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Targeting improved DMFC performance

L.J. Hobson*, Y. Nakano, H. Ozu, S. Hayase

Corporate Research and Development Centre, Toshiba Corporation, 1 Komukai, Toshiba-cho, Saiwai-ku, Kawasaki 212-8582, Japan

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Abstract

Improved DMFC performance through reduction in the extent of methanol crossover in the polymer electrolyte membrane is described. Introduction of a thin barrier layer of polybenzimidazole (PBI) at the Nafion®117 surface by screen printing is shown to reduce methanol permeability whilst maintaining proton conductivity at a level comparable to that of the parent material. Experimental trials using these Nafion®117/PBI composite films show improved DMFC performance; an increased working current density range of 42% combined with an increase in maximum power output of 46% over that of the parent material.

Keywords: Direct methanol fuel cell (DMFC); Nafion®117; Polybenzimidazole (PBI); Screen printing; Methanol crossover; Polymer electrolyte membrane

1. Introduction

The reduced performance of the direct methanol fuel cell (DMFC) due to methanol crossover is well established [1–5]. Particularly significant in terms of the liquid feed cell, methanol permeation to the cathode is primarily responsible for reduction in the open current voltage (OCV) of the cell, as illustrated in Fig. 1. As shown experimentally for Nafion®117 films, Fig. 1, a reduction in OCV in the order of 50%, from 0.6462 to 0.3621 V at 6.4 and 20 wt.% methanol, respectively, makes adequate DMFC performance for commercial applications unobtainable.

Aside from Nafion®117, numerous alternatives have been investigated to determine their potential as polymer electrolyte membranes for DMFC, ranging from similar commercial ion exchange membranes [6,7] to those based on polyetheretherketone (PEEK), polysulfone Udel® (PSU) [8] and polyethylene [9]. But to date the challenge of combining inherent conductivity with a low permeability to methanol remains.

Despite factors to advocate the development of new materials, including the current high cost of Nafion®117 and its loss of mechanical properties at elevated temperatures, a high proportion of research in the field is directed at modification of such commercial films. The approaches described are diverse, ranging from treatment with phosphoric acid [10], doping with inorganic ions [11] and formation of Nafion®117 based organic/inorganic composites [12] to the in situ polymerisation of imbedded polymer precursors [13]. We recently reported the use of low dose electron beam exposure to modify the surface structure and create a selectively permeable methanol barrier at the film surface [14]. By this technique improvements of up to 50% were observed in subsequent DMFC performance (in terms of maximum power output) over use of the unmodified parent material, Nafion®117. This strategy relied on establishing a thin methanol impermeable barrier at the film surface. Other recent publications describing a similar approach include applying plasma polymerisation [15] or the application of a polybenzimidazole (PBI) layer by spray coating or the layering of solution cast films [16].

The use of acid doped PBI as a polymer electrolyte membrane is attractive in terms of thermal and oxidative stability but in order to attain the necessary mechanical flexibility and proton conductivity the DMFC has to be operated at temperatures in excess of 200 °C. Working in the operating temperature range of 60–80 °C, despite negligible methanol permeability, the proton conductivity of PBI is too low for it to be considered a viable option as the main component of the membrane. Film conductivity is explainable mechanistically. Nafion®117 is assigned to the vehicle mechanism, by which protons are transported through the membrane accompanied by another molecular species, i.e. H_3O^+, $H_5O_2^+$ or $CH_3OH_2^+$. Materials assigned to this mechanism generally show a high degree of methanol crossover and high conductivity, which accurately describes the properties of Nafion®117. Conversely PBI exhibits low conductivity and a low permeability to methanol (determined experimentally by us to be 2.4% of that of

* Corresponding author. Tel.: +81-44-520-1286.
E-mail address: hobson@sub1.rdc.toshiba.co.jp (L.J. Hobson).

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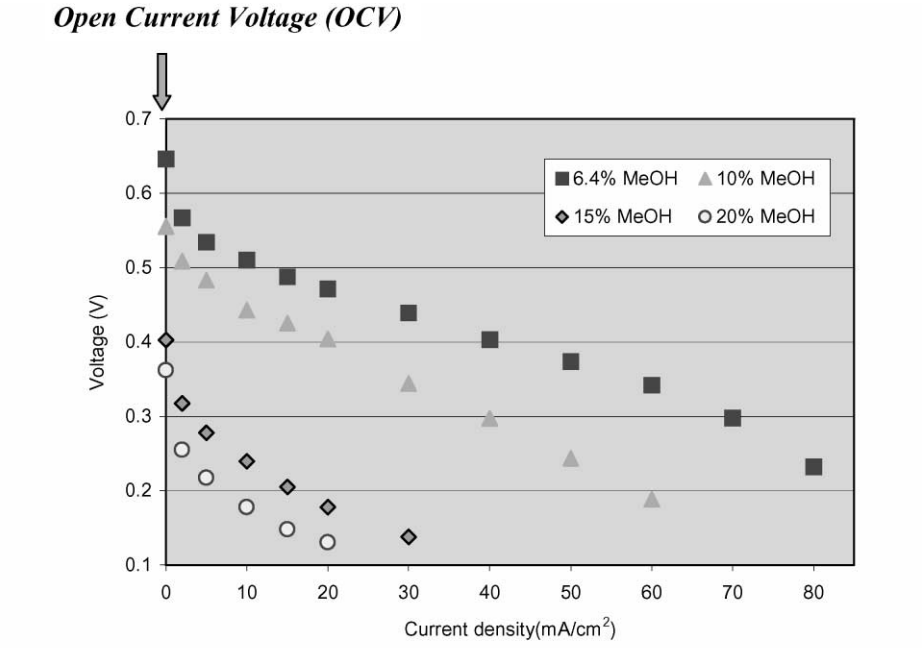

Fig. 1. Effect of methanol concentration on voltage/current density profile for Nafion®117 films.

Nafion®117), behaviour described by the Grottus ''jump'' mechanism [17,18]. Theoretically this mechanism can facilitate high proton conductivity but in practice this is an anomaly. Deluga and Pivovar [16] showed that combination of a thin layer of PBI (∼20 μm) with Nafion®117 (∼50 μm) was more effective than PBI alone. However, despite reducing methanol crossover to the cathode, DMFC performance of these composite membranes was still beneath that of Nafion®117, the accepted benchmark. In contrast herein we report that using an alternative method to combine Nafion®117 and PBI in very different proportions, the treatment of Nafion®117 with dilute PBI/dimethylacetamide (DMAC) solutions, can produce films which exhibit a significantly higher DMFC performance than the parent materials.

2. Experimental

2.1. Materials

Nafion®117 films were obtained from DuPont, USA. PBI was obtained as 10% solution in DMAC from Tokaidenka Kogyo Company Ltd., Japan and used as received, without further purification.

2.2. Sample preparation

2.2.1. Preparation of spin coated films

Nafion®117 films, 6 cm × 6 cm, were boiled in water for 1 h, soaked in 10% H_2O_2 for 2 days at RT, in 10% H_2SO_4 for 1 day at RT, washed with distilled water and dried at RT for 1 day. The films were then dipped in DMAC for 5 min, placed on silicon wafer and spin coated with PBI/DMAC solution (5 s at 500 rpm then 30 s at 2000 rpm). After drying at RT for 2 days, the films were boiled in water for 1 h, dried at RT and pressed at 125 °C for 10 min. After boiling in water for further 1 h the films were dried in air for 3–4 h and rehydrated at RT prior to analysis.

2.2.2. Preparation of dipped films

Nafion®117 films, 6 cm × 6 cm, were dipped in PBI/DMAC solutions of known concentration for 15 min at room temperature. The films were removed from the solutions and line dried in air overnight. Excess DMAC was neutralised by soaking in 5% H_2SO_4 for >48 h. The films were then soaked in distilled water overnight prior to analysis.

2.2.3. Preparation of screen printed films

Nafion®117 films, 25 cm × 25 cm, pre-treated with DMAC, were screen printed with PBI/DMAC solution of known concentration and dried at 70 °C for 1 h.

Film samples 6 cm × 6 cm square were prepared and treated in 5% H_2SO_4 and distilled water prior to analysis.

2.3. Film analysis

Conductance of the film samples was determined from impedance data taken after an appropriate equilibrium period, at a frequency of 1 kHz using a Hewlett Packard 4192A-LF impedance analyser. Using methods previously

described in detail [14] reliable comparative conductance data was obtained, using untreated Nafion®117 membrane as a reference material.

Methanol crossover within the film was measured by gas chromatography. The 5 μl portions were extracted from the cathode reservoir of the DMFC (held at room temperature as a stationary system, using a 10% methanol(aq) fuel system) and analysed for their percentage methanol content. The data is presented as the percentage of the initial 10% methanol starting solution detected as having passed through the membrane.

2.4. DMFC operation

All experimental results quote here for MEA performance were taken using a liquid feed DMFC operated at 60 °C with an air flow rate of 60 cm^3/min and methanol feed of 0.6 cm^3/min. During these experiments neither the other DMFC components nor these operating conditions were optimised in terms of DMFC output.

3. Results and discussion

We describe the preparation of alternative Nafion®117/PBI composite materials using dilute PBI/DMAC solutions and relate subsequent film properties to improved DMFC performance. Literature reports show PBI to be an ideal candidate for the introduction of a selectively permeable barrier layer in terms of permeability, electro-osmotic drag and mechanism for proton conductivity. Application of this material to fuel cell technology has previously been investigated but to date such studies have focussed on films >20 μm thick rather than use of the dilute solutions described here.

From preliminary experiments to investigate the effects of treating Nafion®117 film with dilute PBI/DMAC solutions by spin coating (Table 1) or dipping the films directly (Table 2) we can conclude that the dependence of methanol crossover on % PBI applied is not the simple linear relationship first predicted. First considering films prepared by spin coating, comparison of sample SC1 with the reference film shows that pre-treatment with DMAC actively increases methanol crossover. Having accounted for the initial rise, permeability is subsequently reduced as we increase PBI concentration. At concentrations of 2.5 wt.% and higher, the effect of PBI predominates and methanol crossover falls to levels lower than that of the parent material. Under these specific experimental conditions a 5% PBI solution provides the best result, reducing crossover to 42% of that of the untreated film.

In contrast, behaviour of the Nafion®117 samples dipped in PBI solution is less well defined. From the experimental data recorded in Table 2 we observe a clear minima in the relationship between % PBI applied and rate of crossover, corresponding to 0.1% PBI concentration. By either technique, treatment with PBI can be shown to be effective in reducing extent of methanol crossover. Tables 1 and 2 indicate that crossover can be reduced to in the order of 50% of that of the parent material. However, these materials are unsuitable for polymer electrolyte membranes as their impedance is too high for the benefits of reduced methanol

Table 2
Effect of dipping in PBI/DMAC on methanol crossover in Nafion®117 film[a]

Sample no.	% PBI	GC results, using 10 wt.% methanol solution at RT	
		(% MeOH min^{-1})[b]	% Crossover relative to that of Nafion®117
DP1	0	0.286	100
DP2	0.01	0.186	65
DP3	0.05	0.165	58
DP4	0.10	0.126	44
DP5	0.20	0.133	46
DP6	0.40	0.165	58
DP7	1.00	0.161	56
DP8	2.50	0.187	65

[a] Samples dipped in solutions of PBI in DMAC for 15 min at RT. The films were then allowed to dry hanging under atmospheric conditions before excess DMAC was neutralised by soaking for >48 h in 5% H_2SO_4(aq) followed by water for >24 h.

[b] The units % MeOH min^{-1} refer to the percentage of the initial 10% methanol starting solution detected by gas chromatography as having passed through the membrane.

Table 1
Effect of PBI/DMAC spin coating on methanol crossover in Nafion®117 film

Sample no.	% PBI in DMAC solution	GC results, using 10 wt.% MeOH(aq) at RT	
		(% MeOH min^{-1})[a]	% Crossover relative to that of Nafion®117
Nafion®117-reference	No DMAC pre-treatment	0.296	100
SC1	0	0.391	132
SC2	0.1	0.372	126
SC3	1.0	0.443	150
SC4	2.5	0.224	76
SC5	5	0.124	42
SC6	10	0.180	61

[a] The units % MeOH min^{-1} refer to the percentage of the initial 10% methanol starting solution detected by gas chromatography as having passed through the membrane.

Table 3
Effect of PBI/DMAC screen printing on methanol crossover in Nafion®117 film

Sample no.	% PBI	Film performance			
		GC results, 10 wt.% MeOH(aq) at RT		From impedance data taken at 1 kHz	
		% MeOH min^{-1}	% Crossover relative to that of Nafion®117	Impedance relative to that of Nafion®117	% Conductance ($m\Omega^{-1}$) relative to that of Nafion®117
SP1	0.00	0.290	100	1.00	100
SP2	0.005	0.134	46	0.93	108
SP3	0.01	0.148	51	1.43	70
SP4	0.015	0.287	99	3.07	33
SP5	0.02	0.210	72	2.53	40
SP6	0.03	0.181	62	2.61	38
SP7	0.05	0.101	35	3.61	28

permeability to be reflected in terms of DMFC performance. Even MEAs prepared from films treated by dipping in the most dilute PBI solution showed significantly higher impedance levels. Film DP2 (PBI = 0.01%), which reduced methanol crossover to 65%, registered an impedance of 1850 mΩ, 74 times higher than that of Nafion®117, cf. 25 mΩ.

Attempting to reduce the impedance of the membrane/electrode assemblies (MEA) prepared, applying the PBI coating by screen printing techniques was investigated. By this method there should be significantly less penetration of PBI into the film and hence less dramatic losses in terms of conductance. Initial experiments used 2, 0.2 and 0.02 wt.% solutions of PBI in DMAC. Pre-treatment of the film with DMAC was shown to be advantageous not only in terms of ease of handling but it further reduced the loading of PBI on to the film. Subsequently it was determined that the most effective concentration lay between 0.2 wt.% (DMFC impedance 500 mΩ, relative methanol crossover 40%) and 0.02 wt.% (DMFC impedance 33 mΩ, relative methanol crossover 80%). The film screen printed with 0.02 wt.% PBI was tested in a liquid feed DMFC, operating at 60 °C using 10 wt.% methanol. Considering power output as a function of current density the system showed a 40% improvement in maximum power output when compared with use of the parent material under identical conditions.

In order to further optimise film performance a series of Nafion®117 films screen printed with PBI solutions ranging in concentration from 0.00 to 0.05 wt.% were prepared. Using a simple analytical protocol, previously established to allow film properties to be directly related to subsequent DMFC performance [14], the properties of these films relative to Nafion®117 were determined, Table 3.

The effects of PBI concentration on methanol permeability and film conductance are shown in Fig. 2. After a slight

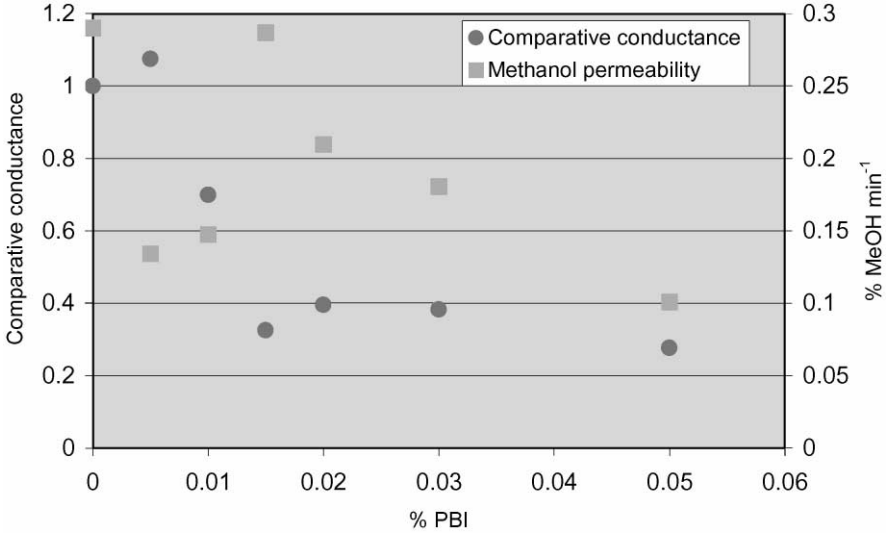

Fig. 2. To show effect of PBI concentration on comparative conductance and methanol permeability. Conductance data ($\Omega\,cm^{-1}$) is reported in terms of arbitrary units, directly compared with conductance measurements recorded for Nafion®117-reference films, (where films of 1.0 are of equal value). Methanol crossover is recorded for a 10% methanol(aq) solution at room temperature in a stationary system. The units % MeOH min^{-1} refer to the percentage of the initial 10% methanol starting solution detected by gas chromatography as having passed through the membrane.

Table 4
Results taken from the comparative DMFC voltage/current density profiles for SP2 and Nafion®117-reference films

Film	MeOH concentration (M)	DMFC impedance (mΩ)	OCV (V)	Maximum power[a] (mW/cm^2)
SP2	2	32	0.6585	21.7
Nafion®117-reference	2	38	0.6462	20.8
SP2	3.2	43	0.610	17.8
Nafion®117-reference	3.2	39	0.555	12.2

[a] Data taken at 60 °C, methanol feed 0.6 cm^3/min, air flow rate 60 cm^3/min.

increase, relative to that of Nafion®117, conductance decreases with increasing PBI concentration until a plateau is reached, corresponding to 0.015% PBI.

In contrast methanol permeability sharply falls at low PBI concentrations, only to return to levels comparable to that of the untreated material at 0.15% PBI and from this point decrease with subsequent increases in PBI concentration. This behaviour pattern at low doses is not unique to PBI, such trends also being observed for the treatment of Nafion®117 films with other chemical modifiers [19].

Film SP2 was identified as exhibiting the film properties most likely to result enhanced DMFC performance; conductance of the same order of magnitude as Nafion®117 combined with reduced permeability to methanol. Its MEA was tested in the DMFC operated at 60 °C (air flow 60 cm^3/min, methanol feed 0.6 cm^3/min) and the results obtained contrasted with those of the untreated film.

Table 4 shows the results of DMFC trials for SP2 and Nafion®117 films, operating at 2 and 3.2 M methanol concentrations. From a comparative study of the voltage/current density profiles for these systems we can show the effect of screen printing with 0.005% PBI on the OCV. At 2 M methanol the improvement is negligible, from 0.6462 to 0.6585 V, which is accompanied by a corresponding decrease in impedance, from 38 to 32 mΩ. Direct measurement of methanol crossover in the DMFC, by monitoring CO_2(g) content of the exhaust gases of the cathode by IR, showed little variation between these two samples. In contrast working at 3.2 M methanol concentration, treatment with PBI is shown to have reduced methanol crossover in the DMFC by approximately 25%. This is also accompanied by an increase in the impedance of the cell, from 39 to 43 mΩ, and an increase in OCV from 0.555 to 0.610 V, of approximately 10%. As during these experiments neither the other DMFC components nor the operating conditions were optimised in terms of DMFC output, it is this relative performance rather than the actual quantitative output of the cell that is of interest.

Fig. 3 shows the comparative power/current density profile for SP2 and Nafion®117 films operating in a liquid feed DMFC at 60 °C. While performance is only nominally better for the screen printed film working at a 2 M methanol concentration, 4% increase in maximum power output over the same range of current density, the situation at 3.2%

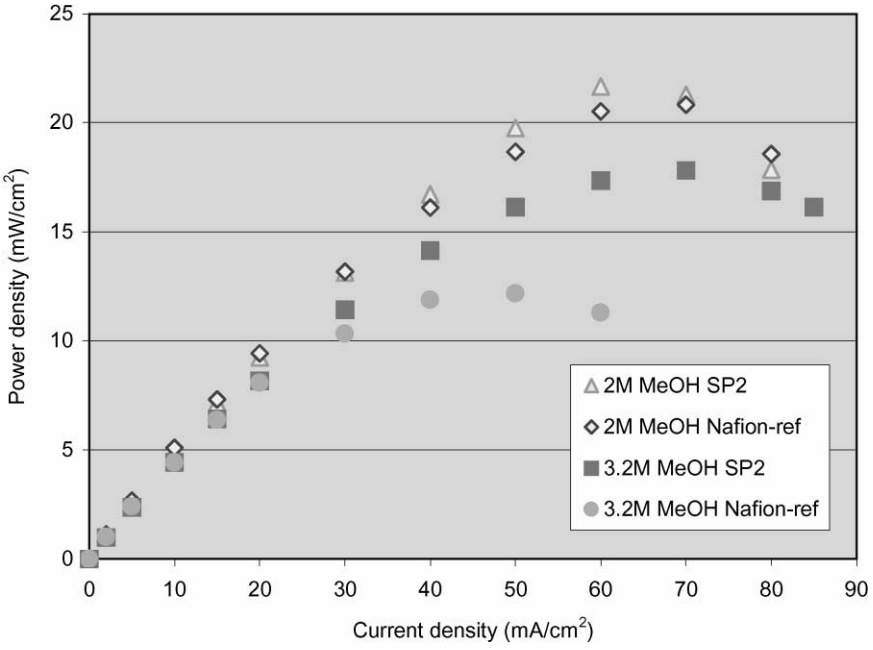

Fig. 3. Power output against current density for SP2 and Nafion®117 films.

methanol concentration is greatly improved. The working current density range is increased by 42% which is combined with an increase in maximum power output of 46% over that of the parent material.

4. Conclusions

In summary we can conclude that treatment with PBI solution reduces the extent of methanol permeability of Nafion®117 films. The semi-permeable barrier created prevents the dramatic reduction in OCV that is synonymous with this material. Screen printing is identified as a viable method to apply the PBI solution which, under the right experimental conditions, does not result in a dramatic increase in the impedance of the resultant MEA. Experimental trials using these materials show improved DMFC performance; an increased working current density range of 42% combined with an increase in maximum power output of 46% over that of the parent material.

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