



A REVIEW ON THE FUEL CELLS DEVELOPMENT

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ABSTRACT

Fuel cells offer a promising alternative to conventional fossil fuel systems, due to their high efficiency, low environmental impact and flexible application. One of the suggested systems for residential, automotive and portable applications is the direct methanol fuel cell (DMFC), which has a proton conducting polymer membrane as electrolyte. While the fuel used most fuel cells is hydrogen (e.g. in the polymer electrolyte membrane fuel cell: PEMFC), the DMFC uses methanol as fuel. Fuel cells are attractive for several applications; however, there are several barriers which must be overcome before they can become an alternative to internal combustion engines.

Key words: Fuel cell, Fossil fuel, DMFC, PEMFC.

INTRODUCTION

A fuel cell is a device in which the energy of a fuel is converted directly into electricity direct current by an electrochemical reaction without resorting to a burning process, rather than to heat by a combustion reaction. The chemical energy of the fuel is released in the form of an electrical energy instead of heat when the fuel is oxidized in an ideal electrochemical cell. Energy conversion by a fuel cell depends largely upon catalytic electrodes, which accomplishes the electrochemical reaction to convert fuel into electric energy without involving the burning process. Efficiencies of fuel cells (40–85%) are considerable high compared to heat engines¹.

The first fuel cell was invented in 1839 by Sir William Robert Grove^{2,3}. He is known as father of the fuel cells. At the London Institution, where he was Professor of Physics (1840–1847), he used his platinum-zinc batteries to produce electric light for one of his lectures. A fuel cell is a device in which the energy of a fuel is converted directly into electricity direct current (DC) by an electrochemical reaction without resorting to a burning process, rather than to heat by a combustion reaction^{4,5}. The energy chemically stored in the fuels is converted into electric current by means of an electrochemical process in the fuel cell.

A fuel cell produces electricity directly from the electrochemical reaction of hydrogen, from a hydrogen-containing fuel, and oxygen from the air. H₂ is the ideal fuel for a fuel cell, the infrastructure for producing and storing. Hydrogen is industrially produced by steam reformation of naphtha oil, methane, and

methanol. High purity hydrogen has been mainly used as a fuel for low temperature fuel cells such as polymer or alkaline electrolyte fuel cells⁶.

Fuel cells offer a promising alternative to conventional fossil fuel systems, due to their high efficiency, low environmental impact and flexible application. One of the suggested systems for residential, automotive and portable applications is the direct methanol fuel cell (DMFC), which has a proton conducting polymer membrane as electrolyte. While the fuel used most fuel cells is hydrogen (e.g. in the polymer electrolyte membrane fuel cell: PEMFC), the DMFC uses methanol as fuel. The advantage of methanol is that the existing distribution infrastructure could be used for fuel supply, unlike for hydrogen⁷.

The proton conducting membrane generally used in the PEMFC and DMFC is the Nafion (Dupont) membrane, a perfluorosulfonic acid. It has excellent chemical, mechanical and thermal stability and high protonic conductivity in its hydrated state. While it has shown very good performance in the PEMFC, Nafion perfluorosulfonic acid polymers are the most commonly used fuel cell membranes. Although it would be desirable methanol could be spontaneously oxidized at the cathode, however, a methanol transport across the membrane has been observed. It causes depolarization losses at the cathode and conversion losses in terms of lost fuel. In order to improve the performance of the DMFC, it is necessary to eliminate or, at least, to reduce the loss of fuel across the cell, usually termed “methanol crossover”. In this sense, the membrane technology is one of the alternatives for trying to solve this problem⁸.

In the DMFC there exists the problem of cross-over of methanol from the anode to the cathode side, leading to secondary reactions, mixed potentials, decreasing energy and power densities and hence a reduced performance. This cross-over is caused by permeation of methanol due to a concentration gradient, indirectly dependent on the operation current and by molecular transport due to electro-osmotic drag, directly related to proton migration through the membrane which increases with increasing current density^{9,10}.

Two different pathways exist to solve this problem of methanol cross-over, the first being the development of ion-conductive membranes based on alternative polymers or polymer composites, the second being the modification of the existing Nafion membrane, in order to prevent cross-over.

Different types of fuel cells

General block diagram of fuel cell is shown in the Fig. 1

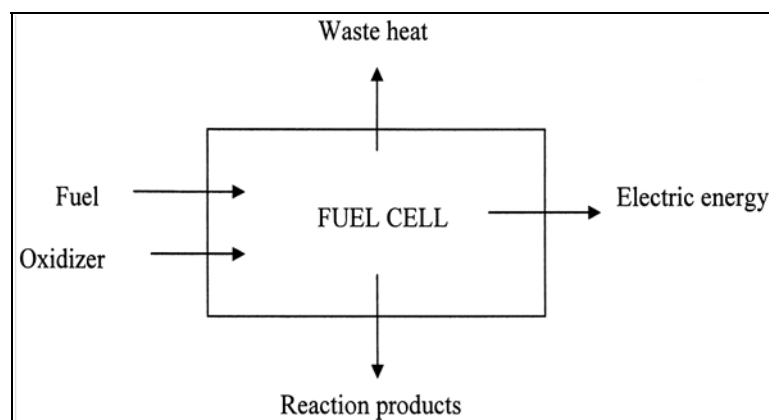


Fig. 1

Various types of the fuel cells have been developed to generate power according to the applications and load requirements (2). Several types of the electrolyte play a key role in types of fuel cells. It must permit only the appropriate ions to pass between the anode and cathode.

Fuel Cells can be classified based on their temperature of operation: high, medium and low temperature fuel cells or based on the type of electrolyte used.

Primarily, the latter method of classification is used for easier understanding and practical reasons and the six common type of fuel cells are Proton exchange membrane fuel cells, (PEMFC), Alkaline fuel cell (AFC), Phosphoric acid fuel cells (PAFC), Molten Carbonate fuel cells (MCFC) and Solid oxide fuel cells (SOFC). The classification determines the chemical reactions that take place, type of catalysts required, operating temperature and fuel used. These factors in turn determine the most suitable applications for each type of fuel cell. The essential characteristics of the major types of fuel cells and their applications¹¹ are reported.

Characteristics of the main types of fuel cells -

Table 1:

Type of fuel cell	Operating temperature, °C	Efficiency, % Cell	Output, kW	Electrolyte	Conducting ion	Fuel
Alkali (AFC)	60-120	60-70	0.3-5	35-50% KOH	OH ⁻	H ₂
Molten carbonate (MCFC)	620-660	60-80	0.10	Molten carbonate melts (Li ₂ CO ₃ /Na ₂ CO ₃)	CO ₃ ²⁻	Hydrocarbons, CO
Phosphoric acid (PAFC)	160-220	40-80	50-200	Con. H ₃ PO ₄	H ⁺	H ₂
Proton exchange membrane (PEMFC)	50-80	40-50	50-200	Polymer Membrane	H ⁺	H ₂ , CH ₃ OH
Solid oxide (SOFC)	800-1000	50-60	50-100	Yttrium-Stabilized ZrO ₂	O ²⁻	Hydrocarbons, CO

The waste heat from the fuel cell, depending on the temperature of operation can be utilized for water and space heating and owing to their cogeneration applications, the overall efficiency of the fuel cell system is increased^{12,13}.

Table 2: Thermodynamic enthalpy, free energy and efficiency of some fuel cell reactions

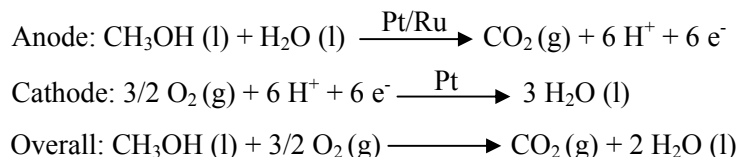
Reaction	ΔH° KJ/KMol	ΔG° KJ/KMol	$\Delta H^{\circ}/\Delta G^{\circ}$ KJ/KMol Efficiency
H ₂ + 1/2O ₂ = H ₂ O	286.0	237.3	83.0
CH ₄ + 2O ₂ = CO ₂ + H ₂ O	890.8	818.4	91.9
CH ₃ OH + 3/2O ₂ = CO ₂ + H ₂ O	726.6	702.5	96.7
CO + 1/2O ₂ = CO ₂	283.1	257.2	90.9

Proton exchange membrane fuel cells (PEMFCs) work with a polymer electrolyte in the form of a thin, permeable sheet. The PEMFCs, otherwise known as polymer electrolyte fuel cells (PEFC), are of particular importance for the use in mobile and small/medium-sized stationary applications¹⁴. The PEM type fuel cells are considered to be the most promising fuel cell for power generation¹⁵.

Efficiency of PEMFCs are about 40 to 50% and operating temperature is about 255 K. The PEMFCs and direct methanol fuel cells (DMFCs) are considered to be promising power sources, especially for transportation applications. The PEMFCs with potentially much higher efficiencies and almost zero emissions offer an attractive alternative to the internal combustion engines for automotive applications. This fuel cell has many important attributes such as high efficiency, clean, quiet, low temperature operation, capable of quick start-up, no liquid electrolyte and simple cell design¹⁶.

Recently, after many years of research and development on fuel cells, the initial euphoria has somewhat vanished, as many problems are yet unsolved. Especially for mobile applications, most material components in fuel cell systems are still too expensive, the systems are more complex than initially anticipated, sometimes difficult to control and still the discussion is far from an end which will be the best fuel for them^{17,18}. While hydrogen is the best fuel in terms of operating the fuel cell itself, its production, storage and distribution is complicated. Alternatively liquid fuels are discussed, like conventional gasoline or methanol. These are easy to store and to distribute, but their conversion in a fuel cell system is difficult. Either one produces hydrogen from them on-board the vehicle to feed a standard Polymer Electrolyte Fuel Cell (PEMFC), or one uses a fuel cell which can convert a liquid fuel directly, like the Direct methanol fuel cell (DMFC)¹⁷.

The complexity of a system combining a hydrogen production unit and a hydrogen-consuming fuel cell have led many people to the conclusion, that the DMFC is the most favorable option for certain mobile and portable applications. The basic operating principle of the DMFC is shown in -



The crossover

Direct methanol fuel cells (DMFCs) are promising candidates for applications in portable power sources, electric vehicles and transport applications because they do not require any fuel processor and can be operated at room temperature¹⁹⁻²¹. However, the DMFC is hindered by methanol crossover through the electrolyte membrane as a result of diffusion and electro-osmotic drag. This results in a mixed cathode potential, as well as a reduction in power output and fuel utilization. Therefore, the suppression of methanol crossover has been a major research focus, and various methods for reducing methanol crossover have been examined including the development of a new electrolyte²², the surface modification of a Nafion membrane²³ and the incorporation of Pt and hygroscopic oxides into the Nafion membrane²⁴.

Methanol crossover arises from electro-osmotic drag and an ion clustering with the membrane. Methanol diffusion or crossover from the anode to the cathode lowers fuel utilization, increases cathode polarization and causes excess thermal load in the cell and consequently lowers the cell performance²⁵.

At the cathode, the reduction of oxygen to water takes place on (usually supported) platinum catalysts. This reaction has been broadly examined in the last twenty years accompanying the development of hydrogen-consuming low-temperature fuel cells (PEMFC)^{26,27}. The reaction is much slower than hydrogen oxidation, therefore it plays a major role in optimizing the performance of these cells. In the DMFC, though, the anode reaction is even slower, so the cathodic oxygen reduction can not be assumed to be the rate determining step under most operating conditions. In the DMFC, a second reaction also takes place at the cathode platinum catalyst: The direct oxidation of methanol permeating through the PEM. This undesired side reaction leads to a mixed potential formation at the cathode, which results in a severely

reduced electrode potential, and therefore also a severely reduced overall cell voltage. Thorsten Schultz et al.²⁸ Compared. The open circuit cell voltage of a DMFC with standard NAFION to the thermodynamic cell voltage according to the Nernst equation. The dramatic voltage difference between thermodynamic and experimental data is to a large extent due to the oxidation of crossover-methanol. Therefore, to establish a better performance, a significant reduction in the methanol permeation through the PEM is necessary. This can either be achieved by PEM materials less permeable for methanol, by optimized (dynamic) methanol feeding strategies, by simply using low methanol feed concentrations (at the moment values around 1 mol/dm³ show best performance²⁹) or by realizing high methanol conversion at the anode (i.e. high fuel utilization). Another important aspect is a possible water flooding of the cathode pore structure due to the water transport through the membrane and the water production at the cathode. Basically, this aspect plays a similar role like for the PEMFC, and can therefore be treated likewise³⁰.

Effect of temperature

Polymer electrolyte fuel cells (PEFCs) and direct methanol fuel cells (DMFCs) using proton conductive ionomer membranes are operated at moderate temperatures (60-80°C) and the most attractive for the applications to electric vehicles, residential power sources, and portable devices. Among the many approaches, higher temperature operation (120°C) seems a preferable solution since it induces higher catalytic activity of electrodes, lowers the susceptibility of Pt catalysts to carbon monoxide contaminated in reformed hydrogen (or intermediate in methanol oxidation) and has a higher efficiency of heat recovery (31,32).

PEMFCs provide the highest power density and specific power among all the other fuel cell types and hence have use in portable devices, transportation and stationary power generation and cogeneration applications. PEM fuel cells based on perfluorinated membrane electrolytes operate in the temperature range between 60 and 80°C while elevating the operating temperature provides improved carbon monoxide tolerance, faster electrode kinetics and simpler thermal management. However, high temperature results in dehydration of the polymer electrolyte leading to increased membrane resistance and degradation of the membrane-electrode interface.

High temperature fuel cell studies were conducted at Princeton University with sol-gel membranes and successful operation has been demonstrated³³. Another approach of modified membranes include incorporation of bifunctional particles, i.e., hydrophilic and proton conducting like zirconium hydrogen phosphates, heteropolyacids and metal hydrogen sulfates. Costamagna et al.³⁴ reported that the inorganic compounds decreased the chemical potential of water in the membrane and created an additional pathway for proton conduction. H₂/O₂ tests were conducted with hybrid membranes at 1300°C and 3 atm. A current density of 1500 mA/cm² at 0.45 V was obtained for the recast composite membranes whereas the unmodified membranes delivered only 250 mA/cm². Nafion 115 composites were prepared by Yang et al.³⁵ by an exchange-precipitation method and obtained power densities of about 380 mW/cm² at 1500°C in a DMFC. While significant research efforts have been made and are in progress for identifying high temperature membranes, very few focus on high temperature and low relative humidity (RH) operation^{36,37} Weng et al.³⁸ studied the electroosmotic coefficient of water and methanol in this polymer at elevated temperatures, showing that both of them must be near zero. Savinell³⁹ et al. incorporated phosphoric acid in Nafion®, where H₃PO₄ acted as a Bronsted base and solvated the proton in the acid group similar to water. A conductivity of 0.05 S/cm⁻¹ at 1500°C was achieved. However, no successful fuel cell studies were performed with these membranes due to anion migration and consequent electrode flooding. Other solvents include heterocycles like imidazole, pyrazole or benzimidazole. Kreuer et.al reported an increase in conductivity for sulfuric acid when mixed with heterocycles⁴⁰. No fuel cell tests have been reported with these membranes in despite of the fact that the increase of the temperature increases the methanol crossover, as was previously mentioned the results found in the literature seem to indicate that the increase of the

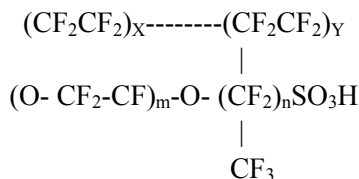
temperature improves the cell performance. For this reason, some authors have studied the possibilities of vapour-feed DMFCs⁴¹.

Jung et al.⁴² found, using Nafion 117 and 2.5 M methanol, an increase of the performance of the cell when the operating temperature increased. They attributed this higher performance to the combined effects of a reduction of ohmic resistance and polarisation. In fact, the ionic conductivity of Nafion membranes, increases with increasing temperature⁴³. This result agrees with those obtained by Surampudi et al.⁴⁴ with Nafion 117 membranes and 2 M methanol fuel cell in the range of 30-90°C, and with the results presented in⁴³⁻⁴⁶, where it is found that a difference in the operation temperature makes a significant difference in the cell performance.

Silicon oxide/Nafion composite membranes were studied by K. T. Adjemian et al.³³ for operation in hydrogen/oxygen proton-exchange membrane fuel cells ~PEMFCs from 80 to 140°C. An increase of the crossover rate with temperature was also found by Narayanan et al.⁴³ for Nafion 117 membranes. They measured the methanol crossover rates by estimating the carbon dioxide content of the cathode exit stream.

Development of membranes

The objectives of new membrane research include: lower cost, higher temperature operation, improved conductivity at lower water contents, and decreased fuel crossover (especially methanol). The heart of the DMFC is the PEM. Ideally it has to combine good proton conductivity with being an insulator for electron transport and being impermeable for all other molecules. Additionally it has to have a very high chemical and thermal stability (operation of up to 150°C). As a matter of fact, there is still only one commercially available product fulfilling at least some of these requirements: NAFION by DuPont Fig. 2.



Chemical Structure of Nafion⁴⁷

Unfortunately, NAFION is only a good proton conductor when it is soaked with water (which makes for a 10% thickness increase due to swelling). This leads to a high water transport through the micropores of the NAFION which is more or less proportional to the proton transport (solvated protons are carried with them, so-called electroosmosis). In hydrogen-fed fuel cells, this problem is not severe, as long as the feed gases are well humidified. Also, using thinner membranes (e.g. the already mentioned PRIMEA by GORE) helps to reduce the problem of water management. A new problem arises for the DMFC, as methanol is easily transported through the NAFION PEM by means of (a) active transport together with the protons and their solvate water (electro osmotic drag) as well as (b) diffusion through the water-filled pores within the NAFION-structure and (c) diffusion through the NAFION itself. This phenomenon is usually called methanol crossover. Its severe implications on cell performance will be discussed in the next section (cathode reactions). More detailed information can be found in⁴⁸⁻⁵⁰.

A further disadvantage of NAFION is its high price ($\gg 500 \pm 1000$ US \$/m²), which contributes significantly to the overall cost of PEM fuel cells. For cost reduction, membrane materials that are chemically and thermally stable even without fluor contents are under development, which are featuring a highly aromatic backbone⁵¹. Sulfonic acid groups, as in NAFION, supply the acidic function. Some of these materials showed lower methanol permeation rates than NAFION, but not sufficiently low to accept the

problems of long-term stability under working conditions. Another approach was proposed by Kreuer⁵². The intercalated water within NAFION (or other proton exchange material) should be replaced by another proton donor/acceptor like imidazole. Protons are mobile in these systems without being solvated, so no other molecules should be transported together with the protons. Also the pores in such PEM materials would be filled up with the substitute leading to an overall reduced water (and methanol) permeability. A quite similar approach was used by the group of Narayanan (California Institute of Technology and Jet Propulsion Laboratory, Pasadena, USA). They investigated composite membranes consisting of an organic supporting matrix of poly vinylidene fluoride (PVDF) which contained an inorganic phase of CsHSO₄ as proton conductor⁵³. The major problem with all the modified membranes presented is the supposedly limited long-term stability, as the proton conducting species may bleed out during the operation of the fuel cell. Presently, tests are carried out to evaluate this possible problem.

The groups of Kerres et al. and Walker et al.^{54,55} have recently combined the already described approaches by using blends of two polymers, one with an acidic function (sulfonic acid groups), one with a basic function (amine, imine or imidazole groups), both featuring an aromatic backbone. These polymer blends have only a small water uptake (swelling) combined with a proton conductivity comparable to NAFION. Also the methanol permeation is lower, for some types only a tenth of the value for NAFION. Tests on longterm stability are under way. Another option to reduce methanol permeation is to modify NAFION (or other material) by coating, i.e. producing an asymmetric composite membrane. A coating can be achieved by either applying a thin (polymer) film onto the membrane surface or by sputtering the surface e.g. with plasma or radiation to modify the NAFION structure⁵⁵. Both measures aim to close the outer water-filled pores, so that no water (and methanol) can enter or leave the membrane. Still the intercalated water (now trapped within the material) provides for the proton mobility. Kerres et al.⁵⁴ and Walker et al.⁵⁵ found significantly lower methanol permeation rates for these types of materials than for unmodified NAFION. First use of these modified membranes in the DMFC is under way, e.g. in the group of Scott with promising first results. But still these materials do not solve the problem of the high production costs as they, momentarily, still rely on NAFION.

K. T. Adjemian et al.³³ studied Silicon oxide/Nafion composite membranes. This made it possible for PEMFCs with the composite silicon oxide Nafion membranes to be operated at 130°C, exhibiting desirable current density levels. Unmodified Nafion 115 and recast Nafion membranes both provided relatively poor performance above 100°C and suffered irreversible heat damage. The advantage of operating a PEMFC at 130°C, rather than at 80°C, is that the CO ~from reformed fuels level can be increased by about a factor of 20 from 10 to 200 ppm. Additionally, elevated temperatures provide the basis for a more efficient and simpler water-management subsystem.

Lei Li et al.⁵⁶ given novel method of Pt catalyst direct deposition on polypyrrole (ppy)-modified Nafion composite membranes for direct methanol fuel cell (DMFC) Both proton conductivity and methanol permeability of the PPy-modified Nafion composite membranes decrease with increasing impregnation time of the Nafion membrane in the pyrrole monomer solution. The methanol permeability of the PPy/Nafion composite membranes was reduced more than the proton conductivity despite the swelling effect of the ionic clusters.

Dong-Hoon Son et al.⁵⁷ Pt/zeolite–Nafion (PZN) polymer electrolyte composite membrane is fabricated for self-humidifying polymer electrolyte membrane fuel cells (PEMFCs) Compared with the performance of ordinary membranes, the performance of cells with PZN membranes is improved significantly under dry conditions. With dry H₂ and O₂ at 50°C, the PZN membrane with 0.65 wt.% of Pt/zeolite (0.03 mg Pt cm⁻²) gives 75% of the performance obtained at 0.6V with the humidified reactants at 75°C.

Li-Chun Chena⁵⁸ et al., prepared Nafion/PTFE (NF) and zirconium phosphate (ZrP) hybridized Nafion/PTFE composite membranes (NF–ZrP), NF–ZrP composite membranes. The effects of introducing porous PTFE film and ZrP particles into Nafion membranes on the DMFC performance were investigated two major polyelectrolyte membranes properties controlling DMFC performance are proton resistance and methanol permeability of membranes. Inserting ZrP into NF composite membranes results in reductions of methanol crossover and proton conductivity of membranes.

Lots of researchers made efforts to reduce methanol crossover by modifying the Nafion membranes via hybridizing Nafion with inorganic nano-particles, such as silicone oxide^{59,60}, tetraethoxysilane⁶¹, diphenyl silicate⁶², zirconium phosphate (ZrP)^{63,64} and phosphotungstic acid, etc.⁶⁵ Methanol might crossover the Nafion membranes either via diffusion or via electro-osmosis through the ionic clusters of Nafion membranes. Mixing inorganic nano-particles into Nafion membranes and leading nanoinorganic particles to locate inside the ionic clusters of Nafion membranes could reduce methanol crossover the membranes⁵⁹⁻⁶⁵.

Recent research reports showed that composite membranes can be prepared by impregnation of a low cost sub- μ porous support material, such as polytetrafluoroethylene (PTFE) membranes with a Nafion solution⁶⁶. It has been reported that Nafion/PTFE (NF) composite membrane had a similar H₂/O₂ polymer electrolyte membrane fuel cell (PEMFC) performance as Du Pont Nafion-112 and a better PEMFC performance than Nafion-117 and Nafion-115 (thickness = 125 μ m)^{67,68}. Modification of pure Nafion membranes using ZrP had been reported by Grot and Rajendran⁶³, Si et al.⁶⁹, and Yang et al.⁷⁰. It had been shown that methanol crossover the Nafion membrane can be reduced by hybridizing the membranes with ZrP.

E. H. Junga et al. show the methanol permeability through the PtRu/Nafion composite membrane as a function of the PtRu loading. The methanol permeability decreased with increasing PtRu loading in the Nafion membrane. It shows the temperature dependence of the proton conductivity in the PtRu/Nafion composite membrane at various PtRu loadings under 100% relative humidity. The proton conductivity increased with increasing temperature, but decreased with increasing PtRu loading.

The concentration of PtRu particles impregnated in the pure Nafion membrane was controlled by the concentration of the impregnation solution. The proton conductivity of the composite membrane decreased with increasing number of PtRu particles embedded in the Nafion membrane, while the level of methanol crossover through the composite membrane was reduced. From the results of the single cell test, the performance of the composite membrane was approximately 28% and 31% higher at an operating temperature of 30 and 45°C than the pure Nafion membrane, respectively. The highest performance was obtained in the composite membrane of 0.05 wt% PtRu/Nafion. This suggests that the PtRu particles embedded in pure Nafion membrane act as a barrier against the methanol crossover through the chemical oxidation of methanol on the PtRu particles as well as by reducing the proton conduction path⁷².

In order to reduce methanol crossover, Uchida et al.⁷³ developed Pt-dispersed polymer electrolyte membrane (PEM) and Prabhuram et al.⁷⁴ modified the Nafion membrane by sputtering Pd and a Pd–Cu alloy. Pt, Pd and Pd alloy oxidize methanol either chemically or electrochemically and impede the migration of water and methanol through the membrane by filling the pores in the membrane. In general, PtRu is an active electrocatalyst for the DMFC anode, while Pt is not because of CO poisoning. Instead of incorporating Pt or Pd in the PEM, PtRu might be a good material for decreasing methanol crossover in the view point of the CO poisoning resistance.

Influence of the thickness of the membrane

As a consequence of its miscibility with water, methanol easily diffuses across the hydrated polymer electrolyte from the anode to the cathode (fuel cross-over) resulting in significant efficiency losses and low power densities. Indeed, to minimize cross-over, relatively thick membranes (~175 μm) and low methanol concentrations (~4% in H_2O) are used in direct methanol fuel cells⁷⁵.

It is a polymer with a fully fluorinated backbone carrying sulfonic acid groups ($-\text{SO}_3\text{H}$) for proton conductivity. Thicknesses between 100 and 200 μm are available, but there are also new developments featuring a mechanical reinforcement to allow for thicknesses down to 20 μm . The thickness might influence the cell's performance; for example, Okada et al.⁷⁶ reported that a thinner membrane is better at containing water than a thicker one because more back diffusion occurs due to a steeper water concentration gradient in a thinner membrane. They reported the effect of membrane thickness on the performance of PEMFCs by using water distribution measurement in PEMs with varying PEM thicknesses.

Studied the effect of membrane thickness on performance of PEMFC by water distribution and observed that the thinnest membrane 56 μm has the highest voltage for a given current density this is because thinner membranes have a lower resistive loss. Results show that the water content in the 56 μm thick membrane is smaller than in the 117 μm thick membrane, and the 117 μm thick membrane has smaller water content than the 340 μm thick membrane. Thus, the thinner membrane does not contain more water than a thicker membrane. However, Büchi et al.⁷⁷ also experimentally observed that a thick membrane, the thickness of which was 400 μm , showed lower resistivity than thinner ones. The resistance of all membranes increased with current density, particularly for the thickest membrane. The thickest membrane increased by about 60 mV for an increase of the current density by 0.3 A/cm^2 , whereas the thinner membranes increased by less than 10 mV over the same range of current density. These results indicate that electro-osmosis obviously plays a dominant role in the thick membrane but not in the thinner membranes.

As it was previously said, methanol crossover decreases when the thickness of the membrane increases. This fact agrees with the results found by Jung et al.⁴¹ and Narayanan et al.⁴² about the increase of the open circuit voltages with increasing membrane thickness. The electrical performance of fuel cell with membranes of various thicknesses shows that the performance trend is probably determined by the combined effects of ionic conductivity and fuel crossover. As a result at higher thicknesses, the ohmic resistance of the cell could be determining the cell voltage, although there would have been some enhancement of the cell voltage due to reduced crossover⁷⁸.

A 1200 EW Nafion membrane exhibits lower water and methanol absorption than an 1100 EW membrane. Adjusted for the thickness difference, the methanol crossover rate through a 1200 EW membrane is only half of that through an 1100 EW membrane. We verified that a DHE in an operating DMFC could provide a stable reference potential. Using the DHE, we found that, with our DMFC configuration and with 1.0 M methanol feed, there is a noticeable methanol concentration polarization in the anode due to the anode backing employed when the cell current density is $>200 \text{ mA}/\text{cm}^2$. The anode of a DMFC using a N120 membrane exhibits slightly better polarization curves than that of DMFC using a N117 membrane. An increase in the methanol crossover rate reduces the air cathode potential at open circuit. Such an increase in methanol crossover can be caused by a feed solution of higher methanol concentration, a more methanol-permeable membrane, or a higher cell temperature. Although the cathode of a H_2/air cell using a N120 membrane is considerably poorer than that of H_2/air cell using a N117 membrane (due to poorer membrane hydration), the cathode of a DMFC using a N120 membrane has much better performance than that of a DMFC using a N117 membrane. This is explained by the lower permeability of MeOH solution through the N120 membrane. The high methanol solution permeation through a N117 membrane can more easily cause cathode flooding in DMFC operation. By operating the DMFC at a temperature above 80 $^\circ\text{C}$

Hybrid membranes with different thicknesses, prepared by V.S. Silva et al.⁷⁹ with sulfonated poly(ether ether ketone) as polymeric matrix (sulfonation degree, SD = 71 and 87%) and 0, 2.5, 5.0 and 7.5 wt.% of ZrO₂ incorporation were characterized regarding proton conductivity, water uptake, methanol and water permeation fluxes and water/methanol selectivity. Nafion® 112, 1135 and 117 were used as reference materials. The results show that, for the studied membranes, increasing the membrane thickness leads to:

- A decrease of the Nafion® and sPEEK (SD = 87%) membranes proton conductivity. In contrast, the membrane thickness seems to have almost no influence in the sPEEK composite membranes proton conductivity, for SD = 71%. This last feature can be assumed as an advantage for DMFC applications.
- A slight increase in the water uptake of the sPEEK composite membranes. For Nafion® the increase in the water uptake is much more noticeable.
- A decrease in the water and methanol permeation fluxes for most of the studied membranes and a decrease of the water/methanol selectivity.

On the other hand, the results show that the zirconium oxide incorporation via the hydrolysis of the zirconium tetrapropylate enables the preparation of hybrid membranes with decreased water swelling, proton conductivity and water and methanol permeation. In contrast, the selectivity towards water/methanol increases with the inorganic content.

Influence of the concentration of methanol

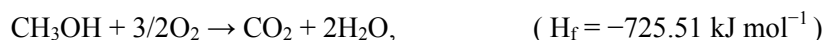
Beck Kyun Kho et al.⁸⁰ studied properties of passive DMFCs, focusing on the internal temperature and the open circuit voltage (OCV), which change as a consequence of the methanol crossover phenomenon. When the methanol was injected in to the reservoir, the OCV experienced an abrupt jump from 0 to 0.9 V and then it dropped immediately to 0.72 V after 2 min duration and it decreased steadily down to 0.57 V over the next 25 min. After passing through the lowest voltage it increased again slowly up to 0.63 V after 3 h. But, the cell temperature went through a reverse track to that of the OCV and it rapidly increased from 25 to 40°C during the first 30 min and then it decreased steadily. The changes found in OCV and temperature are directly related to the methanol crossover phenomenon from the anode to the cathode, which leads to a decrease in OCV by producing a mixed potential through an anodic oxidation of methanol at the cathode and an increase in temperature by combustion of methanol to release heat and water at the cathode compartment. The reversal of the OCV and the temperature at 30 min is estimated to be caused by reduced methanol crossover rate due to decreased methanol concentration in the anode methanol reservoir. As the methanol crossover rate decreases, the temperature declines and the OCV rise.

The change in methanol concentration in the anode compartment is a unique feature of the passive DMFC. When the methanol starts to diffuse into the cathode and is consumed there, the cathode potential decreases and the temperature increases even at open circuit state. The oxygen is supplied from the ambient air through the holes in the cathode plate. As the combustion reaction of methanol proceeds on the cathode and methanol is consumed, the methanol concentration in the reservoir decreases and a concentration gradient sets in across the membrane, reducing the methanol crossover rate. At time t_2 , a further decrease in methanol concentration at the reservoir results in a significant reduction in methanol crossover rate, consequently leading to the reversal of changes in OCV it could be confirmed that the crossed-over methanol is oxidized to produce heat and undergoes anodic oxidation to generate a mixed potential at the

cathode, consequently leading to an increase in cell temperature and a decline of cathode potential only in the presence of oxygen and platinum catalyst. Since methanol crossover rate is dependent on the methanol concentration in the reservoir, it is expected that OCV and temperature vary with methanol concentration^{81,82}. Experiments were carried out with various concentrations of methanol in the reservoir from 1.0 to 5.0 M. It was observed that the OCV has decreased and the temperature has increased with increasing methanol concentration. They all have the same shape of curves though the extent of change varies depending on methanol concentration.

The sharp decrease in temperature might be attributed to two reasons: (1) heat loss by endothermic oxidation of methanol in the anode, (2) reduction of heat production rate due to instantaneous depletion of methanol and oxygen in the cathode.

The increase in cell temperature at open circuit state is due to oxidation of methanol on the cathode as mentioned previously. At the cathode the methanol is oxidized in the presence of oxygen to produce carbon dioxide and water along with heat by a combustion reaction as described in the following equation. This reaction is not electrochemical, but purely chemical, and thus it produces only heat, not electricity:



A higher concentration of methanol in the feed to the anode would decrease the cell voltage as a result of potentially higher rates of transport through the membrane.

Narayanan et al.⁴² also studied the dependence of the crossover rate on the current density, finding it to decrease with increasing current density due to an increased utilization of methanol at high current densities.

In fact, it has been observed that the open circuit voltages decrease with increasing methanol concentration⁸³. This lower performance of the cell at higher methanol concentrations is attributed to the fuel crossover phenomenon^{42,84}. It was found that the cathode electrode performance is significantly lowered at higher methanol concentration⁸⁵. However, at high current densities, it is observed a lower performance of the cell at lower concentration of methanol. This is probably due to the concentration polarisation effects. It is necessary, thus, to find the optimal concentration under the operating conditions of the fuel cell⁸⁶.

Fuel crossover through the proton conducting membrane severely reduces the performance and fuel utilization efficiency of direct methanol fuel cells (DMFC's). The current practice for minimizing crossover is to use extremely diluted fuel solutions (on the order of 1 M or 4% methanol by volume). This work examines a novel feeding strategy that permits use of concentrated methanol solutions, thus helping preserve the high fuel energy density that is one of the more attractive features of the direct liquid-feed fuel cell technology. Methanol dilution can help reduce crossover either by using a constantly diluted feed stream, or by alternately supplying a slightly more and a slightly less diluted solution⁸⁷. However, the greatest benefit of these strategies have only been demonstrated at current densities on the order of 50 mA/cm², and either case requires the same amount of excess water to be fed through the DMFC

Influence of the pressure

The experimental works found have shown that there is a significant effect of increasing the O₂/air pressure on cell performance which cannot be predicted from thermodynamic or kinetic behaviour. Scott and Taama⁸⁵ and Scott et al.⁸⁸ developed a model of a DMFC based on a solid polymer electrolyte membrane which took into account the methanol crossover. This model could explain the cell voltages were

significantly lower and decreased when the oxygen pressure was reduced to a range of practical operating current densities up to approximately 350–400 mA/cm². This influence was also observed by Cruickshank and Scott⁸⁴ who stated that pressurizing the oxygen reduced the crossover of methanol, leading to higher cell voltages. Narayanan et al.⁴² observed that the effect of pressure on the voltage is more significant at low rates than high flow rates. Likewise, the effect of flow rate was less significant at higher pressures. The impact of working at ambient pressure on the cell voltage was the greatest at low flow rates and low temperatures.

Catalysts Used in Fuel Cells

The fuel-cell-powered cars will operate conventional fuels. A lot of work has been reported in the literature by different workers on catalysts used in preparation of the catalytic electrodes of the fuel cells⁸⁹⁻⁹². The new catalysts will be used in the on-board fuel reformer of an automotive fuel cell system to convert gasoline, or other hydrocarbon fuels, into hydrogen-rich gas. Carbon supported platinum (Pt) and platinum–ruthenium (Pt–Ru) alloy are one of the most popular electrocatalysts in polymer electrolyte fuel cell (PEFC). Pt supported on electrically conducting carbons, preferably carbon black, is being increasingly used as an electro-catalyst in fuel cell applications⁹⁰. Carbon supported Pt could be prepared at loadings as high as 70 wt% without a noticeable increase of particle size. Unsupported and carbon supported nanoparticle Pt–Ru atom (Pt–Ru ad) catalysts prepared using the surface reductive deposition technique were evaluated as anode catalysts in liquid feed PEM–DMFCs. It was found that the surface composition of unsupported Pt–Ru ad nanoparticles has a significant influence on their activities as anode catalysts in direct methanol fuel cells (Cao and Bergens⁹¹. Carbon supported Pt–Ru ad catalysts display higher mass activities than unsupported Pt–Ru ad. The electrochemical deposition of Pt–Ru nanoparticles on carbon nanotube electrode and their electrocatalytic properties have been investigated by He et al.⁹² Preferential oxidation of CO in a simulated reformed gas to CO₂ by using selective CO oxidation catalysts was investigated. The effects of preparation method, O₂, water vapor, and CO₂ concentration in feed stream on the selective CO oxidation over Au/CeO₂ catalysts were investigated in the temperature range of 323–463 K⁹³. The activity of Au catalyst depends very strongly upon the preparation method, with co-precipitation prepared Au/CeO₂ catalyst exhibiting the highest activities. The direct methanol fuel cell (DMFC) is an extremely promising power source for portable applications due to its simple handling and processing of fuel. The performance of DMFC has improved markedly in the past 5 years⁹². Research into the electrocatalysis of methanol has been stimulated by intense interest in advancing fuel cells. Methanol oxidation reaction at Pt and Pt alloy electrodes has attracted considerable attention during the last decades

CONCLUSION

The FC is a very promising power generation system with several possible applications. The increasing research activity of the past ten years has resulted in a considerably improved cell performance. Nonetheless the most important problems (methanol crossover, anode kinetics, carbon dioxide evolution) are as yet unsolved. Possible solutions are being investigated though these are still far from final application; their stable long-term operation has yet to be proved.

Current efforts in PEMFC research are focused on (1) reducing membrane cost via the use of non-fluorinated polymer electrolytes and (2) reducing system complexity via the development of ‘water-free’ electrolytes that do not require cumbersome hydration paraphernalia. Such electrolytes would additionally enable operation under ‘warm’ conditions (i.e. above 100°C) and be impermeable to methanol. Additional PEMFC research is very much directed towards the development of high activity cathode electrocatalysts and CO tolerant anode electrocatalysts, which would furthermore be well-suited to direct methanol fuel cells. Dramatic reductions in the Pt content in PEM fuel cells have been achieved over the past 20 years, however complete elimination of Pt remains a goal.

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