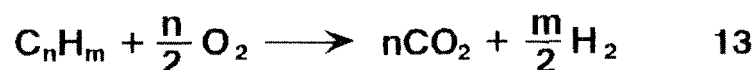


Where m and n are integers depending on the physical structure of the fuel.

The diesel fuel must have the sulphur content reduced either at the refinery or onboard in desulphurising units, before being supplied to the reformer. Sulphur will reduce the performance of the reforming catalysts, which are normally nickel, and will poison the fuel cell catalysts. The process also requires careful control to avoid carbon deposits building up and plugging the reactor. Steam reformers typically yield 75 % but the endothermic reaction proceeds slowly and requires considerable energy, DAMS et al.¹⁸

Partial oxidation

The partial oxidation of the fuel is an exothermic reaction that leads to the



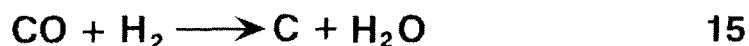
production of hydrogen.

The use of air means that the carbon disposition is far less of a problem. The side reaction that lead to carbon disposition are the same as those in a steam reformer namely:

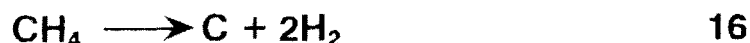
(a) Boudouard carbon formation (carbon monoxide disproportionation)



(b) Reduction of carbon monoxide



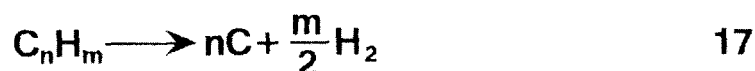
(c) Thermal cracking



Partial oxidation has some advantages over steam reforming: less water is required, the equipment is more compact allowing faster start-up and the high temperature reactor can tolerate some sulphur. As in the steam reformer, a number of shift reactors are used. The partial oxidation process yields a reformat gas with a hydrogen content of around 42 %. The reaction is exothermic and responds quickly to changes in load.¹⁸

Pyrolysis

This process decomposes hydrocarbons to hydrogen and carbon by heating the fuel to high temperatures in the absence of any air.



The reaction will occur without the use of a catalyst but high temperatures are required. Methane is also produced in the reformer, which is difficult to crack. A Catalyst is normally used to overcome this problem. The amount of hydrogen produced can be as great as 95 % but the life of the catalyst is very low at around one hundred hours.¹⁸

Auto-Thermal Reformers

An auto-thermal reformer is a hybrid of the steam and partial oxidation reformation methods. It balances the endothermic requirements of the steam method with the exothermic release from the partial oxidation. The net result is heat balanced reformation method with better load following characteristics and a 75 % hydrogen yield.¹⁸ However, auto-thermal reformers are complex and in their infancy, with considerable work required before they will be commercially available.

Clean gas supply

Both steam and pyrolysis reformers produce a reformat gas that contains both hydrogen and carbon dioxide. The addition of carbon dioxide will reduce the effective hydrogen partial pressure, which reduces the cell output voltage. The partial oxidation and auto-thermal reformat gases will also include nitrogen. Combining the effects of carbon dioxide and nitrogen, at reasonable operating pressures, reduces the hydrogen partial pressure to an unacceptable level. The presence of nitrogen on both sides of the membrane will also effect the membrane diffusion characteristics increasing the diffusion polarisation. It is necessary to use some form of hydrogen separation, with these methods, to increase the yield.

All of the methods discussed produce more than 10ppm carbon monoxide. The solid polymer electrolyte is sensitive to carbon monoxide and will be poisoned by carbon monoxide levels greater than 10ppm. It is necessary to fit a gas clean-up reactor to reduce the level of CO before supplying the gas to the fuel cell stack.

The fuel will first require the sulphur removing, even trace quantities of sulphur would poison the catalyst. Currently there is no marinised system for desulphurising diesel. Industrially sulphur is removed at refineries using fluidised beds. It would be more economical for sulphur to be removed by the refineries and distributed using the current infrastructure but until there is sufficient demand from ship operators, this is unlikely to occur.

The diesel fuel will then need to be reformed to produce hydrogen. Whatever reformation method used the hydrogen rich gas will need to have the carbon monoxide removed from the reformed gas stream. This can be achieved by oxidation in a gas clean up reactor. The hot gas will then need cooling.

The gas at this point could be supplied directly to the fuel cell but if the hydrogen percentage is below approximately 75% the effective partial pressure of hydrogen in the fuel cell will be too low for efficient power densities. The reformation methods that allow high yields of hydrogen (steam and pyrolysis) require high energy to operate and increase the parasitic losses significantly. A pressure swing molecular absorber could be used to separate the hydrogen from the reformed gas. The disadvantages of using gas separation are: increased complexity of the system, it is more difficult for the fuel cell to respond to transient load and the absorber requires considerable compressor power increasing the parasitic load and cost of the system. Finally, the air and hydrogen supplied to the fuel cell have to be humidified.

In order for the system to be efficient, it will be necessary to carefully balance the heat loads and maximize the use of the waste hydrogen by using heat exchangers and gas burners. In spite of the parasitic load, the efficiency of the overall system will exceed that of an internal combustion engine.

Conclusions

Sir William GROVE first invented the fuel cell in 1839. The slow development of the fuel cell is primarily due to the complexity of the chemistry governing its operation and the relative simplicity of the internal combustion engine. The alkaline fuel cells developed for the NASA space programme are too expensive for terrestrial use. The solid polymer fuel cell is the most likely to be used as a maritime power source in the medium term and either solid oxide or molten carbon cells in second-generation systems.

Emission regulations are becoming stricter and there is pressure on engine manufactures to produce cleaner designs. All the major car manufactures are actively developing fuel cell powered vehicles. Fuel cells offer a number of advantages that favour their use in ships, low emissions, high thermodynamic efficiency, very low noise levels, and low maintenance to name a few.

It is clear that considerable development and integration issues exist before a Solid Polymer Fuel Cell System will be a practical reality in a surface ship.

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Nomenclature

E_y	Reversible Thermodynamic potential	V
E^0	Reference potential at unit activity	V
E_0^0	Standard state reference potential	V
F	Faraday constant	C/mol
$P_{H_2}^*$	Effective partial pressure of hydrogen	atm
$P_{O_2}^*$	Effective partial pressure of oxygen	atm
R	Gas constant	J/mol K
T	Temperature	K
T_0	Standard room temperature	K
T_l	The low temperature of a system	K
T_h	The high temperature of a system	K
n	Number of electrons involved in the reaction	
ΔG	Change in Gibb's free energy	W
ΔG_T	Change in Gibb's free energy at temperature T	W
ΔG^0	Standard state change in Gibb's	W
ΔH	Enthalpy change	W
ΔH^0	Standard state enthalpy change	W
ΔH_0	Heat of Combustion of fuel at standard conditions	W
ΔS^0	Standard state entropy	J/mol K
ϵ	System efficiency	%/p.u
ϵ_{CARNOT}	Carnot efficiency	%/p.u
ϵ_t	Thermodynamic efficiency	%/p.u
η_{act}	Activation polarisation	
η_{dif}	Diffusion polarisation	
η_{Ω}	Ohmic polarisation	

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