POLYMERS FOR ADVANCED TECHNOLOGIES
Polym. Adv. Technol. **13**, 381–390 (2002)
DOI:10.1002/pat.202

Comparison of Fuel Cell Performance of Selected Fluoropolymer and Hydrocarbon Based Grafted Copolymers Incorporating Acrylic Acid and Styrene Sulfonic Acid

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ABSTRACT

Fuel cell tests have been carried out on ion exchange membranes produced by the radiation grafting of either acrylic acid or styrene monomers (followed by a sulphonation reaction) onto selected hydrocarbon and fluoropolymer films. Relationships between the membranes' intrinsic properties, composition, ion exchange capacity and equilibrium water content and their respective fuel cell performance have been established. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: solid polymer electrolyte fuel cells; graft copolymers; styrene sulfonic acid; acrylic acid

INTRODUCTION

The idea and basic concepts of a fuel cell are becoming very familiar to the popular press as a possible environmentally-friendly method for producing power as an alternative to the internal combustion engine (ICE) [1, 2]. The solid polymer electrolyte fuel cell (SPEFC) has been suggested as one of the best systems to achieve this aim. This fuel cell, with a solid electrolyte, runs at temperatures from ambient to ~100 °C, has a relatively high power density and the only waste by-product (if the cell is run on hydrogen and oxygen/air) is water [3]. However, for the SPEFC to be a viable option to replace the ICE, the cost of the power has to be comparable (~\$50–60/kW) [4]. Although much research has been carried out on the components for SPEFCs, a drastic cost reduction is essential for them to be considered a viable option. One of the more expensive components is the solid polymer electrolyte (SPE) or ion exchange membrane.

Traditionally, the membranes used in SPEFCs, e.g. in the Gemini missions in the 1960s, were based on membranes such as Nafion™ [3], a polymer with a PTFE backbone and perfluorosulfonic acid side chains. These were designed originally for the chloro-alkali process. Today specialist membranes are being developed specifically for fuel cells, e.g. Gore-Select®, BAM3G. However, due to the nature of these materials and the relative market monopoly, their cost remains high, in the order of \$600–800 m^{-2}. For the membranes to be cost effective, this has to be reduced by an order of magnitude [5].

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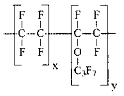
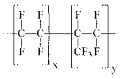
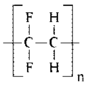
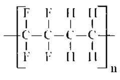
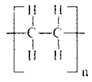
Received 14 May 2001
Revised 11 July 2001
Accepted 17 July 2001

TABLE 1. Base Polymers used for Grafting

Polymer	*Abbreviation*	*Structure*
Tetrafluoroethylene-perfluoroalkoxy vinyl ether	PFA	 $-[CF_2-CF_2]_x-[CF_2-CF(OC_3F_7)]_y-$
Fluorinated ethylene propylene	FEP	 $-[CF_2-CF_2]_x-[CF_2-CF(CF_3)]_y-$
Polyvinylidenefluoride	PVDF	 $-[CF_2-CH_2]_n-$
Ethylene-tetrafluoroethylene	ETFE	 $-[CF_2-CF_2-CH_2-CH_2]_n-$
Low density polyethylene	LDPE	 $-[CH_2-CH_2]_n-$

One method of producing ion exchange membranes is by radiation grafting. Polymers with the appropriate mechanical properties can be modified with suitable monomers to convey the desirable chemical properties. The grafting of acrylic acid (AA) onto hydrocarbon polymers has been used extensively to produce successful ion exchange membranes for the alkaline battery industry [6]. The grafting of styrene onto a polymer backbone, followed by subsequent sulfonation of the grafted groups has also been studied by many groups [7–9] as a possible contender for fuel cell membranes.

This paper looks at the fuel cell performance of a range of AA and styrene (sulfonated) grafted polymers. It will show that the fuel cell performance can be correlated with the membrane's intrinsic properties, such as composition and ion exchange capacity (IEC).

The fuel cell testing and membrane electrode assembly (MEA) preparation reported in this paper was kindly carried out at Loughborough University of Technology.

EXPERIMENTAL

Membrane Preparation

A range of membranes was synthesized using the radiation grafting technique using the polymers shown in Table 1. Essentially, the polymers are irradiated using a Cobalt 60 gamma source to a known total dose, either in the presence of monomer (mutual or simultaneous grafting), or in air to form peroxy radicals which are then reacted at temperature in the presence of a monomer (pre-irradiation grafting; PIG). The preparation and characterization of the membranes has been described elsewhere in more detail [10, 11].

Mutual Grafting Technique

Pieces of polymer were interleaved with a non-woven material, placed in a glass grafting tube and filled with monomer solution until the complete roll was saturated and covered. The oxygen in the vessel was then removed by purging with nitrogen. The irradiation was carried out at $23 \pm 1\,^{\circ}C$ in a Cobalt 60 gamma source for a predetermined time at a known dose rate. Once grafted, the films were washed to remove any homopolymer prior to drying to constant weight. The degree of grafting (DOG) was then calculated.

Pre-irradiation Grafting (PIG) Technique

The polymer films were first irradiated using a Cobalt 60 source in air at $23 \pm 1\,^{\circ}C$ at a known dose rate to set total doses. The films were then either grafted straight away or stored in a freezer at $-18\,^{\circ}C$ until required.

For the grafting process, pieces of the pre-irradiated polymer were placed in a glass grafting vessel and monomer solution was added until the polymer was covered. The vessel was then purged with nitrogen for 2 hr, sealed and placed in a water bath at a set temperature for a known length of time. The grafted polymers were retrieved, washed and dried to constant weight. The DOG could then be calculated.

A range of copolymers with different DOG using both the techniques could be formed by varying the grafting parameters, such as monomer concentration, dose rate, grafting time, total dose and grafting temperature.

Sulfonation Procedure

Unlike the AA copolymers, the styrene grafted copolymers need to undergo a further reaction, sulfonation, in order to function as ion exchange membranes. A standard sulfonation procedure that was suitable for all the copolymer types was developed and used for all the styrene-grafted films. The dry grafted polymers were immersed in a solution of 5% (v/v) chlorosulfonic acid in dichloromethane, for 2 hr at ambient temperature, after which the films were washed to neutrality using demineralized water.

The AA membranes described in this paper were formed using the mutual technique and the styrene grafted ones using the PIG method.

Characterization Techniques

All the membranes synthesized were characterized by four basic techniques, the DOG (i.e. the composition of the copolymer), electrolytic resistivity (the membrane's ability to conduct ions through its thickness), IEC (the capability of the grafted groups to exchange ions with an outside media) and equilibrium water content (EWC) (the amount of water the copolymer can hold).

Degree of Grafting (DOG)

The DOG was calculated using the following formula:

$$\frac{W_1 - W_0}{W_1} \times 100 = \mathrm{DOG}(\%)$$

where W_1 is the weight of grafted polymer, W_0 is the weight of original polymer.

The result has a maximum of 100% and is a measure of the amount of monomer present, i.e. a copolymer with a DOG of 50% consists of 50% original polymer and 50% grafted monomer.

Areal Electrolytic Resistivity

The electrolytic resistivity of the membranes was measured using a technique similar to that employed by Salkind and Kelly [12]. The membrane was placed in a thermostatically controlled cell at a temperature of 25 ± 1 °C An external torque clamp was used to ensure that the membranes were not compressed during testing.

The membrane samples were equilibrated in the chosen electrolyte (0.1 M HCl) for a minimum of 16 hr. The resistivity measurements were taken using a Wayne Kerr Universal Bridge, Model B642 at a frequency of 1591.5 Hz, over a known test area. For each membrane, two samples were tested and the results averaged. The membrane resistivity was then calculated, taking into account the resistivity of the electrolytic path with no membrane present and the area of the sample.

Ion Exchange Capacity (IEC)

The method used to measure the IEC was developed from procedures described in the literature [13–15]. Approximately 0.5 g of the membrane was equilibrated in 0.1 M HCl solution for at least 24 hr at ambient temperature. The sample was then blotted dry and placed in 50 ml of a known molarity NaOH solution (nominally 0.1 M) and allowed to exchange for a further 24 hr at ambient temperature with occasional swirling. Aliquots of the exchanged solution were then titrated to a phenolphthalein end-point against a known molarity HCl solution. The molarity of the NaOH solution after the exchange was then calculated. The procedure was carried out in triplicate and the results averaged. The sample pieces in the exchange were then blotted dry and placed in a vacuum oven at 105 ± 5 °C and weighed to constant weight.

Equilibrium Water Content (EWC)

The EWC of the membranes was measured by immersing the membrane ($0.1\ \mathrm{m} \times 0.15\ \mathrm{m}$) in demineralized water for a minimum of 16 hr at ambient temperature. The hydrated membrane was blotted dry, weighed and measured using a ruler and then dried to constant weight. The dry membrane was then re-weighed and re-measured. The EWC was then calculated as a function of the hydrated state, i.e.,

$$\frac{(\text{hydrated weight}) - (\text{dry weight})}{(\text{hydrated weight})} \times 100 = \mathrm{EWC}(\%)$$

The equilibrium water content influences both the electrolytic resistivity in aqueous media, the IEC and the dimensional changes which occur in the material on hydration.

The membranes chosen for the fuel cell study were those that showed promising properties, including low electrolytic resistivity, high IEC and high EWC. A list of the membranes used and some of their properties is given in Table 2.

Membrane Electrode Assembly (MEA) Preparation

As there was no previous experience of forming these types of membranes into MEAs, they were fabricated in a similar fashion to that developed

TABLE 2. Membranes Submitted for Fuel Cell Testing

Base polymer thickness (μm)	Experiment number	Composition	DOG (%)	IEC (meq g^{-1}) (Na^+ form) (SD)	Electrolytic resistivity in 0.1 M HCl (Ω cm^2)	EWC (%)
50	2651	FEP-g-AA	31	4.197 (0.121)	2.186	—
50	2657	PFA-g-AA	26	2.611 (0.061)	3.924	58
125	2697P	LDPE-g-styrene (sulfonated)	9	0.719 (0.054)	0.280	25
50	2685P	ETFE-g-styrene (sulfonated)	14	0.700 (0.021)	0.338	22
50	2688P	PFA-g-styrene (sulfonated)	17	1.070 (0.045)	<0.001	28
50	2689P	FEP-g-styrene (sulfonated)	19	1.300 (0.035)	<0.001	36
50	2690P	ETFE-g-styrene (sulfonated)	34	2.235 (0.046)	<0.001	45
50	2691P	PVDF-g-styrene (sulfonated)	33	1.509 (0.131)	<0.001	46
175	Nafion® 117	Commercial membrane	—	0.876	—	—

and used for the standard Nafion® membranes [16].

The membranes were first equilibrated in demineralized water for 24 hr at ambient temperature and dried. The gas diffusion electrodes (E-TEK®, 0.35 mg cm^{-2} Pt) were coated with solubilized Nafion® 1100 solution (9 mg cm^{-2}). The membranes were sandwiched between them and bonded at high temperature (100–120 °C) and pressure (2–6 MPa). The resultant MEA had an electrode area of 7 cm^2.

This preparation technique was shown to be fairly harsh and some of the membranes did not form laminated MEAs, although this may have been exaggerated by previous damage to the polymer backbone during the radiation grafting process.

Fuel Cell Testing

Both types of membrane were tested under similar cell conditions, i.e. unhumidified hydrogen and oxygen at temperatures between 25 and 55 °C. The AA based membranes were run at 1 bar hydrogen (gauge) and 2 bar oxygen (gauge), and the sulfonic acid membranes at 1 bar hydrogen (gauge) and 1 bar oxygen (gauge). Although carried out under slightly different conditions, for each fuel cell test a Nafion® 117 membrane was used as a standard. The MEAs were placed in the single cell, and after in-cell conditioning for several hours, polarization data were recorded at various cell temperatures. These conditions were standardized for fuel cell operation at Loughborough and were not specifically optimized for these membranes.

TABLE 3. Summary of Fuel Cell Test Results

Experiment number	MEA produced	OCV (V)				25°C, I (mA cm^{-2})		55°C, I (mA cm^{-2})	
		21°C	50°C	25°C	55°C	0.7 V	0.5 V	0.7 V	0.5 V
Nafion 117 (1)	Yes	0.9	0.9	—	—	—	—	—	—
2651	Yes	0.190	—	—	—	—	—	—	—
2657	Yes	0.650	0.750	—	—	—	—	—	—
Nafion 117 (2)	Yes	—	—	0.969	0.953	37	137	67	197
2697P	Yes	—	—	0.952	0.933	25	52	30	62
2685P	Yes	—	—	0.822	0.862	47	197	106	327
2688P	No	—	—	—	—	—	—	—	—
2689P	No	—	—	—	—	—	—	—	—
2690P	Yes	—	—	0.738	0.787	21	276	100	532
2691P	Yes	—	—	0.873	0.900	70	296	120	504

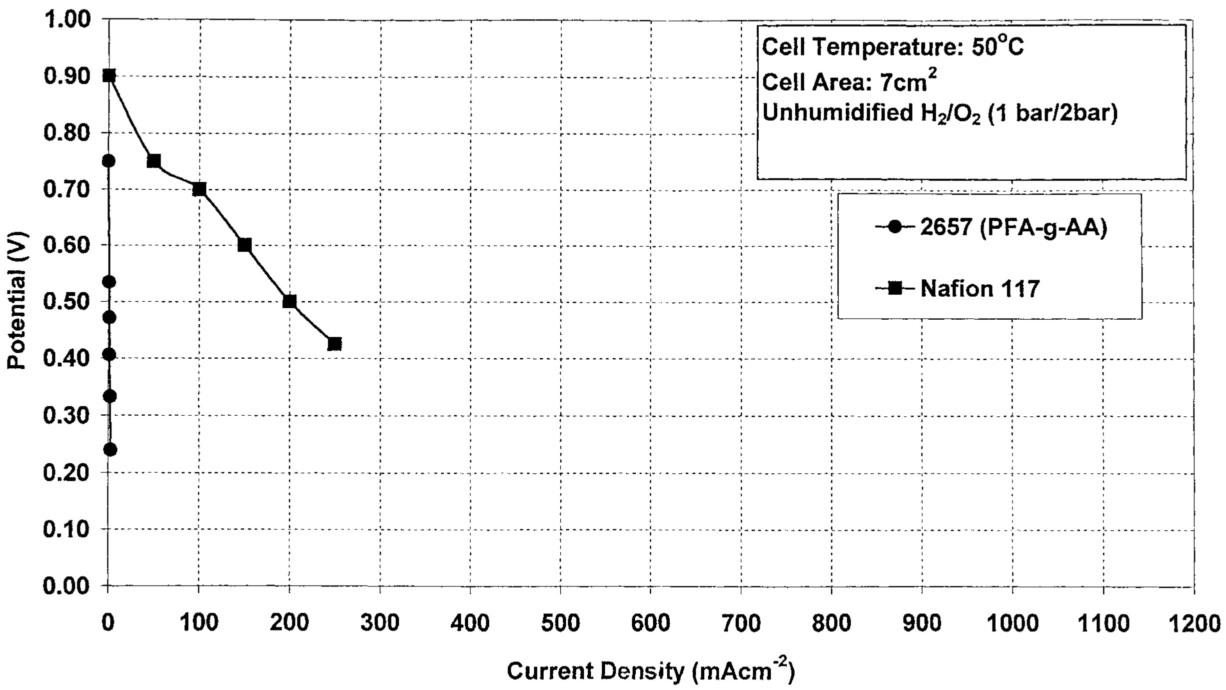


FIGURE 1. Polarization curve of AA grafted membrane.

RESULTS

Fuel Cell Results

A summary of the results can be seen in Table 3. The AA based membranes showed very poor fuel cell performance. The MEA fabricated with membrane 2651 (FEP-g-AA) had a very poor open circuit voltage (OCV) of 0.190 V (cf. Nafion® 117 MEA OCV ~0.9 V) and was unable to sustain any current flow.

The other AA based MEA, 2457 (PFA-g-AA) showed a slightly higher OCV (~0.6–0.75 V) and was able to sustain a very small current flow of ~1 mA cm^{-2} at a cell voltage of 0.5 V. This is clearly shown in the polarization curve in Fig. 1.

The sulfonic acid based membranes were more successful, although two of the membranes based on PFA and FEP failed to form satisfactory MEAs. This is thought to result from the grafting process. It is believed that these polymers are prone to scission reactions when irradiated in the presence of oxygen and other workers have reported similar problems [17].

From Table 4 and the polarization and power density curves (Figs 2–5), three of the sulfonic acid membranes gave performances (under the given conditions) at current densities superior to that of Nafion® 117.

Relating Fuel Cell Performance to Membrane Properties

Previous work [11] has shown that for the styrene grafted sulfonic acid membranes, properties such as IEC and EWC can be related to the DOG as well as to each other. This can be shown even for the limited number of membranes under investigation here (Figs 6 and 7). It was thought that these properties might also relate to the membrane performance. From the power density curves (Figs 3 and 5), the maximum power density achieved by

TABLE 4. Maximum Power Density Achieved by the Sulfonic Acid Membranes

Experiment number	*Maximum power density @ 25°C(mW cm^{-2})*	*Current density (mA cm^{-2})*	*Maximum power density @ 55°C (mW cm^{-2})*	*Current density (mA cm^{-2})*
2697P (LDPE)	23	40	23	80
2685P (ETFE)	112	250	179	380
2690P (ETFE)	280	1000	352	1100
2691P (PVDF)	182	650	363	1100
Nafion® 117	79	175	106	280

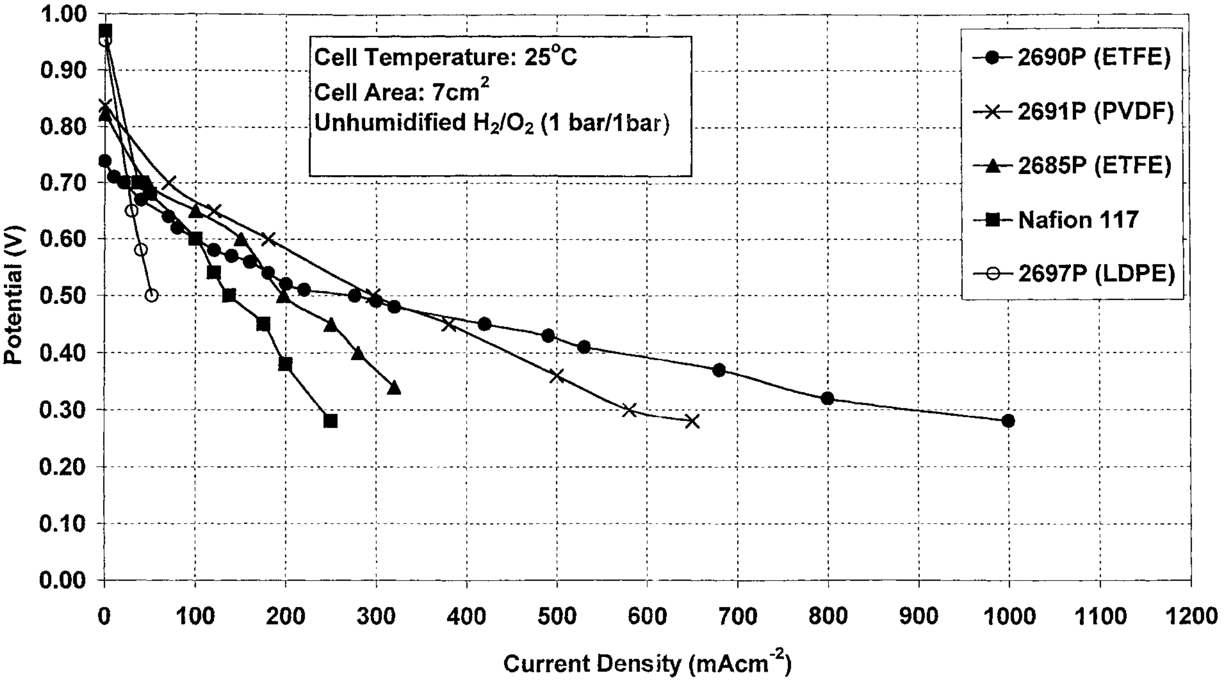


FIGURE 2. Polarization curve of styrene sulfonic acid grafted membranes at 25 °C.

each membrane can be determined. The values are shown in Table 4 compared with their respective current densities. Plotting the maximum power against the measured IEC for each membrane, results in the graphs shown in Figs 8 and 9. It can be seen that there appears to be a clear relationship between the measured IEC and the membrane's fuel cell performance in all cases except for the membrane based on LDPE.

DISCUSSION

Although other work [18] alludes to the fact that strong acid SPEs are required for fuel cell use, no literature could be found to suggest that the carboxylic acid group would not work in an SPEFC. However, the tests on the AA based membranes were unsatisfactory; showing a very low OCV and a poor current density of ~1 mA cm^{-2}.

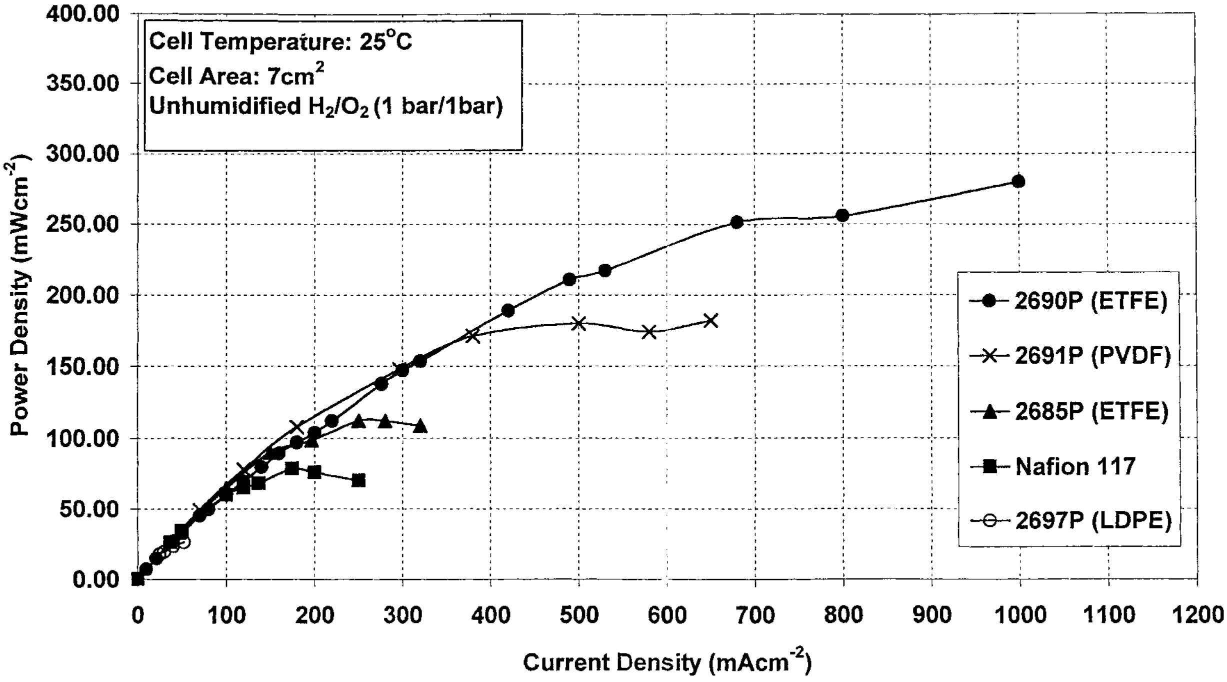


FIGURE 3. Maximum power density v. current density for the styrene sulfonic acid grafted membranes at 25 °C.

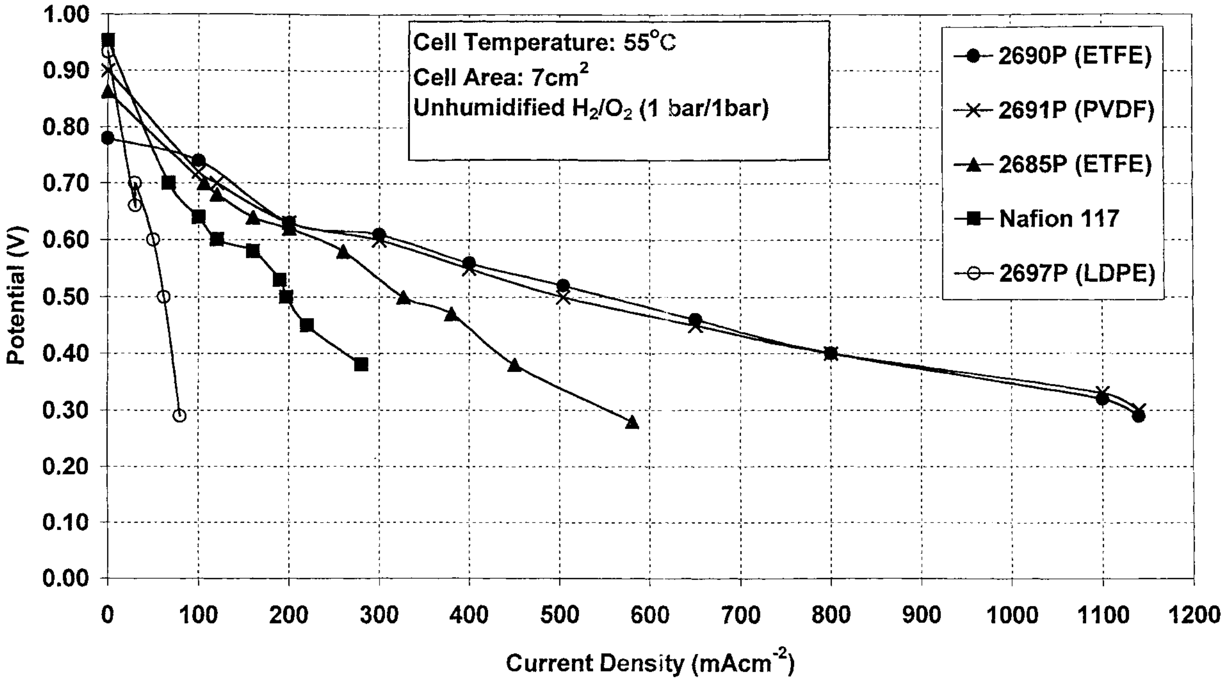


FIGURE 4. Polarization curve of styrene sulfonic acid grafted membranes at 55 °C.

The reason for this poor performance is thought to be because the carboxylic acid group is a weak acid. Hence in the proton-rich environment of the fuel cell, the carboxylic acid group does not dissociate, and so there is no mechanism for proton conduction. A current flow cannot therefore be sustained.

Tests with the sulfonic acid based membranes were much more successful. The fluoropolymer membranes gave better polarization curves than Nafion^(TM) 117, especially when the fuel gases were not humidified. It is well known that Nafion^(TM) 117 requires a certain level of hydration for it to function well in a fuel cell if the pore-cluster model [19] is to be believed. The grafted membranes had a high IEC and it has been shown that

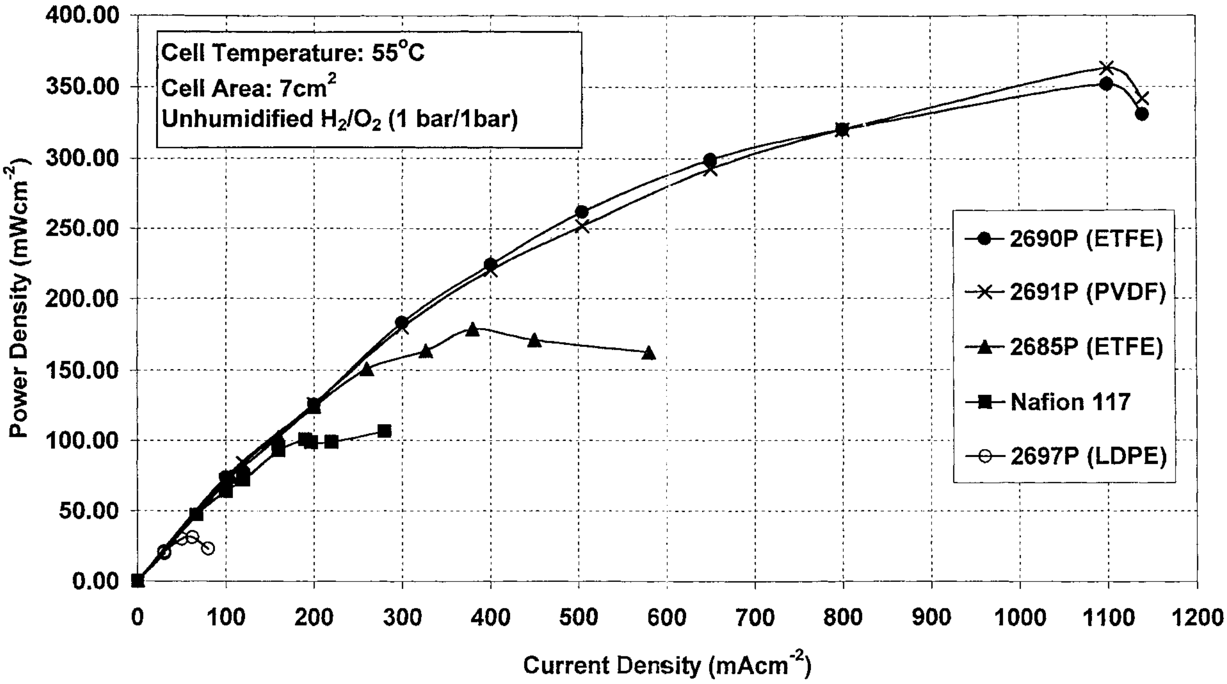


FIGURE 5. Maximum power density *v.* current density for the styrene sulfonic acid grafted membranes at 55 °C.

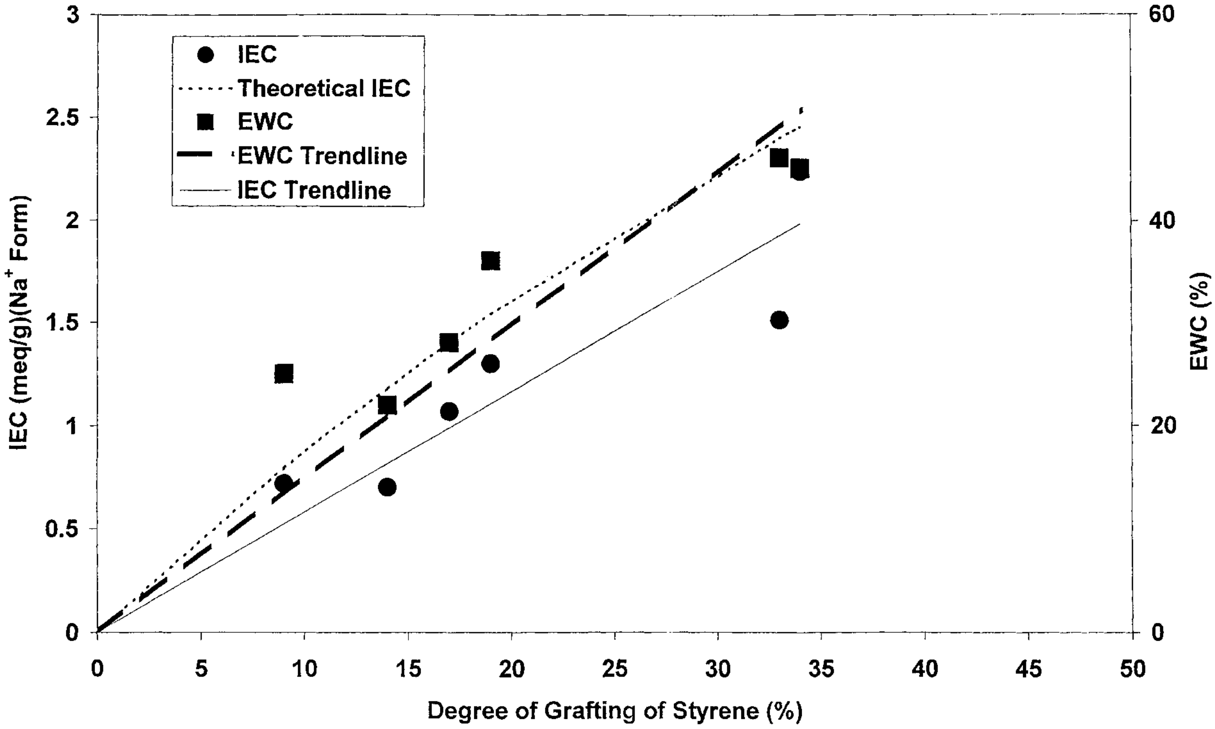


FIGURE 6. Relationship between IEC, EWC and DOG of styrene.

this is related to the membranes' EWC [11]. Hence, the styrene sulfonic acid grafted membranes reported here can absorb water more easily than Nafion® 117 and this gives them a better comparable performance in a water-starved environment, i.e. when the fuel gases are unhumidified. The thickness of the Nafion® 117 (175 μm) and LDPE based copolymer (125 μm) compared to the other

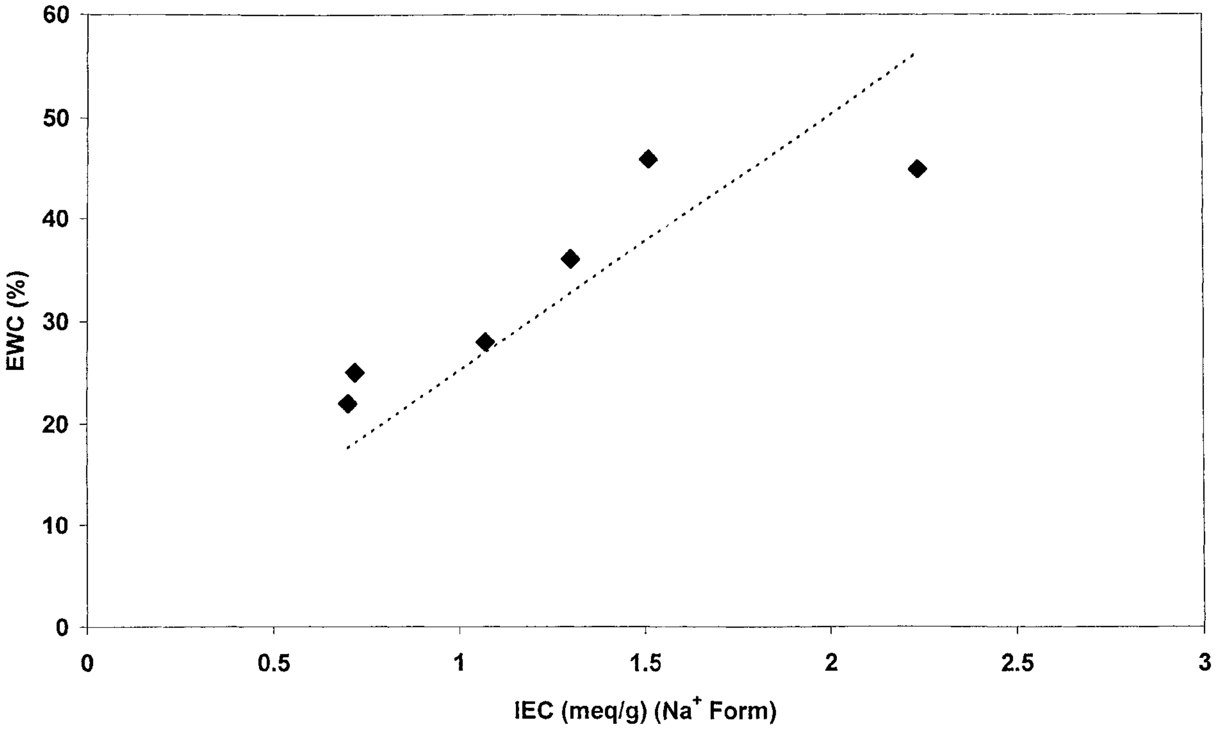


FIGURE 7. Relationship between measured IEC and measured EWC.

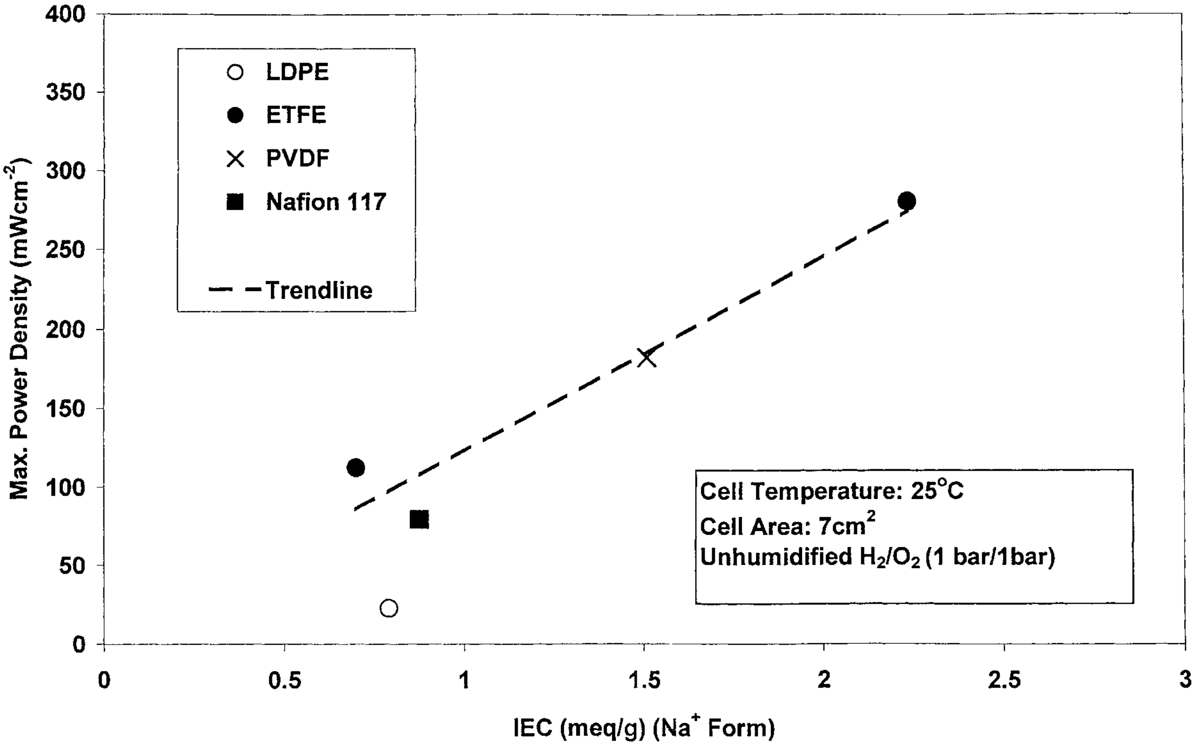


FIGURE 8. Relationship between measured IEC and maximum power density achieved in fuel cell at 25 °C.

membranes (50 µm) should also be taken into account, as their resistivity should be higher as thickness is related to conductivity and may be contributing to the poorer performance.

In order to compare the membrane properties with fuel cell performance, the maximum power density can be plotted against the measured IEC of the test membrane. From the limited number of fuel

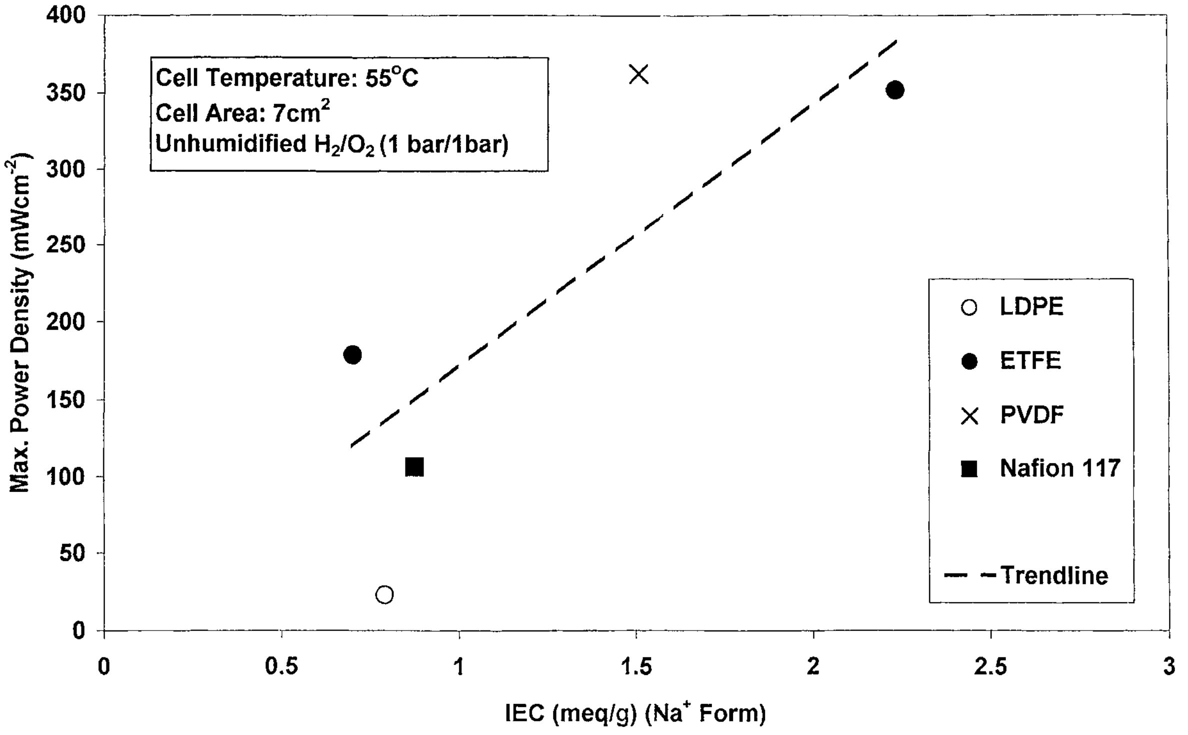


FIGURE 9. Relationship between measured IEC and maximum power density achieved in fuel cell at 55 °C.

cell tests performed, it can be seen in Figs 8 and 9 that there is a strong indication that as the IEC of the membrane increases, then so does the maximum power density. It is also found that Nafion™ 117 fits the trend, but the hydrocarbon based membrane does not. It is therefore suggested that it is important to have fluorine present in the polymer backbone. Its electronegative nature may enhance the membranes performance compared to the hydrocarbon membrane. However, other than this, these results suggest that it is not the backbone polymer that decides the membrane performance, but the quantity of sulfonic acid groups available for ion exchange, which in turn affects the EWC. Although the Nafion™ membrane has a very different composition to that of the graft copolymers, the fact that it follows the same trend may be an indication that the mechanism of proton transfer through the membrane is the same irrespective of the membrane's detailed composition. This indicates that the pore-cluster model may also hold for the graft copolymer membranes.

CONCLUSIONS

The AA grafted membranes performed poorly in fuel cells, probably due to their inability to ionize in the strong acid environment of the fuel cell. They were therefore unable to act as a proton conductor.

The styrene grafted and sulfonated membranes gave good performance in fuel cells, generally better than the standard they were tested against (Nafion™ 117) under the conditions used. This is a reflection of their better proton conduction due to their higher IEC and also their ability to absorb higher amounts of water than the Nafion™ membrane, and to a lesser extent, their reduced thickness.

It has been shown that the membranes performance relates to the IEC and therefore to its DOG of styrene and its EWC. Therefore, it should be possible to predict fuel cell performance from these laboratory measurable properties for the fuel cell conditions used.

From the work carried out this relationship suggests that the precise composition of the backbone polymer is not important (as long as some fluorine atoms are present). The membrane's fuel cell performance is based upon the number of sulfonic acid groups available for ion exchange. As this is linked to the DOG, it is concluded that the backbone polymer is only acting as a "scaffold" for the sulfonic acid groups. Therefore, as long as a stable graft copolymer can be synthesized to the desired DOG, the backbone polymer can be chosen for its other desirable properties, e.g. low cost, mechanical strength, high chemical resistance.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the help of Dr Jon Moore, Dr Damian Davies and Mrs Philippa Gladding of Loughborough University of Technology for MEA preparation and fuel cell testing. This work was funded by EPSRC under grant number GR/K 31848.

REFERENCES

1. Easton K. Fuelling some of the people some of the time. *The Times* 25 November 2000.
2. English A. The car that will save the world. *The Sunday Telegraph* 20 March 1999.
3. Blomen LJLM, Mugerwa MN (eds). *Fuel Cell Systems*. Plenum Press: New York, 1993.
4. Chalk SG, Venkateswaran SR. *Breaking Down the Barriers to Commercialization of Fuel Cells in Transportation through Government-Industry R&D Programs*. Proceedings of the 1996 Fuel Cell Seminar, 17–20 November, Orlando, FL, 1996; 258–261.
5. Inzelt G *et al.* Electron and proton conducting polymers: recent developments and prospects. *Electrochim. Acta* 2000; **45**: 2403–2421.
6. Charlesby A. UK Patent 1,588,6254, 1976.
7. Gupta B *et al.* Cation exchange membranes by pre-irradiation grafting of styrene into FEP films. I. Influence of synthesis conditions. *J. Polym. Sci.: Part A: Polym. Chem.* 1994; **32**: 1931–1938.
8. Nezu S *et al. High Performance Radiation-Grafted Membranes and Electrodes for Polymer Electrolyte Fuel Cells*. Proceedings of the 1996 Fuel Cell Seminar, 17–20 November, *Orlando*, FL, 1996; 620–627.
9. Holmberg S *et al.* Synthesis and properties of sulfonated and crosslinked poly[(vinylidene fluoride)-graft-styrene] membranes. *Polym. Adv. Technol.* 1998; **9**: 121–127.
10. Horsfall JA, Lovell KV. Synthesis and characterisation of acrylic acid grafted hydrocarbon and fluorocarbon polymers using the simultaneous or mutual grafting technique. *J. Appl. Polym. Sci.* submitted for publication.
11. Horsfall JA, Lovell KV. Synthesis and characterisation of sulphonic acid-containing ion exchange membranes based on hydrocarbon and fluorcarbon polymers. *European Polym. J.* submitted for publication.
12. Salkind A, Kelly J. *Characteristics of Separators for Alkaline Silver-Oxide/Zinc Secondary Batteries*. US Air Force Manual, 1964.
13. Wycisk R, Trochimczuk WM. Polyethylene-poly-(methacrylic acid-co-divinyl benzene) interpolymer-type carboxylic membranes. *J. Appl. Polym. Sci.* 1991; **43**: 1727–1735.
14. Byun HS *et al.* Sulfonation of cross-linked asymmetric membranes based on polystyrene and divinylbenzene. *J. Appl. Polym. Sci.* 1994; **52**: 825–835.
15. Mohammadi T, Skylls-Kazacos M. Characterisation of novel composite membranes for redox flow battery applications. *J. Membr. Sci.* 1995; **98**: 77–87.
16. Lee SJ *et al.* Effects of Nafion™ impregnation on performances of PEMFC electrodes. *Electrochim. Acta* 1998; **43**: 3693–3701.
17. Kiefer J *et al. Radiation-Grafting: A Versatile Membrane Preparation Tool for Fuel Cell Applications*. Proceedings of Portable Fuel Cells, 21–24 June, *Lucerne*, 1999; 227–235.
18. Scherer GG. Polymer membranes for fuel cells. *Berichte der Bunsengesellschaft fur Physikalische Chemie* 1990; **94**: 1008–1014.
19. Eisenberg A, Yeager HL (eds). *Perfluorinated Ionomer Membranes*, ACS Symposium No. 180. American Chemical Society: Washington, DC, 1982.