

Polymer electrolyte membrane fuel cells: Principles and advances

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Abstract

Polymer electrolyte membrane fuel cells (PEMFC) are currently under intensive development for a range of power generation application in transportation, stationary and portable power. The PEMFC can produce electricity at high fuel efficiency and high energy density. The PEMFC is typically based 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 performance and considers their limitations in relation to the source and types of fuel used to generate power.

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 60–100 °C and is suitable for transport and portable applications, and for power co-generation in buildings (Larminie & Dicks 2000). 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.

The current, well-developed PEMFC technology, is based on perfluoro-sulphonic acid (PFSA) polymer membranes (e.g. Nafion[®]) as electrolyte, and 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. Introduction to fuel cells

2.1. 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 (Figure 1). 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 immobilised 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.

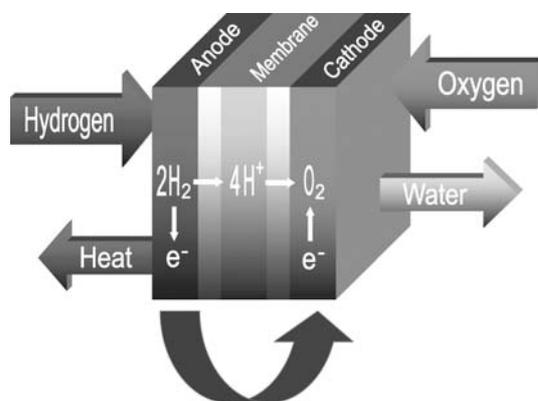


Figure 1. The principle of a fuel cell.

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:



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 fuel cell efficiency is not limited by the Carnot Cycle. 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 :

$$\varepsilon = \frac{\Delta G}{\Delta H} = \frac{-2FE^\circ}{\Delta H}, \quad (3)$$

where F is Faradays constant and E° , 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, ε_e , can be defined as the actual voltage achieved divided by the Gibbs free energy:

$$\varepsilon_e = \frac{-2FE}{\Delta G}, \quad (4)$$

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 Figure 2, due to several voltage losses. These voltage losses are produced from electrode polarisation, internal cell and external resistances, mass transport limitations and limitations in cell materials:

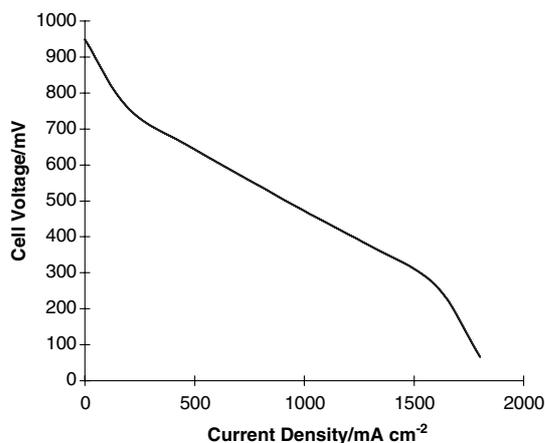


Figure 2. Variation in fuel cell potential with current load and the cause of voltage loss.

1. Electrode polarisation 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 Figure 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) 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 (Figure 2). The peak power produced by the fuel cell is often used to characterise and compare performance.

2.2. Types of fuel cells

There are several types of fuel cell which have been researched and undergone commercial development (Kordesch & Simader 1994). The fuel cells are usually classified in terms of the electrolyte used in the cell and occasionally in terms of the fuel used. The principle designs of fuel cells, which are based on the use of hydrogen, as fuel, are alkaline fuel cell (AFC), phosphoric acid fuel cells (PAFC), proton exchange or polymer electrolyte fuel cell (PEMFC), solid oxide fuel cell (SOFC) and molten carbonate fuel cells (MCFC). More recently, fuel cells based on methanol as fuel have been introduced and are rapidly approaching commercial application. The methanol fuel cell uses a polymer electrolyte membrane (proton conducting) and relies on the direct oxidation of methanol and is thus referred to as the direct methanol fuel cell (DMFC). Other types of fuel cells are based on fuels such as ethanol, propanol, formic acid, dimethylether, sodium borohydride and propane etc. and can use polymer electrolyte membranes. As we will see in the next section the polymer electrolyte membrane takes the place of an acid (proton conducting electrolyte). It should be noted that it is also possible to use a hydroxide conducting polymer electrolyte to replace the alkaline 'liquid' electrolyte (Yu 2003).

3. The polymer electrolyte membrane fuel cell

3.1. PEMFC membranes

The PEMFC, shown in Figure 3, uses a solid proton conducting polymer membrane as the electrolyte. They are designed as low temperature cells (< 100 °C) and were used in the first Gemini space missions as auxiliary power sources. 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

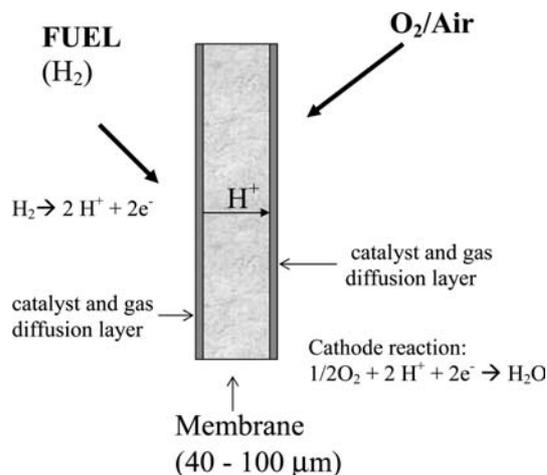


Figure 3. Schematic of the cross section of a polymer electrolyte fuel cell.

cell. The first PEMFC used a polystyrene sulphate polymer which through its lack of long term stability led to the downfall of the PEMFC in space exploration; the AFC was subsequently used. 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 (Gierke & Hsu 1982) is shown in Figure 4.

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.

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

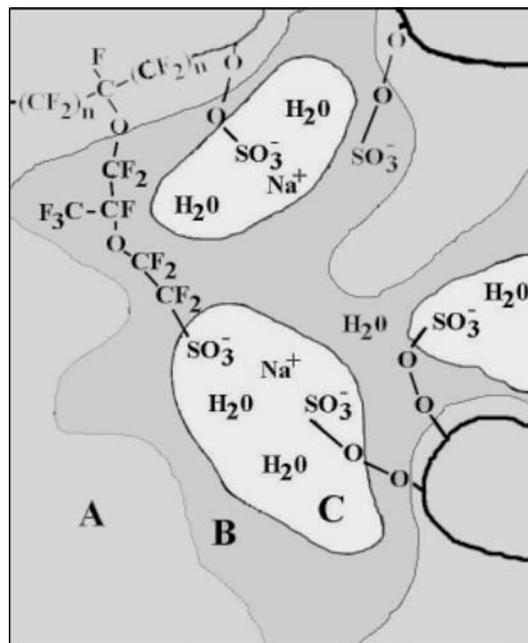


Figure 4. Structure of Nafion polymer. The Yeager Three Phase Model is based on a three-phase clustered system with interconnecting channels within the polymer. The three regions consist of (A) a fluorocarbon backbone, (B) an interfacial region of relatively large fractional void volume containing some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

PTFE is used to reinforce and support the Nafion ionomer and results in a much thinner membrane with reduced ionic resistance (Kolde et al. 1995).

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.

3.2. 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 electrocatalysts. 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

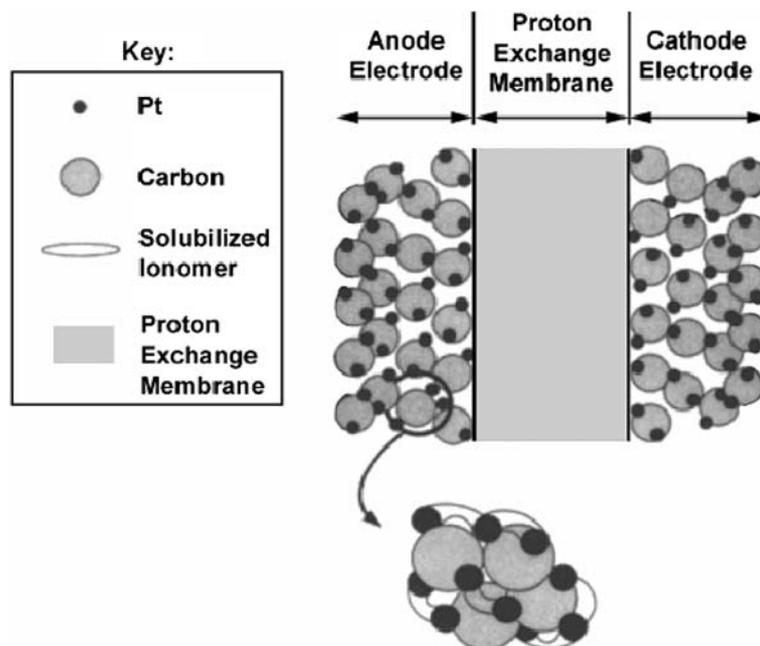


Figure 5. Supported catalyst electrode and the three phase boundary of active catalyst.

typical for the electrocatalyst to be deposited onto a carbon support, as shown in Figure 5, 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 electrocatalyst 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.

3.3. 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 connect-

ing 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 Figure 6. 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.

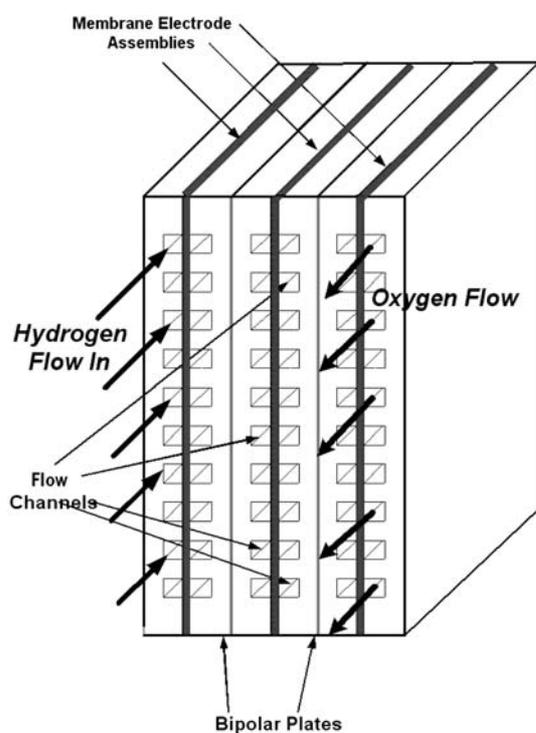


Figure 6. Bipolar connection of MEAs in fuel cells.

One of the simplest flow field designs consists of a series of narrow parallel rectangular channels (Figure 7), 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 (Figure 7) (Scott 2003). 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, two porous structures are separated by a thin conducting metal, or carbon, non-porous sheet,

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 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 force 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.

3.4. 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 (Wilkinson & St-Pierre 2003) are:

- water loss from the electrolyte, causing loss of conductivity

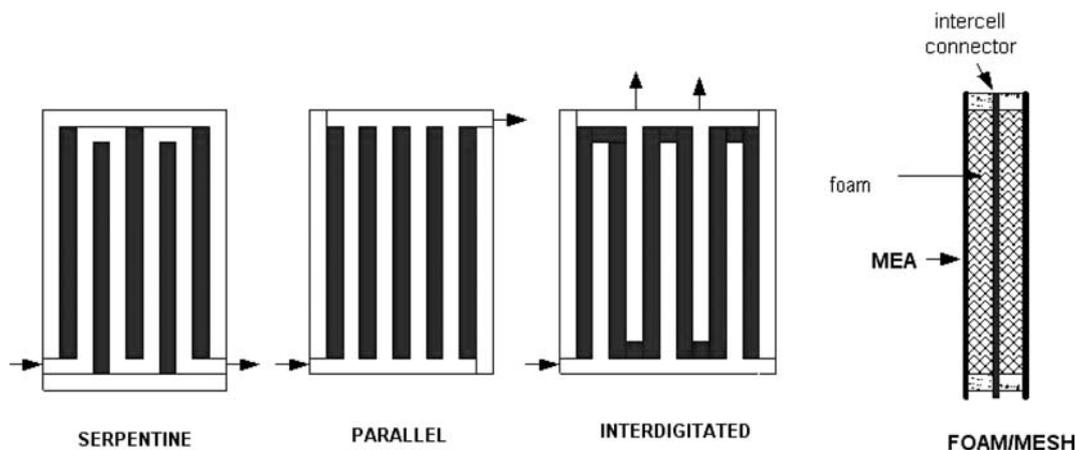


Figure 7. Flow field designs used in fuel cells.

- 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 (Gottesfeld & Pafford 1988). However peroxide brings with it the risk of membrane degradation. Alternatively, problems of contamination can be reduced by improved catalysts. CO tolerant cata-

lysts, based on Pt alloys, e.g. Pt-Ru, have been shown (Gasteiger et al. 1995) 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 $150\text{ }^\circ\text{C}$ would enable CO tolerance levels to be increased to several hundred ppm. The operation of PEMFC at elevated temperatures above $100\text{ }^\circ\text{C}$ will also enhance the kinetics of the cathode and anode reactions. However the ionic conductivity of Nafion falls considerably above $80\text{ }^\circ\text{C}$ due to evaporation loss of water, which is necessary for its conductivity. Alternative polymer membranes, e.g. based on PBI (Quinfeng et al. 2000) that exhibit fast proton transport at elevated temperatures are needed for PEM fuel cells operating in the $100\text{--}200\text{ }^\circ\text{C}$ temperature range.

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 DMFC (Scott et al. 1998). These fuel cells have the advantage that they can operate on liquids which are easily stored in tanks. However the

power performance does not as good as that achieved with hydrogen.

4. Conclusions

Polymer electrolyte membrane fuel cells are currently operated at low temperatures of less than 80 °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 as methanol also comes much more attractive and the use of bio-fuels could become an option for fuel cell derived power.

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