

Performance of the direct methanol fuel cell with radiation-grafted polymer membranes

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Abstract

This paper reports performance data for the direct methanol fuel cell (DMFC) using membrane electrode assemblies using radiation-grafted proton exchange membranes based on polyethylene and ETFE. These membranes exhibited low methanol diffusion coefficients and were thus felt to be potentially useful in reducing possible methanol cross-over from anode to cathode. The membrane electrode assemblies were based on Nafion[®]-bonded carbon-supported catalyst; platinum/ruthenium for the anode and platinum for the cathode. The cell voltage performance of the DMFC, for short duration (<100 h) testing, with these low cost membranes is as good as, or superior to, that of cells based on Nafion[®] under identical operating conditions. However, the stability of contact between the membrane and the catalyst layer requires improvement before these membranes become real alternatives to materials such as Nafion[®], for the DMFC. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Direct methanol fuel cell; Polymer electrolyte membrane; Zeolite; Methanol diffusion

1. Introduction

Solid polymer fuel cells (SPFC) use a polymer membrane as the electrolyte. The membrane, typically 50–250 μm thick, provides an electrolyte capable of withstanding high-pressure differentials with no free corrosive liquids. Besides functioning as an acid electrolyte, the membrane separates the fuel from the oxidant gas. Early activity in this field used membranes based on sulphonated polystyrene and co-polymers of styrene and divinylbenzene [1,2]. Today's membranes are typically solid, hydrated sheets of a sulfonated fluoropolymer similar to Teflon. The acid concentration

of a particular membrane is characterised by equivalent weight, EW (grams of dry polymer/mole of ion exchange sites). Generally lower EW and thinner membranes result in higher cell performance. However, thinner membranes can result in higher parasitic cross-diffusion of reactant fluids.

There are several methods for the production of ion exchange membranes including co-polymerisation of unsubstituted alkene with a functionalised alkene containing an ionic group, or a precursor to the ionic group, polymerisation of an alkene and subsequent introduction of the ionomer into the polymer and using sulphonated arylene main chain ionomers and acid–base polymer blends [3–5]. Of these only a few have reached commercial production. A number of commercial ion exchange membranes are produced by grafting in which new monomers are co-polymerized

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onto a pre-formed polymeric structure, eventually forming a new polymeric structure that is grown from the substrate [6]. Grafting reactions are carried out by forming polymeric radicals in the substrate, a process that can be induced chemically or by ionising radiation. The polymer used as substrates is usually fluorinated or non-fluorinated polyolefin. The grafting procedure is carried out to incorporate a styrene, chloromethylstyrene or reactive olefin group into the substrates, and this reactive moiety is subsequently chemically converted into sulfonate or some other desired functional group.

The important exceptions to these materials are NafionTM, manufactured by DuPont, Aciplex[®] from Asahi Chemicals Co. and Flemion[®] from Asahi Glass Co. [7,5]. These materials are similar and are made of a non-cross-linked perfluorinated olefin backbone with pendant 'perfluoroether' side-chains bearing sulfonate groups. The material swells in water, which results in the formation of two separate regions: one comprising the hydrophobic polymer backbone (a PTFE-type structure) held together by van der Waals interactions, and the other region consisting of well-defined clusters of hydrophilic sulfonate groups protruding into 'micropools' of sorbed water. This morphology with discrete hydrophobic and hydrophilic regions gives the material very valuable properties. Since the concentration of the sulfonate groups in the water channels penetrating the material is very high, the transport of counter-ions will be fast, and the Donnan exclusion of co-ions is very effective. This accounts for the exceptional transport efficiency in hydrated NafionTM. These properties, and the fact that the material is chemically very inert, due to the perfluorinated structure, have rendered it useful in several applications at high current densities.

The high cost of Nafion[®] has prompted efforts to develop membrane materials with the same desirable chemical and mechanical features but which can be produced more cheaply. A cheaper membrane can be prepared by doping an inexpensive, non-conductive material (which serves the mechanical/structural function) with a small amount of an ion-transporting polymer (which allows the membrane to accomplish its chemical function). One example is the impregnation of the commercially available porous polytetrafluoroethylene membranes (PTFE, Gore-Tex) with small quantities of NafionTM bearing sulfonate groups.

Native Gore-Tex materials are not wetted by water although in an aqueous supporting electrolyte solution NafionTM is impregnated and the membrane becomes water-swollen and ionically conductive [8,9].

A significant membrane development since the introduction of Nafion[®] was a new perfluorosulfonic acid membrane, with a shorter side-chain, made by Dow Chemical [10]. The Dow material is prepared by the co-polymerisation of tetrafluoroethylene with a vinyl ether monomer. The polymer can be described as having a Teflon-like backbone structure with a side-chain attached via an ether group. The short side chain polymers in the Dow membranes cause completely different permeation rates and other properties relative to those of NafionTM [10]. However, this membrane never progressed through to being a commercial product. Asahi Chemical Industry Co. perfluorinated membranes (Aciplex-S) show excellent performances, because of their high conductivity and long-term stability in PEMFCs [11].

Pall in the USA has also produced a grafted fluorinated membrane which has demonstrated superior behaviour, in terms of cell voltage response, to Nafion[®] when used in hydrogen SPE fuel cells. However, the demonstrated stability of the membrane electrode assemblies (MEA) was inferior to that of MEAs based on Nafion, with de-lamination of the catalyst layer from the membrane surface occurring after several hundred hours of use [12]. Brack and co-workers have also shown that their radiation-grafted membranes can give a cell polarisation performance as good as, if not better than that of Nafion, when used in hydrogen fuel cells [13]. However, the long-term stability in operating fuel cells was not as good as that achieved with Nafion membranes, although it was superior to that of the Pall radiation-grafted membranes, as measured by the in situ membrane resistance in hydrogen fuel cells [14].

The major limitation of the above membranes is that for direct methanol fuel cells they exhibit significant cross-over of methanol from anode to cathode (commonly known as methanol cross-over) which causes a mixed potential and reduces the electrical performance. Thus significant research has been directed to the production of low cost membrane materials with high proton conductivity and low methanol cross-over. Polybenzimidazole (PBI) was suggested for use as a polymer electrolyte when doped with an

amphoteric acid such as phosphoric acid or sulphuric acid. The acid-doped PBI membrane exhibits excellent oxidative and thermal stability, and good mechanical flexibility at elevated temperature (200°C). Compared to Nafion™ membranes, there are several advantages of acid-doped PBI membranes. First, an acid-doped PBI membrane has good protonic conductivity at an elevated temperature. Second, it has an almost zero electro-osmotic drag number compared to the drag number of 0.6–2.0 for the Nafion™ membrane. This unique feature of the acid-doped PBI membrane allows the PBI fuel cell to be operated at high temperature and low gas humidity without membrane dehydration. Third, the acid-doped PBI membrane has low methanol vapour permeability. These proper-

ties suggest that the acid-doped PBI membrane is a promising polymer electrolyte for the DMFC [15–17]. Motogami proposed the use of polyglycidylether [18] as a membrane in fuel cells. Ballard Inc. have recently developed of a new low cost membrane material for use in fuel cells (see e.g. [19]). In all the above cases very little published information is available. Hence specific details about the material nature, performance in a fuel cell environment and availability are as yet scarce [20,21].

Sulfonated and sulfonated/cross-linked proton-exchange membranes have also been fabricated from selected phosphazene polymers for potential use in PEMFCs. In particular, polyphosphazene, poly-[bis(3-methylphenoxy)phosphazene] looks promising

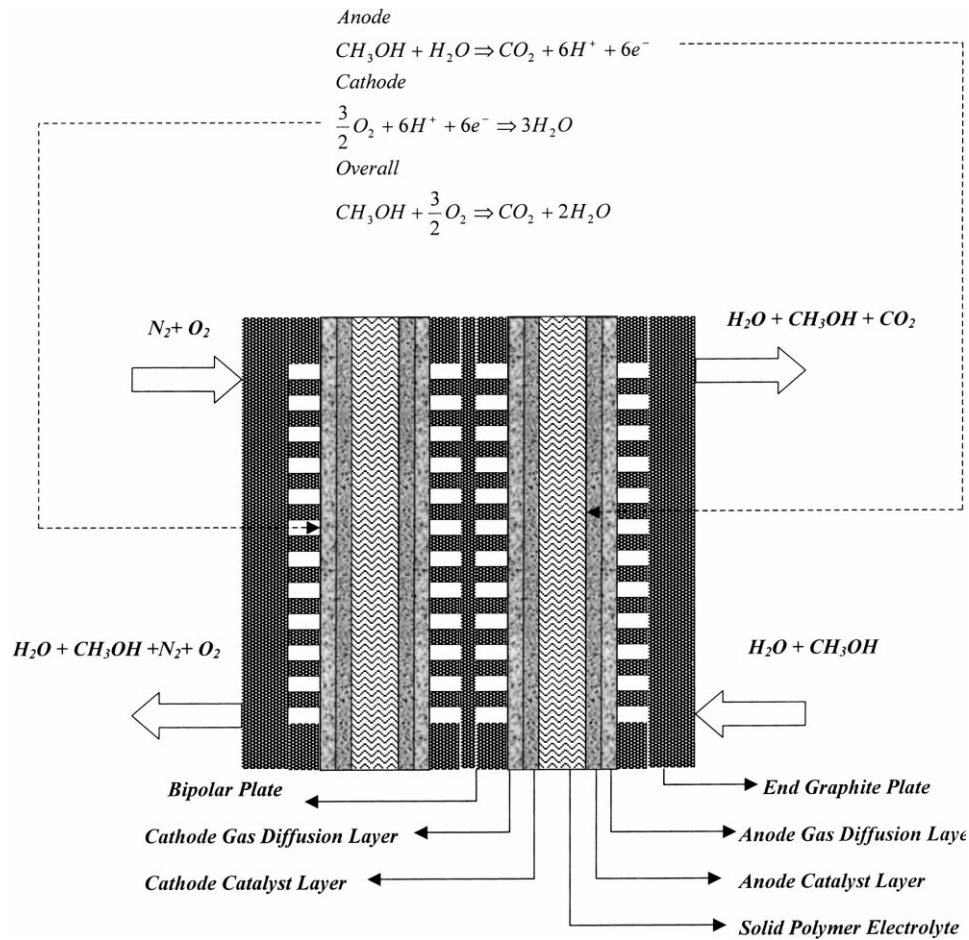


Fig. 1. Schematic representation of the direct methanol fuel cell.

for direct liquid methanol fuel cells. Water and methanol diffusivities in the polyphosphazene membrane are low ($<10^{-7}$ cm²/s) and the methanol cross-over rate was approximately 10 times lower than that for Nafion 117 [22].

Materials for membranes in SPE cells are not limited to polymers and some research is underway using inorganic-type materials. Among such materials zeolites offer interesting characteristics with molecular selectivity which can potentially differentiate between water and the larger methanol molecule. In fact such materials are in commercial use for the separation of alcohols, e.g. methanol from water, in the pervaporation process [23]. We report briefly here the use of such materials in the DMFC.

The focus of this paper is to report methanol permeation data for a range of membrane materials, which were considered as low cost alternatives to Nafion[®] for the DMFC, and performance data for the DMFC (shown schematically in Fig. 1) using SPE membranes based on radiation-grafted low density polyethylene and ETFE, which is compared to that obtained with cells based on Nafion[®] 117.

2. Experimental

2.1. Methanol permeation

The permeation of methanol was determined using two well-stirred glass reservoirs (30 cm³) separated by the membrane material under test. One reservoir was filled with methanol and the other with de-ionised water. Each membrane was soaked in a 2.0 M methanol solution for 48 h, at room temperature, prior to testing. The membrane cross-section area was 8.55 cm². Small aliquots (0.1 cm³) of solution were withdrawn from both reservoirs at suitable intervals over a 3-hour period. Methanol concentration was determined by refractive index using an Abbe refractometer for high methanol solution concentrations (>0.5 mol dm⁻³) and gas chromatography analysis, using an AI Cambridge GLC fitted with a TCD detector at low concentrations (<0.5). Concentration changes in the aqueous phase were significant (up to 9 mol dm⁻³) over this period, as shown in Fig. 2. The temperature of the tests was maintained at 20°C. Each experiment was repeated three times

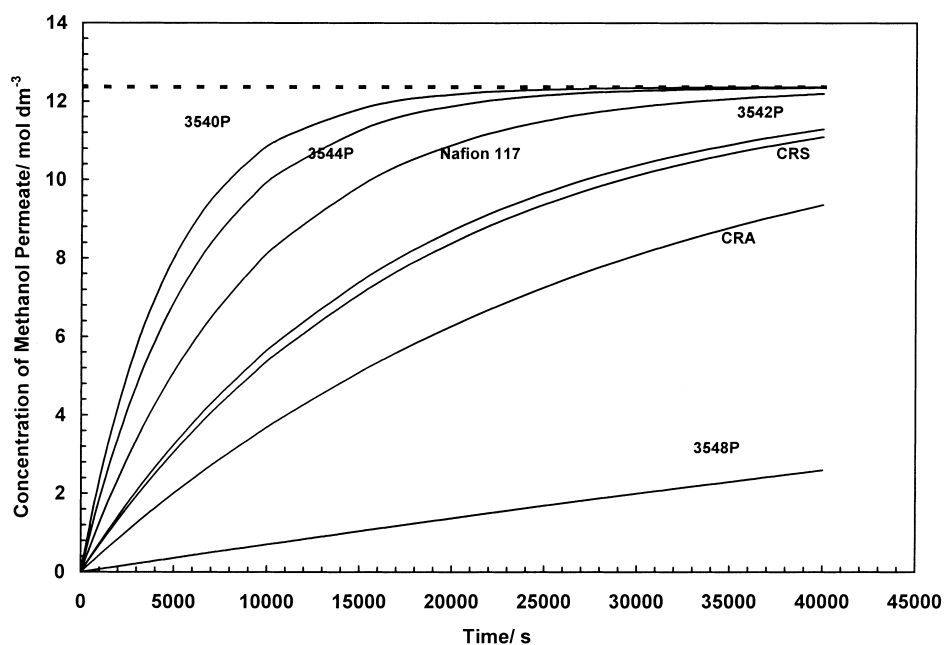


Fig. 2. Variation of methanol permeate solution concentration with time during methanol diffusion at 20°C.

Table 1
Membrane materials

Membrane no.	Base film	Functional group	Nominal thickness (μm)	Supplier	Resistivity (ohm cm^2)	IEC (meq/g, Na^+ form)
Nafion 117	Perfluoro polymer		170	Du Pont	0.04	0.9
CRA	Radiochemically grafted		160	Solvay	1–4 ^a	1.4–2.2
CRS	Fluorinated film		160	Solvay	1–3 ^a	1.7–2.2
R4010	PTFE		20	Pall	0.6	1.2
R1010	PTFE		40	Pall	0.3	1.2
3540P	ETFE	PSSA ^c	50	Cranfield University	0.044 ^b	2.17
3542P	ETFE	PSSA ^c	50	Cranfield University	<0.003 ^b	1.92
3544P	PVDF	PSSA ^c	50	Cranfield University	<0.003 ^b	2.15
3548P	PVDF-Co	PSSA ^c	50	Cranfield University	0.471 ^b	1.26
3553P	LDPE	PSSA ^c	125	Cranfield University	0.454 ^b	0.81
3735P	ETFE	PSSA ^c	50	Cranfield University	0.012 ^b	1.9
3747P	ETFE	PSSA ^c	50	Cranfield University	<0.003 ^b	1.97
3748P	LDPE	PSSA ^c	125	Cranfield University	<0.003 ^b	2.19
3749P	LDPE	PSSA ^c	125	Cranfield University	0.160 ^b	1.38

^a As measured in 10 gdm^{-3} NaCl.

^b As measured in 0.1 M HCl.

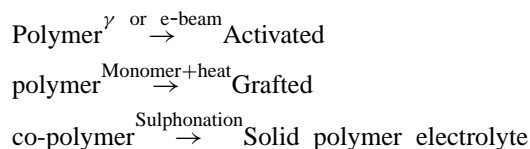
^c PSSA: polystyrene sulphuric acid.

to ensure reproducibility of the data. The diffusion coefficients of methanol were determined from a dynamic model of the system based on Fick's law of diffusion.

The electrical resistance of the membranes was determined using AC impedance. The resistivity of the membranes was measured in a thermostatically controlled cell (25°C). The samples were equilibrated in 0.1 M HCl or 10 g dm^{-3} NaCl at this temperature overnight. The membrane sample is clamped between two reservoirs of the electrolyte in which the Pt electrodes are situated. The resistance measurements were taken using a Wayne Kerr Universal Bridge, Model B624 at a frequency of 1591.5 Hz, over a test area of 0.5 cm^2 . The resistivity value of the electrolyte pathway was measured using a blank of the same thickness as the membrane, with a hole cut in the test area. The blank measurement was subtracted from the measurement obtained from the sample. Two samples were tested for each membrane and their results averaged. Membrane resistivity was calculated taking into account the area of the sample.

The membrane materials investigated in this work, and their properties, are listed in Table 1. Membranes from four sources were used in this work: Cranfield University, DuPont, Solvay SA and Pall-Gelman. The membranes produced at Cranfield University were synthesised by the radiation-grafting technique.

The base polymers were first irradiated using a cobalt-60 source in air to produce peroxy radicals on the polymer backbone. The radicals were then used in a further reaction with styrene (carried out in an inert atmosphere) to form a co-polymer. The grafted co-polymer was then sulphonated and the membrane hydrolysed in hot water. The polymer electrolyte formed could then be dried and used as appropriate. The basic grafting scheme is shown below:



2.2. Direct methanol fuel cell

Membrane electrode assemblies (MEA), shown schematically in Fig. 1, studied in this work were made in the following manner. The anode consisted of a Teflonised carbon cloth support (E-Tek, type 'A'), of 0.35 mm thickness, upon which was spread a thin layer of uncatalysed (ketjenblack 600) carbon, bound with 10 wt% Nafion[®] from a solution of 5 wt% Nafion[®] dissolved in a mixture of water and lower aliphatic alcohols (Aldrich). The catal-

ysed layer, Pt–Ru dispersed on carbon (2 mg cm^{-2} metal loading) and bound with 10 wt% Nafion[®], was spread on this diffusion-backing layer. A thin layer of Nafion solution was spread onto the surface of each electrode. The MEA was obtained by hot-pressing the anode and cathode on either side of the pre-treated membrane. The thickness of the MEA is approximately 0.8 mm depending on the diffusion layer thickness.

The Pt–Ru anode catalyst used was: 35 wt% Pt, 15 wt% Ru. The cathode was constructed using the same method as for the anode, a diffusion layer bound with 10 wt% PTFE and a catalyst layer consisting of 10 wt% Pt on a carbon catalyst with a loading 1 mg cm^{-2} Pt black (Johnson Matthey) with 10 wt% Nafion[®]. The electrodes were placed either side of a pre-treated Nafion[®] 117 membrane. The Nafion 117 membrane pre-treatment involved

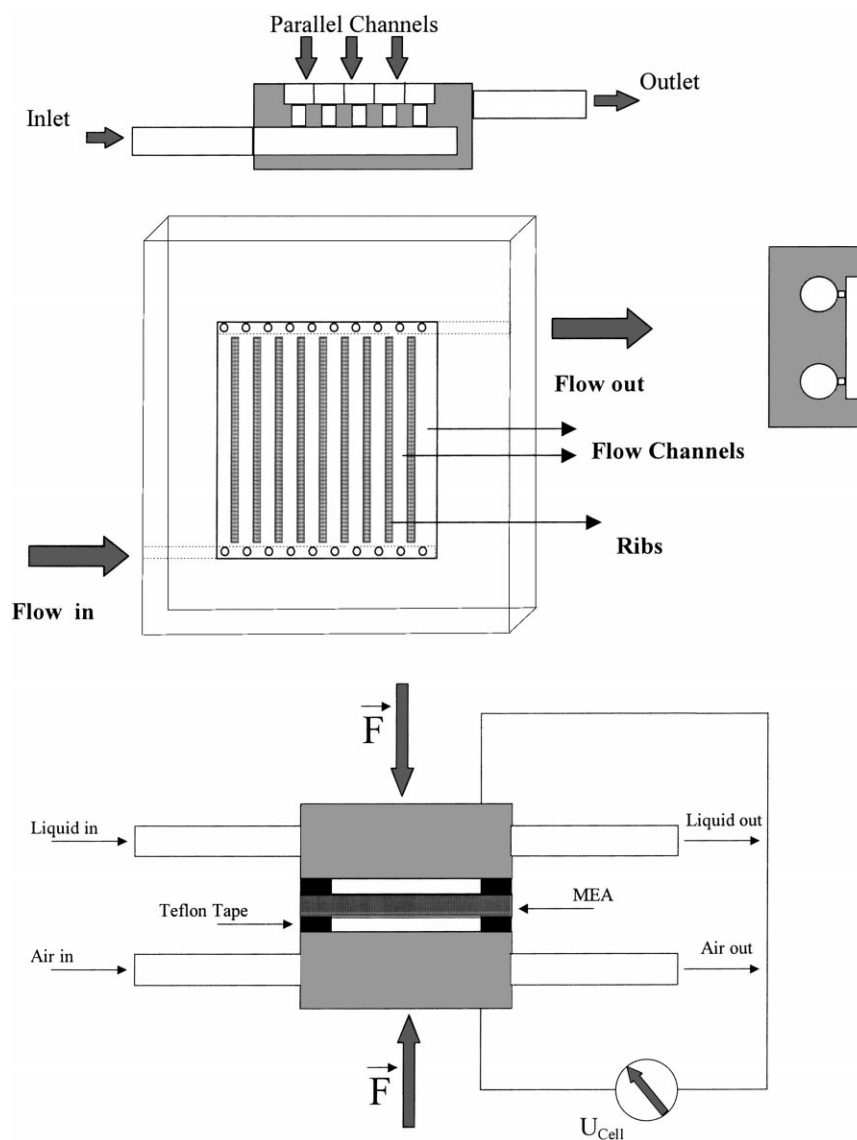


Fig. 3. Experimental fuel cell.

boiling the membrane for 1 h in 5 vol% H₂O₂ and 1 h in 1 M H₂SO₄ before washing in boiling Millipore water (>18 mΩ) for 2 h with regular changes of water. The other membranes, 3747P and 3748P, used in this study were only pre-treated with 0.5 M H₂SO₄ before washing in boiling Millipore water (>18 mΩ) for 2 h with regular changes of water. The 3747P and the Nafion 117 assemblies were hot-pressed at 100 kg cm⁻² for 3 min at 135°C, while the 3748P was hot-pressed at 75°C. This difference is due to the fact that 3748P has a degradation temperature below 100°C. Consequently operation of this membrane in the DMFC was limited to a temperature of 70°C. The resulting MEA was installed in the cell after pressing, and hydrated with water circulated over the anode at 75°C for 48 h. The majority of data reported here was obtained after allowing 48 h to condition a new MEA in the test fuel cell at 75°C and atmospheric pressure with continuous feed of, typically, 2 M methanol solution.

Tests on the DMFC were performed with a cell (Fig. 3) with a cross-sectional area of 9 cm². The cell was fitted with one MEA sandwiched between two graphite blocks which had a flow bed, either in the form of parallel channels or square spots, cut out for methanol and oxygen/air flow. The cell was held together between two copper current collectors, two plastic insulation sheets and two stainless steel or aluminium backing plates using a set of retaining bolts positioned around the periphery of the cell. Electrical heaters, supplied by Watson Marlow, were placed behind each of the graphite blocks in order to heat the cell to the desired operating temperature. The graphite blocks were also provided with electrical contacts and small holes to accommodate thermocouples. The fuel cells were used in a simple flow rig, which consisted of a Watson Marlow peristaltic pump to supply the aqueous methanol solution from a reservoir to a Eurotherm temperature controller to heat the methanol. Oxygen and air were supplied from cylinders, at ambient temperature, and the pressure regulated by pressure-regulating valves. All connections between the cells and equipment were with PTFE tubing, fittings and valves. Cell polarisation curves were obtained galvanostatically.

3. Results and discussion

3.1. Methanol permeation

The measured diffusion coefficients of the membranes are given in Table 2. The diffusion coefficient of methanol through Nafion[®] 117 was $1.72 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$, at 20°C, which compares well with those of 4.8×10^{-6} and $5.6 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ measured at 60 and 70°C, respectively [24], allowing for the influence of temperature on the diffusion coefficient. The diffusion coefficients of the membranes from Pall and Solvay were all lower than that for Nafion[®] 117. However, because the membranes from Pall are also thinner than Nafion[®], the molar flux of methanol through the materials is not significantly lower and thus the expected benefit from reduced methanol cross-over on cathode mixed potential would not be realised. In addition there would be little benefit in electrical performance due to membrane conductivity. Although the membranes from Solvay had low diffusion coefficients the material was not recommended, by the manufacturer, for use in the DMFC.

The membranes from Cranfield showed a large variation in the diffusion coefficient and noticeably two materials, 3548P and 3553P, exhibited very low diffusion coefficients, at least an order of magnitude lower than Nafion[®] ($0.11 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$). However, as illustrated in Table 1, both these materials have high electrical resistivity. Tables 1 and 2 indicate that material 3542P (ETFE) gives a reasonable compromise

Table 2
Membrane diffusion coefficients

Membrane	Diffusion coefficient (cm ² s ⁻¹)
Nafion 117	1.72×10^{-6}
3540P	3.38×10^{-6}
3542P	0.99×10^{-6}
3544P	2.62×10^{-6}
3548P	0.11×10^{-6}
3553P	$<0.05 \times 10^{-6}$
CRA	0.58×10^{-6}
CRS	0.92×10^{-6}
3747P	1.34×10^{-6}
3748P	1.32×10^{-6}
R1010	0.6×10^{-6}
R4010	1.2×10^{-6}

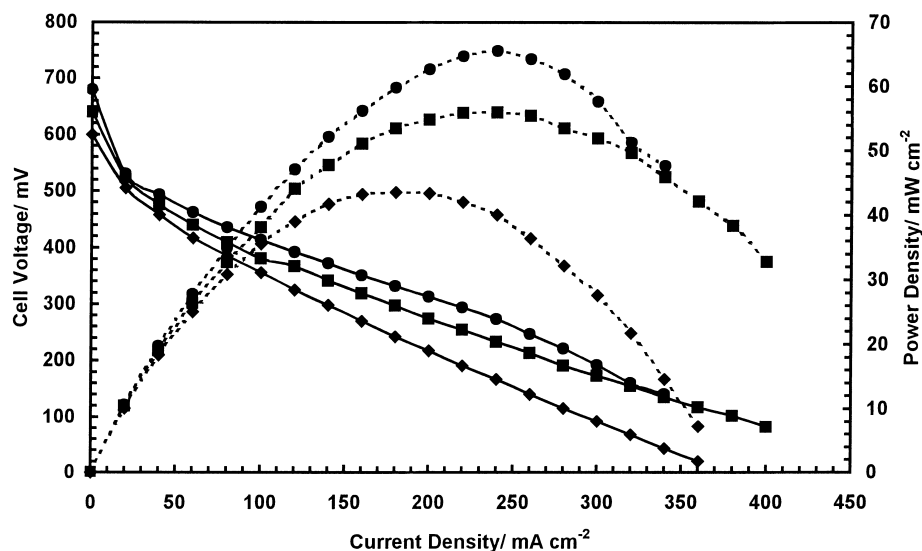


Fig. 4. The effect of conditioning period on the cell voltage and power response of the ETFE (3747P) MEA. 90°C, 2 bar air, 2 mol dm⁻³ methanol, 1 cm³ min⁻¹. ♦: 24 h, ■: 48 h, ●: 72 h.

between electrical resistivity and methanol diffusivity. Thus this material, or rather in fact a slightly modified version of this membrane, i.e. 3747P was proposed for DMFC studies. In addition, because of the low methanol diffusivity of membrane 3553P (LDPE) a modified version of this material, i.e. 3748P, with much lower resistivity was tested in the DMFC. Noticeably, however, this material now exhibited quite high methanol diffusivity.

3.2. Direct methanol fuel cell performance

One of the major advances made in the research of SPE cells including the DMFC was the introduction of Nafion[®] as a binder in the catalyst layer as a replacement to Teflon[™]. In general it is believed that this material penetrates the catalyst layer and serves as an ionic bridge between the active sites of the electrocatalyst and the membrane surface thus facilitating proton removal. Ralph et al. [25] presented a comprehensive study on the effect of dissolved Nafion[®] loading in SPEMFC electrodes when at the same time significant research has focused on investigating the exact mechanism of performance improvement achieved through Nafion addition to the catalyst layer [26–30]. This

major breakthrough probably poses the greatest limitation in trying alternative membranes. If the membranes differ significantly in terms of chemical composition from Nafion[®] then the dissolved Nafion[®] solution may be incompatible. It generally may not promote good electrical contact or good adhesion between the different composite layers forming MEA. Membranes commercially available today are generally not available in a dissolved form nor can they be dissolved and re-cast.

Two major requirements for a membrane material for the DMFC are low methanol cross-over and high ionic conductivity. Two alternative membrane materials (fabricated at Cranfield University) were evaluated for the DMFC operation after initial characterisation in terms of electrical conductivity and methanol permeation. It should be noted that although a membrane material may exhibit low methanol permeation during non-electrochemical tests, methanol transport may still be significant through the process of 'electro-osmosis'.

The performance and the power response of the membrane coded 3747P is shown in Fig. 4. The cell was heated at 90°C, and tested with a 2.0 kmol dm⁻³ methanol solution at a flow rate of 10 cm³ min⁻¹. The effect of the conditioning period on improving the cell performance and power output is shown. After a

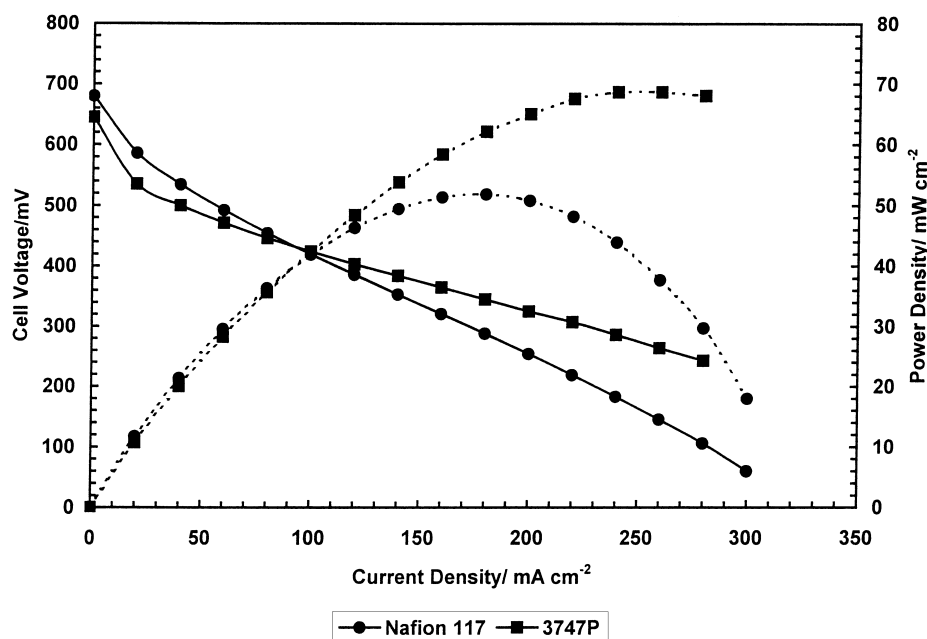


Fig. 5. Comparison of the voltage and power density response of MEAs made with Nafion and ETFE-3747P membranes. 90°C, 2 bar air, 2 mol dm⁻³ methanol, 1 cm³ min⁻¹ ■: 3747P, ●: Nafion 117.

period of 72 h no significant further improvement in performance is achieved.

Fig. 5 compares the performance of MEA with the 3747P membrane and Nafion 117. Noticeable there is a slight improvement in the open circuit voltage, approximately 35 mV, and at higher current densities a significant voltage and power performance improvement is seen. The data indicate that the electrical resistance of MEA with the 3747P membrane is lower than with Nafion[®] (the slope of the voltage current curve is lower). In attempts to assess the effect of high methanol concentration we operated the cell with a 4.0 M methanol solution (Fig. 6). In this case a large reduction in open circuit potential is seen, as anticipated from an increase in methanol cross-over. However, a reasonable power performance compared to the use of 2 M methanol is achieved, which is contrary to that achieved by others with such high methanol concentrations [31]. The effective resistance of MEA does not appear to have significantly changed with the increase in methanol concentration.

After further operation of MEA made with the 3747P membrane the performance degraded quite

rapidly which we accredit to the degradation of the binding between the composite layers of bonded catalyst and membrane forming the MEA. On removing the MEA from the cell there were severe signs of de-lamination between the catalyst and membrane layers. Further research is required to pursue the aspects of lamination and an alternative soluble ionomer to Nafion with suitable adhesion characteristics.

The electrical and power performance of the second membrane from Cranfield (code number 3748P) is compared with that of Nafion[®] 117 in Fig. 7 for a temperature of 70°C. Although its performance is not significantly different from that of Nafion[®] there is an apparent improvement at lower current densities whilst at higher current densities the performance is inferior to that of Nafion, which is accredited to overall inferior electrical conductivity of MEA, due to poor bonding of the catalyst layer to the membrane material at lower fabrication temperatures. An interesting feature of the 3748P membrane is its fast water uptake: the membrane needs only a few seconds in order to become fully hydrated from a dry condi-

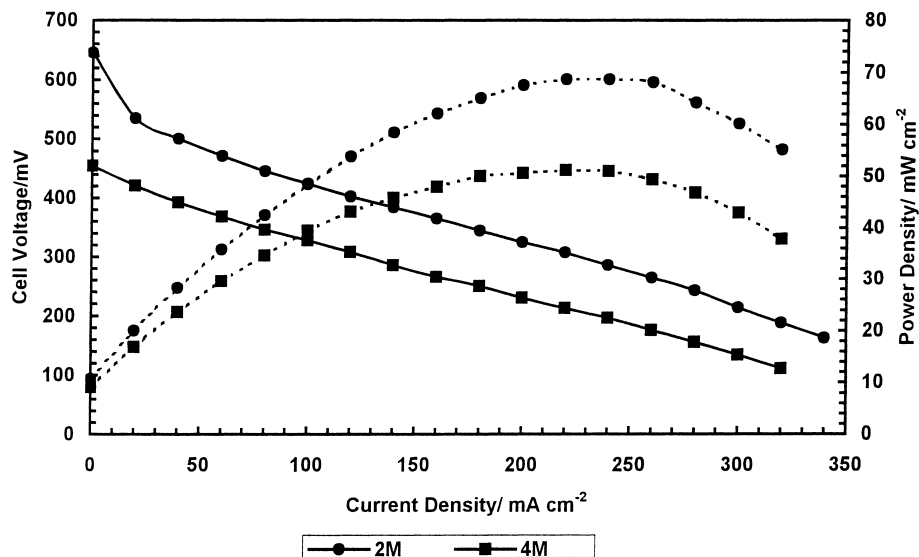


Fig. 6. Effect of methanol concentration on the performance of the ETFE 3747P membrane. 90°C, 2 bar air, 1 cm³ min⁻¹ ■: 4M, ●: 2M.

tion. As shown in Fig. 8 the cell is able to deliver a significant power output immediately after MEA installation, a performance which further improves after a short conditioning phase. The stability of this material is, as with the 3747P membrane, a problem in a

longer term operation, which needs to be addressed in subsequent research.

A material, which has potential use in the DMFC, due to its lack of permeability to methanol, is zeolite. As a first step the use of a zeolite membrane,

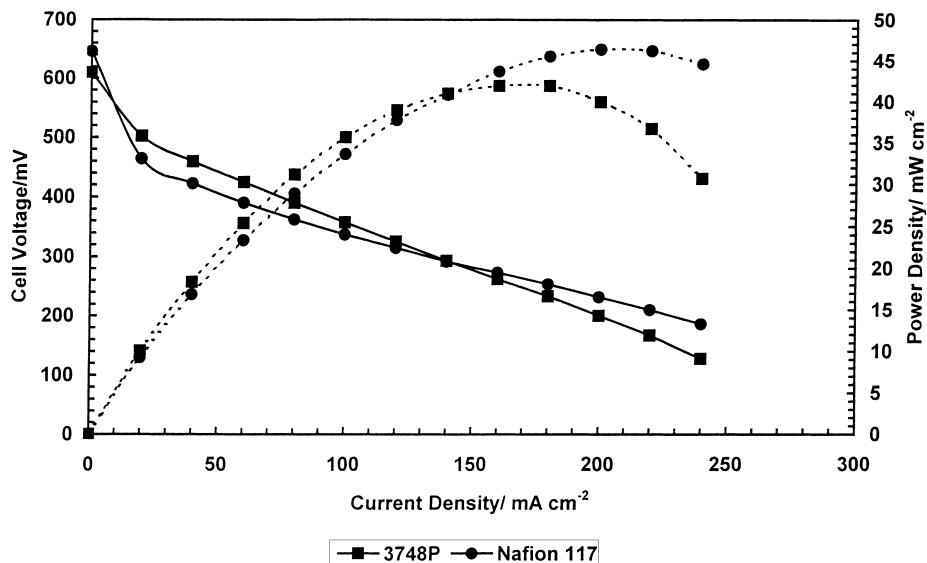


Fig. 7. Comparison of the voltage and power density response of MEAs made with Nafion and LDPE-3748P membranes. 70°C, 2 bar air, 2 mol dm⁻³ methanol, 1 cm³ min⁻¹. ■: 3748P, ●: Nafion 117.

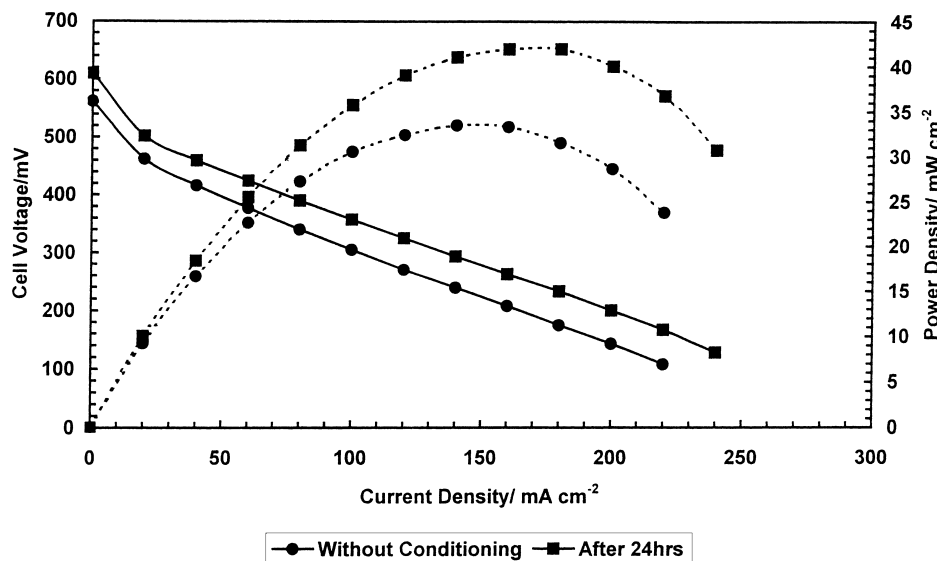


Fig. 8. Effect of conditioning on the voltage and power density response of MEAs made with LDPE-3748P membrane. 70°C, 2 bar air, 2 mol dm⁻³ methanol, 1 cm³ min⁻¹.

designed as a pervaporation membrane and not as a proton-conducting material was investigated. This material exhibited zero permeation of methanol under conditions of operation used in this study. The feasibility of using zeolite materials was demonstrated in the DMFC, at 90°C with a 1.0 M methanol solution, with a potential of 120 mV at a current density of 2 mA cm⁻². Although the performance is negligible it is attributable to the high resistance of the zeolite membrane and relatively poor wetting characteristics. The performance improved when the cathode side was flooded with water: an action which gave a performance up to 10 mA cm⁻². Further research will be needed to produce high proton-conducting forms of zeolite membrane for potential use in the DMFC.

4. Conclusions

This research has characterised radiation-grafted solid polymer membrane materials, which have potential applications in the DMFC. The power performance of MEAs constructed from these materials is as good, and superior at higher current densities, as those made with Nafion. A major issue is the stability

of MEA in terms of lamination of catalyst layer to the membrane surface.

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