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Polymer electrolyte fuel cells, advances in research and development

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Polymer electrolyte membrane fuel cells (PEMFC) are currently under intensive development for a range of power generation application in transportation, stationary and portable. The PEMFC can produce electricity at high fuel efficiency and high energy density. The PEMFC is typically base on Nafion® or similar polymers and operates at low temperatures of less than 80 °C. This article reviews the design principles of the PEMFC, the advances made in their performances and considers their limitations in relation to the types of materials used to generate power.

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1. Introduction

Fuel cells convert the chemical energy of a fuel directly into electricity. The process is an electrochemical reaction akin to a battery, but unlike batteries, fuel cells do not store the energy within the chemicals internally. Instead fuel cells use a continuous supply of fuel from an external storage tank. Accordingly, fuel cell systems have the potential to solve the most challenging problems associated with the currently available battery systems, namely their insufficient energy at a given weight (specific energy density) or volume (volumetric energy density). Besides, while the leading battery technologies are reaching the practical limits of their energy storage capabilities, commercial fuel cells are still in their infancy. Furthermore, since fuel cells operate without a thermal cycle, they offer a high energy efficiency and virtual elimination of air pollution without the use of emission control devices as in conventional energy conversion.

An important type of fuel cell is the Polymer Electrolyte Membrane Fuel Cell, (PEMFC), also called Proton Exchange Membrane Fuel Cell, which operates typically in the range 60°C-100°C and is suitable for transport and portable applications, and for power co-generation in buildings [1]. The PEMFC could also find applications in power generation in providing peak power and avoiding grid-reinforcement and are currently being tested on the 250 kW scale with hydrogen as the fuel [2].

The current, well-developed PEMFC technology is based on perfluoro-sulfonic acid (PFSA) polymer membranes (e.g. Nafion®) as electrolyte. It has limitations due to the low temperature of operation, namely; conductivity and water management issues, slow oxygen reduction reaction (ORR), a low tolerance to fuel impurities, e.g. CO and S as well as serious cooling problems and poor heat recovery (for residential applications). In contrast, operating at higher temperature gives several benefits including enhanced tolerance to CO and greatly reduced humidification issues. To achieve this goal requires a new range of polymer electrolyte membrane, which exhibit stability and high conductivity in the absence of liquid water.

This article reviews the advances made in the performance of PEMFC since their inception and considers their limitations in relation to the source and type of fuels to be used to generate power.

2. Operating principle of fuel cells

A fuel cell consists of two electrodes, an anode to which the fuel and a cathode to which the oxidant are supplied externally, and the electrolyte which separates the two electrodes and allows the ions to flow across it (Fig. 1).

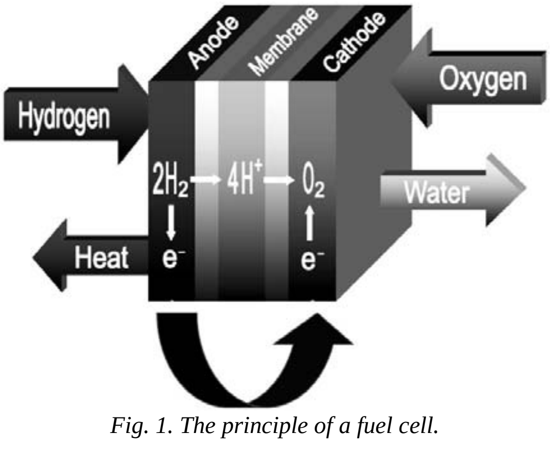

Fig. 1. The principle of a fuel cell.

In practice, a fuel cell consists of a thin composite structure of anode, cathode and electrolyte. Good electrochemical performance of the cell requires effective electrocatalysts. The electrocatalysts in a fuel cell are positioned on either side of an electrolyte, typically in the form of a polymer, ceramic or immobilized acid or alkali, to form the cell assembly. The reaction gases are, in practical operation, fed to the back faces of the electrodes. Flow fields are used to supply and distribute the fuel and the oxidant to the anode and the cathode electrocatalyst, respectively. The distribution of fuel and oxidant flow over the electrodes should ideally be uniform to try to ensure a uniform performance of each electrode across its surface. The flow field allows gas to flow along the length of the electrode whilst permitting gas transport to the electrocatalyst normal to its surface, through a diffusion layer.

The fuel cell converts the chemical energy contained within the fuel to electrical energy by virtue of the electrochemical reactions in the cell. Fuel cells typically use hydrogen as the fuel but a range of other fuels such as methanol and ethanol can be used as well nevertheless the best performance in terms of power output is achieved with the reaction of pure hydrogen with oxygen. In the case of an acid electrolyte the cell reactions are:

$$\begin{aligned} &H_2 \rightarrow 2\,H^+ + 2\,e^- \;,\quad E_0 = 0\text{ V} \\ &0.5\,O_2 + 2\,H^+ + 2\,e^- \rightarrow H_2O\;,\; E_0 = 1.229\text{ V} \end{aligned} \qquad (1)$$

The standard theoretical cell potential for the fuel cell is thus approximately 1.23 V. One of the attractions of the fuel cell is the potential high efficiency of conversion of the chemical energy into electrical energy. Unlike the combustion engine, where the heat of combustion of the fuel is first converted into mechanical energy, which is then converted into electrical energy, the Carnot Cycle does not limit the fuel cell efficiency. In a fuel cell the maximum (theoretical) electrical efficiency, ε, at standard conditions of temperature and pressure, is given by the ratio of the Gibbs free energy change, ΔG, of the reaction to the enthalpy change, ΔH:

$$\varepsilon = \frac{\Delta G}{\Delta H} = -\frac{2FE^0}{\Delta H} \qquad (2)$$

where F is Faradays constant and E^o, the standard cell potential.

For a fuel cell at low temperature, where the product is liquid water, the efficiency is approximately 83%. In almost all practical fuel cells, the theoretical efficiency is not achieved due to irreversible voltage losses associated with the flow of current and due to the actual construction of the cell. For a fuel cell the electrochemical efficiency, $\varepsilon_{e,}$ can be defined as the actual voltage achieved divided by the Gibbs free energy:

$$\varepsilon_e = \frac{-2FE}{\Delta G} \qquad (3)$$

where, E, is the actual potential produced by the fuel cell.

The potential produced by the fuel cell typically decreases with the current drawn from the cell, as depicted in Fig. 2, due to several voltage losses.

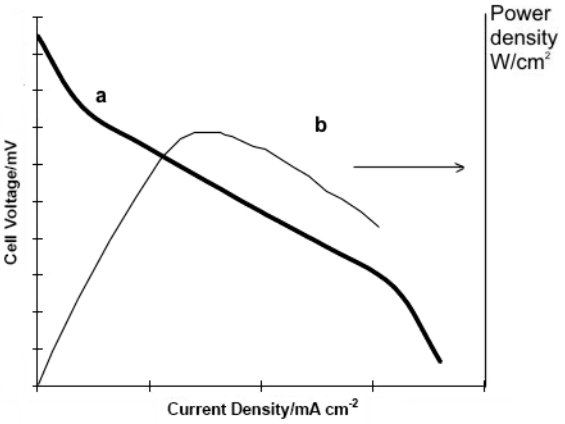

Fig. 2. Electrical caracteristics for a fuel cell; a) Voltage losses b) Power density.

These voltage losses are produced from electrode polarization, internal cell and external resistances, mass transport limitations and limitations in cell materials:

1. Electrode polarization arises when current flows and the electrode potential deviates from the standard potential. This deviation in potential corresponds to the electrical work performed by the cell. The deviation in potential is referred to as the overpotential, η, and its typical variation with current or current density (the current per unit cross section area of the electrode) is shown in Fig. 2, as the initial rapid change in potential of the electrode reactions. In the case of the hydrogen fuel cell, the largest voltage loss is produced by the reduction of oxygen (reaction 2 in eq 1) which is kinetically much slower than the oxidation of hydrogen.

2. Internal resistances in the cell produce Ohmic voltage losses. These resistances are due to the electrolyte used to ionically connect the two electrode reaction and the electronic resistance associated with the connection of electrode material in the cell.

3. At high currents there may be a rapid fall in potential which is due to a number of mass transport limitations. These limitations are due to the inability of reactants to diffuse to the electrocatalysts in the electrodes at a rate sufficient to meet the requirements of the electrochemical reaction rate. Typically this is due to low partial pressures of oxygen, in the presence of nitrogen (in air) and water vapour (formed by the cathode reaction) and to the formation of liquid water which covers the electrocatalysts and floods the porous structure of the electrode.

Overall in a fuel cell, the power (or power density) produced by the fuel cell exhibits a maximum with an increase in current density (Fig. 2b). The peak power produced by the fuel cell is often used to characterise and compare performances.

3. PEMFC membranes

Perfluorinated membranes

The PEMFC, shown in its constructive components, Fig 3, uses a solid proton conducting polymer membrane as the electrolyte.

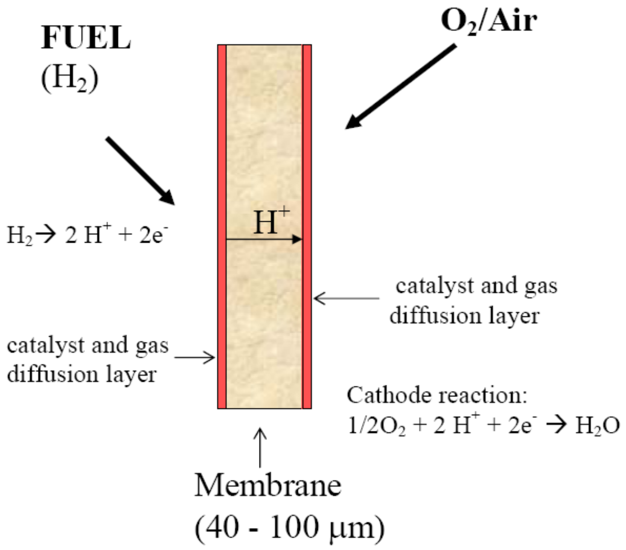

Fig 3. PEMFC, components and their functions.

A critical component of the PEMFC is the polymer membrane itself, which must exhibit good stability in the relatively harsh operating environment of a fuel cell. The first PEMFC used a polystyrene sulphonate polymer which through its lack of long term stability led to the downfall of the PEMFC. However following the invention of the Nafion® series of membrane by DuPont, a major breakthrough in PEMFC development occurred. The Nafion membranes consist of a polytetrafluoroethylene (PTFE) based structure which are, not electronically conducting, stable and chemically inert in the oxidising and reducing environment of the fuel cell. The structure of the Nafion ionomer material [3] is shown in Fig. 4a.

The material consists of a PTFE backbone with vinyl ether side chains which terminate with sulphonic acid groups. The PTFE results in hydrophobic regions, which may be envisaged as surrounding a hydrophilic zones formed by the clustering of the sulphonic acid groups which attract water, under normal fuel cell operating conditions. These clusters of acid regions are responsible for the high ionic (proton) conductivity of the membrane and thus its use in the PEMFC. The membrane has a relatively small temperature range of stability although in operation the upper limit is dictated by the requirement for humidification.

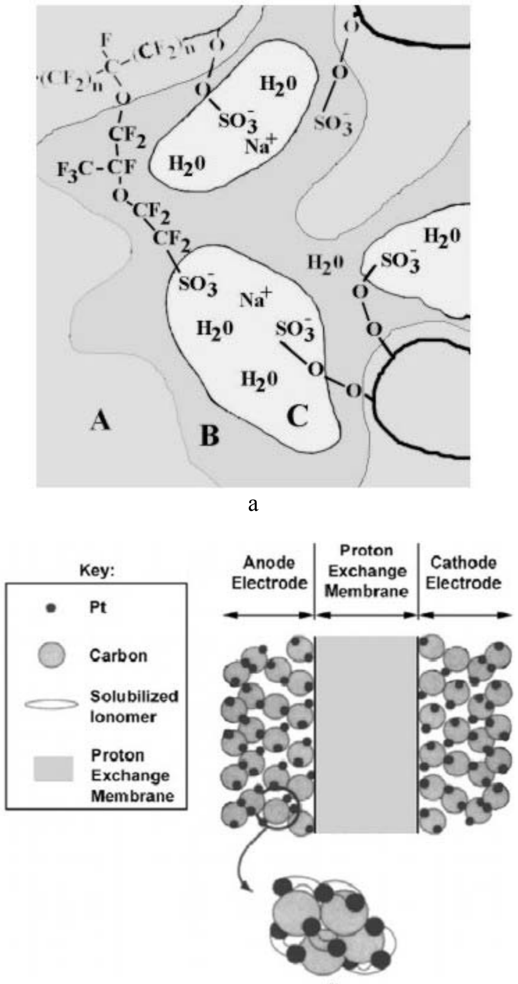

Fig 4. a) Structure of Nafion polymer. The Yeager Three Phase Model is based on a three-phase clustered system with interconnecting channels within the polymer. The three regions consist of (A) a fluorocarbon backbone, (B) an interfacial region of relatively large fractional void volume containing some pendant side chains, some water, and those sulfate groups and (C) the clustered regions. b) Supported catalyst electrode and the three phase boundary of active catalyst.

Since the application of Nafion in fuel cells several other variants, from companies such as Dow, Asahi Chemicals and Gore of the material have been used. An approach used by Gore and Asahi is to fabricate composite structures in which PTFE is used to reinforce and support the Nafion ionomer and results in a much thinner membrane with reduced ionic resistance [4]. The presence of water is a prerequisite for ionic conduction through the membrane. The limitations of Nafion related to the need to maintain a well humidified membrane has promoted significant research into alternative materials which are discussed later. Once with Nafion a new field in chemical physics came up, protonic conductors and superprotonic conduction.

The operation of PEMFC will be enhanced by elevated temperatures above 100 °C by improved kinetics of the cathode and anode reactions and the reduction of the adsorption of poisoning species such as CO. However, the ionic conductivity of Nafion falls considerably above 80 ^{o}C due to evaporation loss of water, which is necessary for its conductivity. Composite membranes that exhibit fast proton transport at elevated temperatures are needed for PEMFC operating in the 100 to 200°C temperature range. Several approaches have been pursued to resolve this issue, such as utilising different proton-conducting ionomer polymers, including polyphenylene sulphide sulphonic acid, sulfonated polyimides the perfluorosulfonyl imide form of the Nafion membrane, sulphonated polyether ether ketones and other novel sulfonated polymeric membranes [5]. The influence of temperature and humidity on the proton conductivity of these systems was frequently similar to that for Nafion membranes, but they often exhibited inferior performance.

Another approach is the use of proton-conducting membranes based on acid-impregnated ionomer polymers such as polystyrene sulphonic acid membranes imbibed with sulphuric acid, Nafion membranes impregnated with 85% phosphoric acid [6], or non-volatile heteropolyacid-impregnated Nafion membranes [7]. A related strategy is to utilise acid-doped non-ionomeric polymers such as phosphoric acid-doped polybenzimidazol (PBI) [8] or trifluoromethane sulfonic acid-doped polyvinylidene fluoride-hexafluoropropylene P(VdF-HFP) copolymers [9]. With the acid doped, or impregnated, membranes there are potential problems with acid migration, corrosion of cell components, adsorption of anions on the catalyst and acid volatility.

Ionomer polymer membranes, which derive proton conductivity from fixed acid sites, solvated by water, are unlikely to achieve conductivities greater than 0.1 S cm^{-1}, at temperatures far higher than the boiling point of water. However, because the Nafion membrane requires only a dipolar solvent medium for conduction, high ionic conductivity has been achieved in other solvents (not purely aqueous) including water-organic solvent mixtures, alcoholic solvents and some aprotic dipolar solvents

Consequently, a new group of polymer membranes, based on impregnation with ionic liquids, with high ionic conductivity over a wide temperature range and with low solvent volatility, have been investigated. Recently, proton conducting sulfonated polyether ketone membranes, imbibed with pyrazole or imidazole liquids under anhydrous conditions, have been produced with conductivities close to 0.01 S cm^{-1} at 200 ^{o}C [10] and a high temperature proton conducting membrane based on a Nafion-Ionic liquid composite [11]. Ionic conductivities in excess of 0.1S cm^{-1} have been demonstrated using the ionic liquid 1-butyl, 3-methyl imidazolium trifluoromethane sulphonate at temperatures of 180 ^{o}C. The membranes used in this study were the Nafion (117 and NE105) membrane (1000 equivalent weight (EW)), an 890 EW and also the 805 EW Dow (XUS) membrane. Comparisons between the ionic-liquid-swollen membrane and the neat liquid itself indicate substantial proton mobility in these composites. The demonstration of a perfluorinated ionomer membrane, such as the Nafion membrane, swollen with ionic liquids to give composite free-standing membranes with excellent stability and proton conductivity in fuel cell applications while retaining the low volatility of the ionic liquid has yet to be seen.

PBI Membranes.

PBI (polybenzimidazole) is a relatively low cost commercially available polymer (150-220 euro/kg) which has excellent stability in reducing and oxidising environments. PBI is a basic polymer (pKa ≈ 6.0) which readily sorbs acid and helps to further stabilise the polymer. The PBI membranes are conductive above 100 ^{o}C even when dry. Acid doping of 50% by weight can be achieved without adverse effects to its mechanical properties. One of the main attractions of PBI is that the solution form of the polymer can potentially be used to cast membranes and be used as an ionomer ink in the preparation of bonded catalytic electrodes for fuel cells. For example, the work [8] prepared PBI membranes containing 15 w/o Pt by casting from a mixture of PBI and fuel cell grade platinum black.

Two procedures for preparation of acid (phosphoric) doped PBI membranes have been researched. First referred to as type I, membranes were cast from a solution of the polymer and doped by immersion in a solution of phosphoric acid, typically 11.0 M in concentration. The membrane films typically contained 5.0 H_3PO_4 molecules per repeat unit in the polymer. The second method casts the membrane films from a solution of polymer in phosphoric acid in a suitable solvent. The membranes, type II, contained 6.0 H_3PO_4 molecules per repeat unit. In general compared to a Nafion membrane, acid doped PBI membranes have several advantages. They have good proton conductivity and mechanical flexibility at elevated temperature, and exhibit excellent oxidative and thermal stability.

The actual status in the membranes development

Ballard developed a range of membranes for PEM fuel cells which have delivered excellent long term performance and in particular polymers based on sulphonated trifluorostyrene (BAM3G) [12]. High performance PEM fuel cell operation has been achieved with a cell based on phosphotungstic acid (PWA) as proton conducting electrolyte immobilised in a glass fibre matrix [13]. Excellent power densities for PEM cells of up to 700 mW cm^{-2} have been achieved at 25 ^{o}C. This was partly attributed to the promotion of the oxygen reduction reaction by the PWA electrolyte. An adaptation of the use of this heteropolyacid was its immobilization into a Nafion membrane [7]. Preliminary fuel cell data indicated an improved performance with this membrane in comparison with Nafion alone when operating at temperatures of 110 to 120 ^{o}C. Nafion membranes immobilized with silicotungstic acid and thiophene were used in PEM cells to improve the performance. The conductivity of the new membranes was approximately 8 times that of equivalent Nafion 117 membranes [14]. Ionomeric membranes made from sulphonated polysulphone filled with 8% phosphatoantimonic acid, which have conductivities of 0.06 S cm^{-1} at 80 ^{o}C have been proposed for high temperature PEM cells [15].

Interest in the immobilization of a range of ionic conductors in porous supports for PEM cells continues with recent reports of immobilization of sulphuric acid inside glass fibre matrices and polysulphone membranes [16]. Micro-fibre glass fleece with immobilized 5.0 M H_2SO_4 or Nafion 117 exhibited conductivity comparable to Nafion, i.e. 0.53 S cm^{-1}. Polysulphone containing immobilised sulphuric acid gave conductivity superior to Nafion. PEM fuel cell performance, using electrodes produced by a "cold-pressing", was as good as that achieved with Nafion membranes. Kerres et al. [17] prepared acid-base ionomer blends of sulphonated polyetherketone and sulphonated poly-sulphone (PSU) with PBI, $PSU(NH_2)_2$ and poly(4-vinylpyridine). Polymer membranes were produced, 30 and 60 μm thick, from blends of PEEK and $PSU(NH_2)_2$ which had ion exchange capacities of 1.34 and 1.58 with ionic resistances of 0.1 Ω cm2. Hasiotis et al. [18] have tested membranes from blends of PBI and sulphonated polysulphone (SPSU). Membranes cast from the latter polymer are known to have good mechanical strength and flexibility. On doping with phosphoric acid, the effect of an increase of SPSU was to decrease the doping acid content. The ionic conductivity of the blend membranes increased with temperature. For blends with 44% SPSU and low acid doping of 30 mol% H_3PO_4, conductivity increased from 0.002 to 0.01 S cm^{-1} with an increase in temperature from 30 to 180 ^{o}C. Conductivity of the blend membranes also increased with relative humidity and acid doping level. The blend membranes exhibited superior conductivity to PBI alone under similar test conditions. Typical conductivities of highly doped blend membranes were in the range of 0.01 to 0.07 S cm^{-1}, at temperatures from 20 to 180 ^{o}C and were comparable to those achieved with the Type II PBI membranes discussed above. The blend membranes have been fabricated into viable MEAs for PEM cells and exhibited good power densities at temperatures as high as 190 ^{o}C [19,20].

A list of alternative membrane materials that have been used in the PEMFC is presented in Table 1.

Table 1. Membranes for the PEMFC, general features.

Membrane	Characteristic Type	Features
Perfluorinated ionomer	Homogeneous, e.g. Nafion®	High conductivity and chemical and mechanical stability. High methanol crossover
	Micro-reinforced, e.g. PTFE filled, GoreSelect Composites with heteropolyacids, e.g. Nafion® containing phosphotungstic acid.	Thin, very high conductivity but high crossover of methanol High conductivity
Partially Fluorinated ionomer	Grafted membranes, e.g. PVDF-Styrene co-polymer	High conductivity, reduced methanol diffusion. Stability unknown
	Based on poly(α,β,β, trifluorostyrene) and co-polymers), e.g. Ballard BAM® membranes	Lower cost replacement to Nafion for PEM. Excellent PEM performance, good lifetime
Non-fluorinated ionomer	Sulphonated divynyl benzene-cross linked polystyrene	Poor stability
	Sulphonated styrene/ethylene-butylene/styrene tri-block polymer, DAIS Corp	Good proton conductivity. Low cost. Sulphonated hydrocarbon polymer ink available for electrode bonding
	Polyphosphazene	High conductivity
	Homogeneous partially sulphonated (het)arylene main chain polymers, e.g. polyetherketone	Low methanol diffusion coefficient Good chemical and mechanical stability especially when cross-linked
	Covalently cross-linked arylene main-chain ionomers and ionomer blends, e.g. Victrex^{R} poly(ethersulphone) with sulphonamide cross-linking	High temperature operation. Questions over chemical and material stability
	Ionically cross-linked ionomer networks, e.g. PBI with sulphonated poly(ethersulphone).	High thermal stability and reduced methanol crossover with good conductivity
High-molecular/flow molecular composites	Polymer/inorganic mineral acid composite, e.g. phosphoric acid doped PBI	Water free proton conductivity, suitable for high temperature DMFC
	Acidic polymer/flow-molecular amphoter composites, e.g. sulphonated PEEK with imidazole	Good proton conductivity at temperatures $>100^{o}$C. Good DMFC performance
Inorganic	Organic/inorganic hybrid polymers, e.g.(organically modified silane electrolyte (ormolytes)	Good conductivity
	Nano-porous membrane with immobilised acid, e.g, SiO_2/PVDF binder/ sulphuric acid	Cheap, high conductivity, low methanol crossover

4. Fuel cell electrodes

The structure of the PEMFC requires the electrodes to be porous so that there is adequate space for the diffusion of gas to the active zones of the electocatalyts. The typical catalyst used in the PEMFC is based on platinum. The electrode itself must provide a high surface area of catalyst to maximise the reaction rate (current density) and minimise the electrode polarisation. Thus, there is a need for small particles which provide high surface area per unit volume, whilst also keeping the mass of catalyst used and thus the cost low. It is typical for the electrocatalyst to be deposited onto a carbon support, as shown in Figure 4b, which enables the porous gas diffusion electrode (GDE) structure to be produced, whilst achieving electronic communication within the electrode as a whole. However, it is also important, particularly for the cathode (where water is formed), that the GDE is hydrophobic so that gas "channels" are formed and so that the electrode does not become flooded with water resulting in mass transport limitations. In the early GDEs, the hydrophobicity was introduced by binding the carbon supported catalyst with PTFE. However, this meant that only the catalyst next to the membrane were in ionic contact, and the majority of the electocatalyst was not actually used electrochemically and consequently power densities of the PEMFC were relatively low. In fact what is required is a "three phase boundary", in which electrocatalyst are in ionic contact with the membrane and in electronic contact whilst access to reactant gas is provided.

The solution to the problem was achieved by the introduction of ionomer into the electrode structure as a binder. The method of production is to form an ink of carbon supported catalyst in water and isopropyl alcohol and solubilised ionomer (with possibly PTFE). The ink can then be spread onto the membrane and then be covered with a carbon backing (diffusion) layer. After applying an ink to both sides of the membrane the overall structure is pressed under pressure and elevated temperature to form a membrane electrode assembly (MEA). The carbon backing layer acts as a gas distributor and the means of current collection for the electrode. An alternative to casting the ink onto the membrane is to cast the inks onto the gas diffusion layers, which are subsequently hot-pressed onto the membrane. The end result of this process is nanometre sized catalyst particles which are in electronic contact through the carbon support and which are in ionic contact through a thin coating of ionomer. A thin coating is essential so that the amount of water absorbed into the ionomer, or present on the surface, is small and does not present a large barrier for gas diffusion to the electrocatalyst. This is particularly important in the case of oxygen at the cathode.

5. Catalysts for the PEMFC

Platinum is acknowledged as the best catalyst for the oxidation of hydrogen. Carbon supported Pt catalysts feature widely as catalyst for oxygen reduction in PEMFC and in direct methanol fuel cells (DMFC). Although much research has been directed to finding alternative non-precious metal based catalysts, the performance of Pt has not been matched. Because of the sluggish kinetics of the oxygen reduction reaction, the loading of Pt in the cathode catalyst is significantly greater than in the anode; of the order of 0.4 -0.5 mg cm^{-2}. Pt supported catalysts do, however, show a loss of activity with time due to catalyst sintering. To reduce the impact of cathode de-activation alloys of Pt have been researched for the PEMFC largely as a result of the earlier equivalent work on Pt alloys for phosphoric acid fuel cells. Pt alloys using Cr and Fe have been shown to exhibit higher activity than Pt alone and exhibit improved stability [21]. In practical applications the hydrogen is generally not pure and can contain traces of CO, NH_3 and sulphur species. Additionally, the hydrogen is typically formed by a reformation process and has a typical "reformate" composition of, ca. 70% H_2, 30% CO_2 with at least 0.5%CO. CO is one of the major poisons for low temperature fuel cells and poisoning occurs by adsorption of the species onto the active catalyst sites. On Pt, CO adsorbs readily and leads to a surface covered with CO which blocks the sites for oxidation of hydrogen. With Pt catalysts, there is a severe detrimental effect to hydrogen oxidation at levels of CO as low as 5-10 ppm. Avoiding CO contamination in the PEMFC is thus a major issue and can be achieved by a number of methods:

i. Gas clean-up in which CO is physically removed from the gas stream to a level which does not affect cell performance

ii. Addition of oxygen or peroxide to the fuel stream to chemically oxidise the CO. However, peroxide brings with it the risk of membrane degradation [21]

iii.Improved catalysts. CO tolerant catalysts based on Pt alloys, e.g. Pt-Ru, have been shown to exhibit good performance in the presence of relatively large amounts of CO up to 100 ppm [22]

iv.Bilayer anode. In a bilayer anode, a CO oxidation catalyst is placed next to the Pt based electrocatalyst (near the feed side) and serves to reduce the CO content with a reduced input of oxygen.

v. Higher temperature operation improves the CO tolerance of Pt. Operation at temperatures above 150 ^{o}C would enable CO tolerance levels to be increased to several hundred ppm.

6. Practical issues in fuel cells

In most practical systems, fuel cells are connected in series to produce useful overall voltages. In principle, this can be achieved by simply connecting the edges of the electrodes. However, because the electrode structures are thin and of relatively low electrical conductivity, they would introduce a small but significant loss of voltage, especially at high current loads. Thus, electrical connection in stacks is usually achieved using bipolar plates, which make electrical connection over the surface of the electrode. A second function of the bipolar plates is to separate the anode and cathode gases. Hence, not surprisingly, the functions of the bipolar plate and flow field are incorporated into one unit, sometimes referred to as the "flow field plate". This function is depicted in Fig. 5.

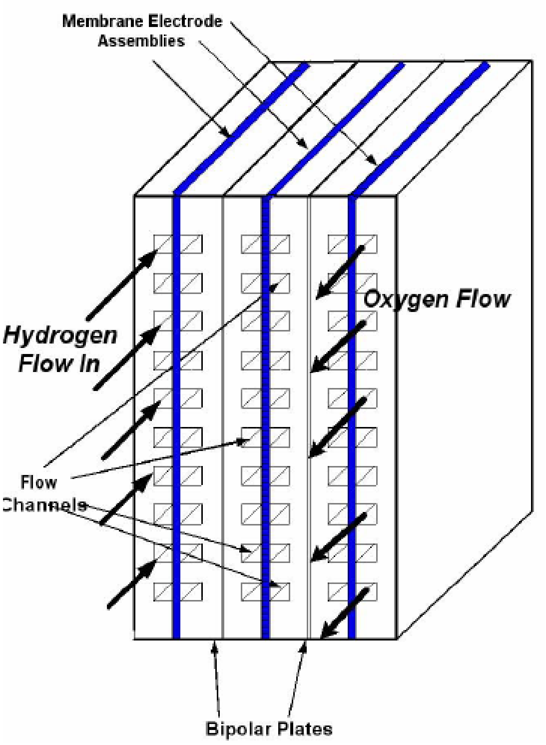

Fig. 5. Bipolar connection of MEAs in fuel cells.

Plates have to be thin, electrical conducting, non-pervious to gases, non-corrosive, low weight and low cost. These factors introduce several challenges in plate selection and design. For example, whilst the flow field enables access of gas to the electrode structure in its open spaces, it prevents electrical contact at these points. Electrical contact should be as frequent and as large as possible to mitigate against long current flow path lengths. However, large areas of electrical contact could lead to problems of access of reactant gases to regions under the electrical contact.

One of the simplest flow field designs consists of a series of narrow parallel rectangular channels (Fig. 6), where fuel or oxidant is fed at one end and exit from the opposite end. Such "ribbed" designs are commonly used in phosphoric acid cells and proton exchange membrane (PEM) cells. The plates can be machined graphite or metal, or produced by compression or injection molding of carbon polymer composites. The direction of anode and cathode gas flows can be parallel, either counter-current or co-current, or at an angle of 90 degrees.

In polymer electrolyte (PEM) cells, flow field designs are based on a number of different concepts; varying from simple parallel channels to serpentine flow to rather complex designs in which flow can be in a zig-zag manner (Fig. 7) [23]. In the serpentine design the flow snakes backwards and forwards, from one edge of the cell to the other, in a small number of channels grouped together. This creates a long flow path for reactants in the cell.

An alternative to the use of open channels is to use a thin porous structure (1-2 mm thick) made from metal foam, sintered metal, metal fibre or mat, which directly contacts the MEA. In practice, a thin conducting metal, or carbon, non-porous sheet separates two porous structures,

An alternative flow arrangement is the so-called interdigitated flow field. This design has inter-linked finger like channels with dead ends. Interdigitated flow fields with the dead end flow design have been reported to improve performance in PEM and direct methanol fuel cells (DMFC). The improvement is attributed to the dead end channels changing the transport mechanism in the porous layers to a forced convection transport rather than predominantly diffusion. In addition, the shear forces of the gas flow helps to remove a large amount of liquid water that may become trapped in the electrocatalyst layers and thus alleviate any potential problems of flooding.

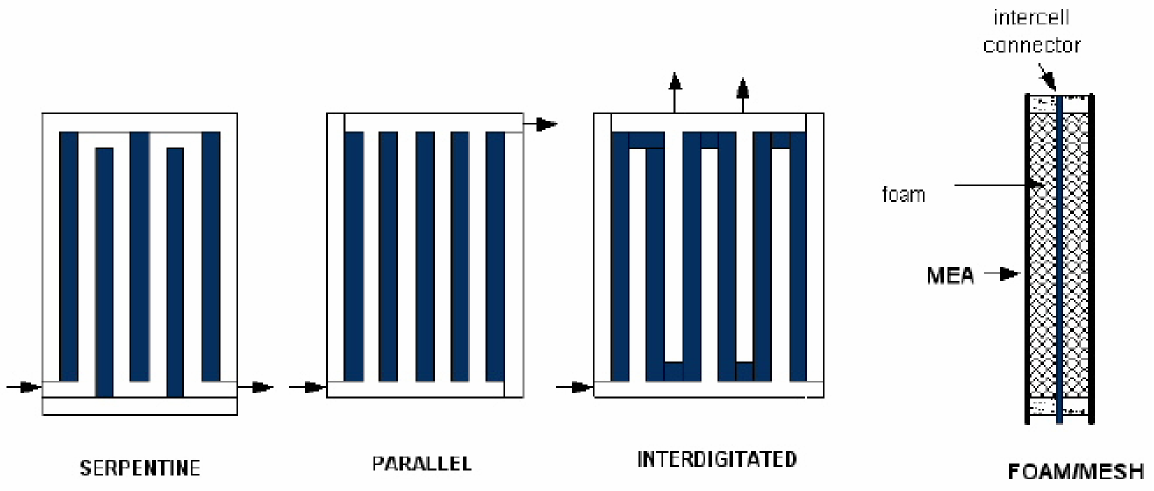

Fig. 7. Flow field designs used in fuel cells.

7. Operating problems with PEMFCs

The good performance of a PEMFC depends on maintaining stable conditions of operation. For long term operation the major problems that are encountered [24] are:

- Water loss from the electrolyte, causing loss of conductivity
- Flooding of electrodes causing loss of available catalyst surface area
- De-lamination of the electrodes
- Poor mechanical strength, especially for very thin electrolytes
- Poisoning of Pt-based anodes by adsorption of CO and other contaminants e.g. sulphur species
- Severe cell corrosion during electrolyte flooding caused by fuel-deficient conditions
- Starvation of fuel leading to carbon corrosion in the catalyst supports and carbon diffusion layers
- Ageing of the cell components from mechanical and thermal stresses due to changing temperature, current density and humidity
- Membrane degradation due to peroxide production at the cathode and regions of high stress or “hot-spots”

Contamination in PEMFCs, particularly from CO, is a major issue, as in practical applications the hydrogen is generally not pure and contains trace amounts of CO, as well as NH_3 and Sulphur species. Avoiding contamination can be achieved by a number of methods, including gas clean-up, in which CO is physically removed from the gas stream to a level which does not affect cell performance and the addition of oxygen or peroxide to the fuel stream to chemically oxidise the CO [21]. However peroxide brings with it the risk of membrane degradation. Alternatively, improved catalysts can reduce problems of contamination. CO tolerant catalysts, based on Pt alloys, e.g. Pt-Ru, have been shown [22] to exhibit good performance in the presence of relatively large amounts of CO (ca 100 ppm). The use of a bilayer anode, in which a CO oxidation catalyst is placed next to the Pt based electrocatalyst (near the feed side), serves to reduce the CO content with a reduced input of oxygen.

Another method to reduce the impact of contamination is to use higher temperatures of operation to improve the CO tolerance of Pt. Operation at temperatures above 150 ^{o}C would enable CO tolerance levels to be increased to several hundred ppm. The operation of PEMFC at elevated temperatures above 100 ^{o}C will also enhance the kinetics of the cathode and anode reactions. However the ionic conductivity of Nafion falls considerably above 80 ^{o}C due to evaporation loss of water, which is necessary for its conductivity. Alternative polymer membranes, e.g. based on PBI [25] that exhibit fast proton transport at elevated temperatures is needed for proton-exchange-membrane fuel cells operating in the 100 to 200°C temperature range. An interesting alternative has been proposed in [26] where studied a composite polypiridyne-nanometric YSZ. An alternative approach to operation of PEMFCs is to use a fuel other than hydrogen. There is a large interest in the application of PEMFC technology with liquid fuels such as methanol and ethanol. These fuel cells operate by the direct oxidation of the fuel, e.g. methanol in the direct methanol fuel cell (DMFC)[27]. These fuel cells have the advantage that they can operate on liquids which are easily stored in tanks. However the power performance does nis not as good as that achieved with hydrogen.

8. Conclusions

Polymer electrolyte membrane fuel cells are currently operated at low temperatures of less than 80 ^{o}C. They produce power at high electrical efficiency with low environmental pollution. However, because of the low temperatures of operation they have several limitations that present challenges for technology development. These challenges include high materials cost (noble metal catalysts, polymer membrane, etc), complex system construction and operation with respect to water and thermal management; appropriate fuel supply, low value of heat energy and limited co-generation of heat and power for stationary applications. The technical problems to developing improved PEMFC technology can be solved by the use of new membranes that operate at temperatures higher than 100 °C. At these higher temperatures the oxidation of fuels such also comes much more attractive. Proton exchange membrane fuel cells (PEMFC) are currently based on Nafion or similar membranes and operate at low temperatures of less than 80^{0} C. The main challenges for research and technology development are: (1) high materials cost (noble metal catalysts, polymer membrane, etc) (2) complex system construction and operation with respect to water and thermal management; (3) fuel supply, i.e. on-board storage and refueling of hydrogen or reformer-purification units for hydrocarbons/alcohols and (4) low value of heat energy, low overall efficiency (~30%) and limited co-generation of heat and power for stationary applications. The technical problems to developing improved PEMFC technology can be solved by the research of new PEMFCs for operation at temperatures significantly higher than 100°C. In terms of applications, there appear two temperature ranges for higher temperature PEMFC operation: i) 110-130^{o}C for automotive operation ii) 150-200^{o}C for stationary operation. At these higher temperatures, the oxidation of fuels comes much more attractive with extension to bio-fuels. At present pure H_2 is being considered as the fuel of choice for PEMFC.

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