TECHNOLOGY OF DIRECT METHANOL FUEL CELL PROGRESS AND FUTURE PROSPECTS

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ABSTRACT

Fuel cell represents a new energy conversion technology, which promises to provide clean source of power. Fuel cells using methanol directly on the electrode or the DMFC are the promising candidates for transportation and portable power source applications. The low operation temperature, fast start-up time and simplicity (i.e. no need for reformer) are some of the advantages of DMFC, which make it attractive for transportation applications. Moreover, liquid methanol has substantial electro-activity on catalytically active anodes of DMFC, has high efficiency, inexpensive and widely available and can be easily handled and distributed. The main poison species for platinum anode of methanol fuel cell is recognized as adsorbed CO. The dramatic improvement in DMFC performance is mainly attributed to the use of polymer electrolyte membrane, Nafion. The best single cell performance reached a power density of 300 mW/cm^2 at a cell voltage of 500 mV. The basic problems in DMFC are still linked to the poor catalytic activities of anode and the methanol crossover through Nafion membranes. In addition, the high price of Nafion membrane also acts as a barrier towards the commercialization. This paper presents the progress made in the direct methanol fuel cell (DMFC) and their future prospects. Also, some novel polymer membrane development work carried out by the author for polymer DMFC and PEM fuel cell will be highlighted.

Keywords: *Fuel cell, methanol, membranes, electrodes, power density, MEA, fuel cell stack.*

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(   )   (DMFC)

(DMFC)   .

.   (   )

(   )

.   (CO)   .

(DMFC)

/   (   )   Du Pont Co. (Nafion   )

/   (   )   .   (   )

(DMFC)   .

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                                                                    .

                                                          .   (DMFC)

                              .(PEM)   DMFC

1. INTRODUCTION

Direct methanol fuel cells using polymer electrolyte membranes are promising candidates for transportation applications and portable power sources such as replacing batteries [Gottesfeld 1999, St-Pierre and Wilkinson 2001]. By eliminating reformer, DMFC offer simple system design and potentially higher overall efficiency than the reformate-fed fuel cells. Significant advances in H_2/air polymer electrolyte fuel cells have been reported including the low electrocatalyst consumption and high power density. However, fuel processor-fuel cell stack system on board the vehicle presents problems of packaging, complexity, and an overall system efficiency significantly lower than that of the fuel cell itself. Moreover, methanol is the liquid fuel that has substantial electroactivity and can be directly oxidized to CO_2 and water on catalytically active anodes in DMFC. In addition to high efficiency and environmental compatibility, liquid methanol is inexpensive, widely available and can be handled and distributed to consumers to such an extent that the present supply networks of gasoline can be used for methanol without difficulty. DMFC systems have been studied extensively over the last 30 years. During the 60`s a 100 W fuel cell system was developed for US military equipments but its durability was limited [Cameron et al, 1988]. Shell extensively studied methanol oxidation catalysts and found platinum/ruthenium system as the most active electrocatalyst. Both Shell and Esso stopped their R&D in the late 70`s, as the catalytic activity which had been developed for methanol oxidation was insufficient for effective commercialization. Other DMFC systems have been investigated during 1965-70 by Cathro and Week, Brown and Boveri, and by the US army for military communication systems [Cameron et al, 1988]. Starting in the mid 80`s interest has again been growing in the development of this type of fuel cell due to increased awareness of energy and environmental concerns. It is estimated that during the period 1987-2001, more than 125 papers have been devoted to the methanol oxidation directed for fuel cell purposes.

There are several conditions, which fuel cells must meet in order to become a real alternative to the internal combustion engines [Appleby 1996]. One of the most important requirements is system size, because of the need to generate sufficient power within limited space on car board. This requirement is not met by liquid electrolyte fuel cells as they have considerably lower power density than solid electrolyte fuel cells. Highly efficient molten carbonate and

solid oxide electrolytes, operating at temperatures in the range 700 to 1000 ^{o}C require extended, power consuming periods to reach working temperature. Therefore, they cannot start rapidly and respond quickly to the change in power demand of the particular vehicle. Using a gaseous fuel (commonly hydrogen) is not suitable for small light duty electric cars due to difficulties with fuel distribution and safe handling, and on-vehicle space and weight constraints. Currently methanol and also other organic fuels are steam reformed to hydrogen-rich gas before entry into the anode area of a cell. This fuel feed usually contains traces of carbon monoxide, which acts as catalyst poison and needs to be purified. Purification of the fuel feed with water gas shift reaction will reduce the overall system efficiency and increase the weight, volume and start-up time of the device. From the point of view of system simplicity and convenience in operation the direct methanol fuel cell where methanol fuel is supplied directly to the anode is a most attractive technological solution for automotive application. The specific advantages in comparison to other fuel cell types such as high energy efficiency (weight and volume) stationary electrolyte, hence no corrosive liquids, self starting at ambient temperature, long-term experience, up to several 10000 h, stability, etc. make the PEM-DMFC the most promising transportation power source.

2. PRINCIPLES OF DMFC OPERATION

A schematic drawing of a fuel cell is given in Fig. 1, which demonstrates the principle of operation of a DMFC. The direct methanol fuel cell works by oxidizing the liquid methanol to CO_2 and water. This eliminates the need for an external hydrogen supply. A proton conducting solid membrane, used both as electrolyte and separator between anode and cathode, is sandwiched between porous carbon structures. The latter serve as current collectors and at the same time as a support for catalyst particles. Before catalyst deposition the carbon collectors are impregnated with polymer electrolyte to provide the intimate contact of the metal particles both with electron and proton conductors. At the anode a methanol molecule reacts with a water molecule liberating CO_2, six protons which are free to migrate through the electrolyte towards cathode, and six electrons (a very high electron yield) which can pass through the external load. The CO_2 produced in the reaction is rejected by the acid electrolyte. The protons, migrating through electrolyte and electrons, moving via external loaded circuit, have to reach a particle of catalyst on the cathode, where oxygen is electrocatalytically reduced producing water. The water produced is removed by the oxygen flowing through the cathode compartment. An electric potential appears between the electrodes because of the excess of electrons at the anode (where they are generated) compared with the cathode (where they are consumed). It is this potential difference that drives current through the external load, making fuel cell a real source of power. The maximum voltage attainable from the overall reaction in the methanol-air fuel cell in theory is 1.18 V with a theoretical efficiency of 96.5%, but in practice it is not achieved due to the poor electrode kinetics and ohmic losses the electrolyte[Lamy & Léger, 1997; Hogarth & Hards, 1996].

The relevant electrode reactions are:

Anode: $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$ $E^0 = 0.046$ V   (1)

Cathode $3/2O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$ $E^0 = 1.23$ V   (2)

Overall $CH_3OH + 3/2O_2 \rightarrow CO_2 + 2H_2O$ $E^0 = 1.18$ V   (3)
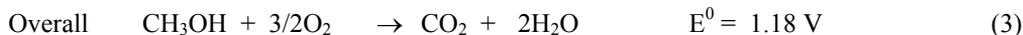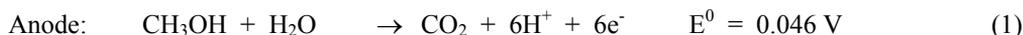
Currently there are some obstacles[Hamnett 1990, 1996] which need to be overcome before large scale commercialization of DMFC: (a) low activity and high cost of anode electrocatalyst, the anode reaction has poor electrode kinetics, particularly at lower temperatures, making it highly desirable to identify improved catalysts and to work at as high a temperature as possible; (b)the reduction of oxygen on cathode is also low though the problems are not so serious as with aqueous mineral acid electrolytes; (c) and perhaps of greatest concern at the moment is the permeability of the current perfluorosulfonic acid membranes(Nafion) to methanol, which allow considerable crossover of methanol from anode region to cathode region. This leads both to degradation of performance, since mixed potential develops at the cathode, and to deterioration of fuel utilization. Methanol vapor also appears in the cathode exhaust, from which it would have to be removed. And the last, but not less significant is the high cost of Nafion membrane in the range of US$ 800-2000/ m^2.

3. DMFC ANODE

The electro-oxidation of methanol requires the presence of Pt based catalyst Platinum is involved in two key steps occurring during oxidation route. One is the dehydrogenation step and the second is the chemisorption of CO. The methanol electro-oxidation reaction is a slow process and it involves the transfer of six electrons to the electrode for complete oxidation to carbon dioxide. Various reaction intermediates may be formed during methanol oxidation [Parson & Van der Noot 1988]. Some of these (CO-like) species are irreversibly adsorbed on the surface of the electrocatalyst and severely poison Pt for the occurance of the overall reaction, which has the effect of significantly reducing the fuel consumption efficiency and the power density of fuel cell. Thus it is very important to develop new electrocatalysts to inhibit the poisoning and significantly increase the rate of electro-oxidation by at least a factor of two to three times.Until now platinum is proved to be the only effective anode catalyst for DMFC. The research in methanol electro-oxidation using Pt anode reached important breakthroughs during the last 15 years. The most significant issue in the development of useful low-cost high efficiency methanol fuel cells for generating electric current is the poisoning of the platinum anode by carbon monoxide that is generated during the oxidation. Carbon monoxide molecules formed from the early steps of methanol oxidation adsorb on and block polycrystalline platinum electrode surfaces and are not oxidized away by the reaction with water to make carbon dioxide unless the anode potential is increased to about 0.6V(SHE). The net result of doing this is an unacceptable loss of cell voltage and efficiency.

It has been found that carbon monoxide can be oxidized at a lower potential by adding oxygen to the system, but the gain in the cell voltage is not large [Bittins et al 1993]. Furthermore, there is a loss of power because no current is generated when carbon monoxide is oxidized by oxygen on the anode surface whereas, on the other hand, oxidation of carbon monoxide by water yields two electrons and two protons and the CO_{ads} poison that forms is oxidized by water

$$CO_{ads} + H_2O \rightarrow CO_2 + 2H^+ + 2e^- \tag{4}$$
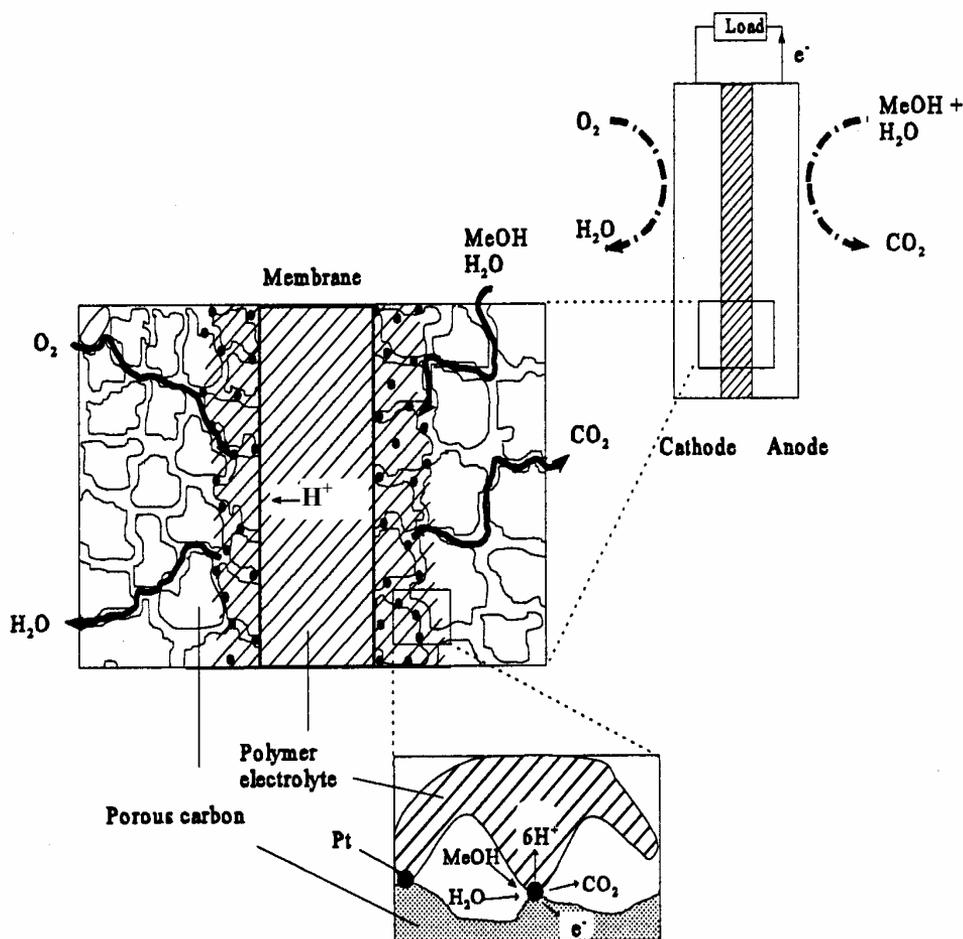
Fig.1. Schematic showing the principle of operation of a direct methanol fuel cell (DMFC) on Platinum electrodes using Nafiion membrane as solid polymer electrolyte.

It was proposed [Gillman 1964] that reaction 4 proceeds by direct attack by a H_2O molecule on the adsorbed CO. A recent molecular orbital study [Shiller & Anderson 1992] on Pt(111) suggested that for this to occur the H_2O molecule would not need to be adsorbed on the surface. Results of the kinetic isotope study were consistent with the formation of an activated complex of H_2O and CO_{ads} for which deprotonation was not rate limiting [Wieckowski 1977]. The involvement of OH_{ads}, formed from H_2O decomposition on electrode surfaces in oxidising organic fuels was proposed three decades ago[Bockris & Wroblowa 1964]. Its formation was advanced as the rate-determining step for the electro-oxidation process.

It is agreed that the coverage of carbonyl decreases as the methanol concentration falls, and at low methanol concentration three electron intermediates such as Pt_3COH, Pt-CHO become more important. The uncertainty about the surface intermediates results in the uncertainty on the reaction mechanism. However, the reaction products are generally fixed. The main reaction product of methanol electroxidation is carbon dioxide, but formaldehyde and formic acid were also detected in small amounts. Methyl formate was also mentioned in one study. Even though the mechanism is not certain, as an example, a mechanism suggested in [Christensen et al 1988] is shown below. The first three steps were initially proposed by [Bagotzky et al 1977].

$$CH_3OH \quad + \quad 2Pt \quad \rightarrow \quad PtCH_2OH \ + \ Pt\text{-}H \tag{5}$$

$$PtCH_2OH \ + \ 2Pt \quad \rightarrow \quad Pt_2CHOH \ + \ Pt\text{-}H \tag{6}$$

$$Pt_2CHOH \ + \ 2Pt \quad \rightarrow \quad Pt_3COH \quad + \ Pt\text{-}H \tag{7}$$
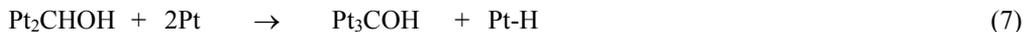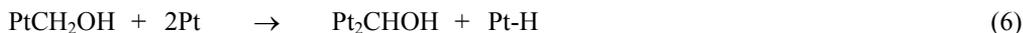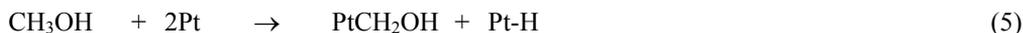
The rate of reaction 9 < reaction 8 < reaction 7 such that Pt_3COH is the major adsorbed species. The Pt-H species are lost to the solution as H^+

$$Pt\text{-}H \quad \rightarrow \quad Pt \ + H^+ \ + \ e^-. \tag{8}$$

In [Gasteiger et al 1993] it is taken for granted that the poison is CO_{ads}. The oxidation of CO_{ads} by OH_{ads} proceeds as follows:

$$CO_{ads} \ + \ OH_{ads} \quad \rightarrow \quad CO_2 \ + \ H^+ \ + \ e^-. \tag{9}$$

The hydroxyl group is formed by oxidation of H_2O on the anode

$$H_2O \quad \rightarrow \quad H_2O_{ads} \tag{10}$$

$$H_2O_{ads} \ \rightarrow \quad OH_{ads} \ + \ H^+ \ + \ e^- \tag{11}$$

The OH_{ads} oxidant has not yet been directly observed on Pt anodes. The possibility of its formation comes from the coincidence of the potential for the onset of H_2O oxidation with the peak for CO oxidation [Gasteiger et al 1994]. A molecular orbital study of the potential dependence of water decomposition on a Pt(111) anode by the reaction below showed proper potential dependence

$$H_2O_{ads} \quad \rightarrow \quad OH_{ads} + H_{ads} \tag{12}$$

The adsorbed H atoms are assumed to discharge spontaneously into solution

$$H_{ads} \quad \rightarrow \quad H^+ + e^-. \tag{13}$$

Studies involving partial substitution of Pt with other transition metals like W, Pd, Ni, Ti, Rh, Mo have not yielded fruitful results[Arico et al 2001]. Accordingly, most work has addressed to the modification of the Pt environment by alloying it with other elements or through the synthesis of multifunctional electrocatalyst. Until now the most successful results have been obtained through the alloying route.

Many attempts have been made in order to increase the catalytic activity and to decrease the poisoning of the electrode by preparation of multiple metal anodes. Platinum containing bimetallic alloy anodes was investigated for Pt-Ru, Pt-Sn, Pt-Pd, Pt-Rd, Pt-Pb, Pt-Ti, Pt-Re [Anderson et al 1996]. It was reported that the addition of Ru, Sn, Ti, and Pb yields a positive effect for the methanol electroxidation. The function of Sn and Ti appears to promote the formation of active Pt-O groups capable of completing the oxidation reaction. It has been shown that alloying of Sn and Ru with Pt gives rise to electrocatalysts, which strongly promote the oxidation of methanol and CO. To date a Pt-Ru electrocatalyst (1:1) wt.% has shown the best results (Gottesfeld, 1999)

Numerous studies have indicated that as the Pt crystallite size increased, the specific activity for oxygen reduction decreased. Hamnett et al (1990) and Watanabe et al (1992) observed the increase in activity with the platinum dispersion, however, their explanation are different.

As mentioned earlier Pt-Ru alloys are the best electrocatalysts for methanol oxidation for DMFC. These catalysts are generally dispersed as small particles on conductive supports such as high surface area carbon black to obtain the optimum catalyst utilization for methanol oxidation in acidic electrolytes. Recently, [Uchida et al 1995] showed that the types of carbon play an important role in the performance of anode for methanol oxidation. Among the carbon blacks tested, the electrode with carbon AB2: acetylene black, which is characterized by a large volume of pores in the 3 to 8 nm size and a rough surface of the primary particles, showed the best performance of 355mV at 60mA/cm^2.

In a study Anderson et al (1996) examined the effects of 42 different alloying atoms, Sc through Se from period 4, Y through Te from period 5, and La through Po from period 6 for a Pt anodes by the presence of substitutional foreign atoms using ASED-MO theory. They have found that substitutional atoms from periods 4,5, and 6 of the periodic table when present in the Pt(111) surface seem to form two groups with respect to their activity for forming OH bonded to them from H_2O molecules. As surface substitutional atoms, no elements to the right of the Pt group are found to attract H_2O strongly enough to activate OH dissociation. The transition metals to the left of Pt group, with the possible exception of Ni, Rh, and Ir, show activity for generating OH_{ads}. Of these, the early first transition series metal appears especially promising and the early second transition series metals are also potentially active in attracting and dissociating H_2O. These are theoretical results and predictions from the model, whether these can be made stable alloy surfaces for DMFC operation is not known, and further experimental investigations are needed to reveal the fact. Past experimental work in the literature suggests promise for some of them.

Also a very recent development is reported by a research group in UK led by Burstein et al 1996 for the new anode material without containing noble metal for electro-oxidation of methanol. They prepared anode catalyst from nickel nitrate and sodium tungstate, and tested it in a electrochemical cell with sulfuric acid as electrolyte. Their results of anode polarization showed the anode oxidation rate is low over the entire potential range covered in the absence of methanol, the maximum observed rate of oxidation of the catalyst was $< 6A/cm^2$ and after 250s was still declining. This corrosion rate is much lower than that found in previous experiment using base catalyst. Thus the electrocatalyst activity of the new material for anodic oxidation of methanol is ambiguous.

4. DMFC CATHODES

In direct methanol fuel cell the oxygen is reduced at the cathode, and so the electrode configuration is the same as that of H_2/O_2 fuel cell because of the same cathodic reaction. So, most of the cathodes developed originally for H_2/O_2 fuel cells are used in DMFC, which is platinum supported on carbon. In direct methanol fuel cell using polymer electrolyte membrane, there is a serious problem of methanol crossover from the anode region to cathode region, which causes a decrease in cathode performance leading to a loss in overall fuel cell efficiency. Not much is known about the chemical and electrochemical processes which methanol is undergoing at the cathode of an operating DMFC. Wang et al (1996) found that methanol is oxidized to carbon dioxide by oxygen in the presence of platinum, which inhibits the oxygen reduction reaction and results in lower cathode potential (depolarization). A loss of 100mV due to the methanol crossover on Pt/C cathode for a DMFC using solid polymer membrane has been reported by several investigators [Kuver et al 1994, Burke 1989]. Keeping in mind that the highest cathode potential is 1V in practice, this kind of loss is certainly a serious problem that needs to be resolved. Some work is being done to develop methanol tolerant catalyst (cathode), however, even if the cathode depolarization is resolved,

the methanol crossover is still an issue of considerable significance, which results in a decrease in fuel cell efficiency. From a practical point of view it should be important to stop this methanol crossover through the membrane.

Beside the methanol crossover, a general problem related with Pt cathode still exists. The equilibrium potential for oxygen gas reduction to water according to equation 2 is 1.23 V(RHE) at 25^oC. In practice the cathode potential on Pt/C electrode does not exceed 1 V. The main reason for this voltage loss is the formation of an oxide film (OH_{ads}) and the presence of strong water dipole, which interacts with positively charged metal surface. It is concluded that the neutral oxygen molecules are unable to displace the water dipoles from the surface when the potential is above 1 V. Consequently, the oxygen molecules are unable to exert their maximum thermodynamic potential in Pt electrode system.

Burke 1989 carried out a study on the Pt/C cathode in DMFC investigated the effect of temperature, O_2 pressure, Pt loadings, and binder content. The cathode performance is favored by high O_2 pressure, high optimum temperature, high Pt loading. Hamnett et al. 1990 showed that the type of carbon and binder also play important roles for the cathodes catalytic performance in a solid polymer electrolyte DMFC. It has been observed that cathode containing Nafion as a binder showed improved performance. The recent achievement of Hamnett group is that Pt loading on cathode has gone down to $0.5mg/cm^2$. The Pt/C cathode recently used by Giner Inc. is claimed to have a structure that is relatively tolerant to methanol.

Cathodes using metals different from platinum were also investigated [Shukla et al 1985]. Some works were also carried on the development of methanol tolerant cathodes. A research group in Case Western university has observed that carbon supported high surface area RuO_2 is a relatively active catalyst for oxygen reduction but showed poor performance for methanol oxidation. A $Ru-MoS_2$ based cathode system is currently being investigated at the New Castle university [Zaidi 1997]. Ye et al 1996 prepared new cathode based on a highly porous carbonized polyacrylonitrile(PAN) foam material with very low platinum loading ($=13\mu g/cm^2$).

5. DMFC ELECTROLYTE-PROTON CONDUCTING MEMBRANES

The efficiency and power density of fuel cells strongly depend however, also on the conductance of the electrolytes. It should be mentioned, that only acidic electrolyte can be used in DMFC to aid carbon dioxide rejection. Alkaline electrolytes are not considered because of fast degradation due to formation of insoluble carbonates, which lead to essentially poor long-term performance. A strongly acidic ion exchange membrane [Scherer 1990] is indispensable as a solid electrolyte in fuel cells (DMFC). Polymer electrolyte membrane designated, as PEM is a kind of proton exchange membrane first proposed by Grubb [Grubb 1959]. A solid polymer electrolyte using H_2 fuel cell has found applications in first manned

space mission Gemini during 1960`s. In the case of DMFC, until now sulfonic acid membranes have been considered promising as proton conductors due to the fact that the sulfonic acid function fully dissociates.

The center of the fuel cell is the polymer electrolyte membranes as it defines the properties needed for other components of the fuel cell. The most widely used membrane today is Nafion manufactured by Du Pont. The main advantage of Nafion is its long lifetime; it can last for several thousand hours at temperatures below 100 ^{o}C. Moreover power densities of 600-700 mW/cm^2 were obtained with Nafion membrane. Thus Nafion membrane allowed the development of fuel cells operating between 80-100 ^{o}C [Scherer 1990]. Even though Nafion is considered to be most effective and efficient PEM for fuel cell, it also has several problems. First and the most important is that the cost of these membranes in the range of US $ 800 /m^2 (Du Pont) and US $ 2000/m^2 (Dow) exclude their applications for the transportation sector. Second, there is a serious problem of methanol crossover from anode to cathode side, which results in decreased performance of the overall fuel cell [Appleby 1996].

Thus, it is very important to modify these by, for example, developing composites or finding alternative proton conductors with the capability of inhibiting methanol transport. It is generally accepted that a solid-state proton conductor is preferable for liquid fuel-fed DMFCs because it hinders corrosion and rejects carbon dioxide (produced during methanol oxidation). The polymer electrolyte should have a high ionic conductivity (5×10^{-2} ohm^{-1} cm^{-1}) under working conditions and a low permeability to methanol (less than 10^{-6} moles min^{-1} cm^{-2}). Furthermore, it must be chemically and electrochemically stable under operating conditions [Rikukawa 2000]. Efforts have been expanded in developing less costly and methanol impermeable membranes for DMFC. Keeping these requirement partially fluorinated hydrocarbon membranes were developed by radiation grafting in the USA and Japan. Some of the membranes investigated so far are: sulfonated poly (ether ether ketone) and poly (ether sulfone), poly vinyledine fluoride, styrene grafted and sulfonated membranes,and/or membranes doped with heteropolyanions acid doped polybenzimidazole [Rikukawa 2000].

Sulfonated poly (ether ether ketone) and poly (ether sulfone) electrolytes show promising characteristics in terms of mechanical strength and acceptable conductivity in their protonic form with low resistance to ion transport and reduced crossover of methanol. The stability and conductivity properties of sulfonated poly ether ether ketones and poly ether sulfones, as ascertained in DMFCs, are at present not developed sufficiently to meet the requirements [Kreuer 2001].

In search of low cost and thermally stable proton conducting membranes Zaidi (2000) developed a series of composite proton conducting membranes by incorporation of solid heteropolyacids (HPA) into sulfonted polyether-ether ketone (SPEEK) matrix. These membranes showed a high conductivity of the order of 2×10^{-2} S/cm, which is higher than

exhibited by Nafion 117. The results of the conductivity studies of some of these membranes are shown in Fig.2. They show a high conductivity upto 150 ^{o}C where conductivity of Nafion membranes falls to low values. In another study composite membranes containing solid inorganic boron phosphate (BPO$_4$) into SPEEK polymer were prepared by Zaidi (2001). In this the loading of the solid conductor was varied from 20 to 60 wt.%. The high loading of solid conductor particles (HPA and BPO$_4$) into the SPEEK polymer is expected to reduce the methanol permeation through these composite membranes. These membranes are chemically stable and mechanically stronger and possess high conductivity. Further work is in progress for their performance in actual DMFC and methanol permeation study.
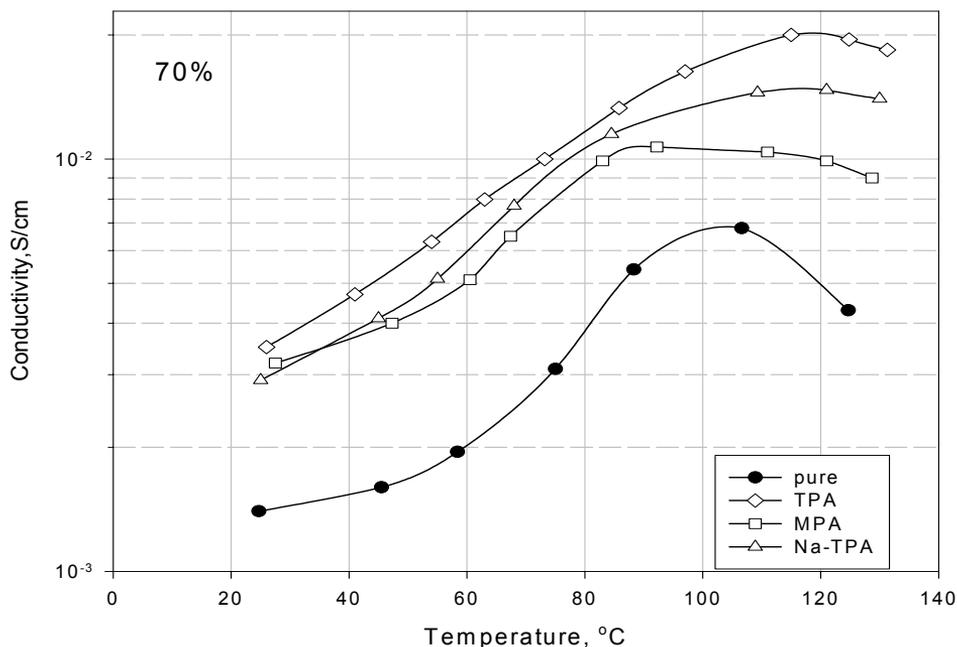

Fig.2. Conductivity of Composite SPEEK membranes containing solid
Heteropolyacids based on 70% sulfonation of PEEK (Zaidi et al 2000)
[TPA: Tungstophosphoric acid; MPA: Molybdophosphoric acid].

6. DMFC PERFORMANCE-TECHNOLOGICAL DEVELOPMENTS

The performance of the direct methanol fuel cell very much depends on the techniques of the preparation of membrane electrode assembly. In practice the polymer electrolyte membrane fuel cell (PEMFC) uses a hydrated sheet of a perfluorinated ion exchange membrane as a solid electrolyte, catalytic membranes are intimately bonded to each side of the membrane. These assemblies are called membrane electrode assemblies (MEAs). The performance of MEA for the PEMFC is much effected by a good network of PFSI-perfluorosulfonate ionomer(Nafion) and uniformity of Nafion on platinum particles in the catalyst layer [Uchida et al 1995].

Over the course of DMFC development many techniques were investigated for forming the MEA in cells based on Nafion membrane to increase the interface between Pt particles and Nafion [Uchida et al 1995, 1996;Ren et al 1996; Ravikumar & Shukla 1996].These include conventional PTFE-treated wet-proofed electrodes, catalyst/ionomer inks applied to carbon cloth, and thin film catalysts formed applying a catalyst/ionomer ink to transfer decals. These various types of catalysts were then bonded to Nafion membranes by hot pressing. The thin films catalysts bonded to the membrane by the decal method provided the best results in terms of catalyst utilization and cell performance. Uchida et a (1996) described a new method for the fabrication of MEAs, called the Paste-method, with high performance as well as an ideal structure of the reaction field in the catalyst layer.

A single fuel cell can be built, once the anode, cathode and electrolyte materials are fixed. However, from an engineering point of view, there are still many factors, which have to be taken into consideration in the design of single cell. The two sides of MEA should be bonded by electrically conductive, corrosion resistance and porous materials, which allow the current collection, the liquid methanol access (anode region) and the gas permeation (cathode region). A carbon cloth containing PTFE is usually the material of choice to satisfy the above requirements

The performance of DMFC is generally reported in terms of the maximum power density and the power density at a particular cell voltage, e.g. 0.5V. It strongly depends on the fuel cell operating conditions and on the characteristics of the fuel cell components. The best single cell (5-5-cm^2 active area) DMFC performances achieved by various groups in the last five years, are 300-450mWcm^{-2} and 200-300 mWcm^{-2} as the maximum power density at 100 ^{o}C with overall Pt loading of 2-5 mgcm^{-2}, in the presence of an oxygen and air feed at the cathode respectively [Arico et al 2001].

A fuel cell stack is a combination of several such single cells. The development of DMFC stacks has gained momentum in the last three to four years. The rated power output of the DMFC stack varies from a few watts in the case of portable power sources up to a few kW for remote power generators and hybrid battery-fuel cell vehicles. The best results achieved with DMFC stacks for transportation are 175 mW/cm^2 at the design of 0.5v/cell. Few companies have published information on building the DMFC stacks and their performances, although fuel cell work is in progress in many laboratories in the USA, Canada, Japan and other countries around the world. The DMFC stacks performances reported in recent years are by Giner Inc, International Fuel cells (IFP), Siemens Los Alamas National Laboratory (LANL), Korean Institute of energy research (KIER) in Table 1 [Zaidi 1997; Arico et al 2001].

Table 1: Performance of DMFC Stacks

Stack Developer	No. of cells/ active area	Rated Power, W	Max. Power Density, mW/cm^2	Power Density @0.5V, mW/cm^2	T, ^{o}C	Oxidant/P atm
Siemens John Matthey	16/550	850	100	42.5	104	Air/1.5
Los Alamas	5/45	17	75	50	60	Air/0.7
Los Alamas	5/45	47	220	175	100	Air/3
Giner inc.	5/-	-	80	56	69	Oxygen/1.3
IFC	2/-	-	100	60	104	Oxygen
KIER	3/150	40	90	20	90	Oxygen/3

7. CONCLUSIONS

Fuel cells appear close to realizing widespread commercialization based on current developments. Its low operation temperature, fast start-up time and simplicity make direct methanol fuel cell an ideal power source for a number of portable and stationary applications. These applications include battery replacement for portable telephones, and computers, power sources in remote areas and military installations. DMFC promises to be very attractive for applications especially in transportation sector due to the ease of the handling of liquid fuels. In view of their ability to achieve power levels comparable to those of today's internal combustion engine, PEM fuel cells are considered to be the most promising candidates for the electrical propulsion systems. During the previous years a dramatic improvement in DMFC performance is mainly attributed to the use of polymer electrolyte-Nafion. The best single cell performance reached a power density of 300mW/cm^2 at cell voltage of 500 mV. A recent stack study indicates that a power density of 175 mW/cm^2 can be achieved with a stack of 5 cells. Based on a power density of 100 mW/cm^2 and Pt loading of 4 mg/cm^2, the stack cost is estimated as Can.\$ 8,510/kW, which is already comparable with the price of SPFC stacks with reformer. The basic problems in DMFC are still linked to the poor catalytic activity of the anode and the methanol crossover. In spite of these difficulties, DMFC does have the capability of being very cheap and potentially very competitive with the internal combustion engine. With continued advances fuel cells will become increasingly competitive with conventional combustion engine technologies. The cost of fuel cells will decrease as their lifetimes lengthen, power density increase and overall reliability rises. Though fuel cell commercialization is under way, the rate of market growth will depend on the rate of technological improvement. Basic and applied research can play large roles in solving problems about fuel cell technology, thereby helping to improve the technology and expand its market opportunities.

ACKNOWLEDGEMENT

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