Nafion/polyaniline/silica composite membranes for direct methanol fuel cell application

Chih-Yuan Chen [a,b], Jairo I. Garnica-Rodriguez [a,b], Mikel C. Duke [a],
Roni F. Dalla Costa [c], Andrew L. Dicks [b], João C. Diniz da Costa [a,b,*]

[a] *FIMLab, Films and Inorganic Membrane Laboratory, School of Engineering, The University of Queensland, Brisbane, Qld 4072, Australia*
[b] *ARC Centre for Functional Nanomaterials, School of Engineering, The University of Queensland, Brisbane, Qld 4072, Australia*
[c] *Universidade Petrobras, RH/UP/ECTEP, Av. Antônio Carlos Magalhães, 1113 – Itaigara, Salvador BA 41.856-900, Brazil*

Abstract

This work investigates the characterization and performance of polyaniline and silica modified Nafion membranes. The aniline monomers are synthesized in situ to form a polyaniline film, whilst silica is embedded into the Nafion matrix by the polycondensation of tetraethylorthosilicate. The physicochemical properties are studied by means of X-ray diffraction and Fourier transform infrared techniques and show that the polyaniline layer is formed on the Nafion surface and improves the structural properties of Nafion in methanol solution. Nafion loses its crystallinity once exposed to water and ethanol, whilst the polyaniline modification allows crystallinity to be maintained under similar conditions. By contrast, the proton conductivities of polyaniline modified membranes are 3–5-fold lower than that of Nafion. On a positive note, methanol crossover is reduced by over two orders of magnitude, as verified by crossover limiting current analysis. The polyaniline modification allows the membrane to become less hydrophilic, which explains the lower proton conductivity. No major advantages are observed by embedding silica into the Nafion matrix. The performance of a membrane electrode assembly (MEA) using commercial catalysts and polyaniline modified membranes in a cell gives a peak power of 8 mW cm^{-2} at 20 °C with 2 M methanol and air feeding. This performance correlates to half that of MEAs using Nafion, though the membrane modification leads to a robust material that may allow operation at high methanol concentration.
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1. Introduction

The direct methanol fuel cell (DMFC) is a specific type of a polymer electrolyte fuel cell (PEMFC) that uses an aqueous solution of methanol as a fuel instead of pure hydrogen. In a DMFC, protons and electrons are produced by the oxidation of methanol at the negative electrode (anode) whilst at the positive electrode (cathode) oxygen reacts with electrons taken from the electrode and with protons from the electrolyte (which in state-of-the-art DMFCs is a Nafion^{TM} membrane) to produce water [1,2]. During the last decade, DMFC research and development has focused on portable power applications such as mobile phones, laptop computers, and portable cameras and games. The long-term goal is to replace high-performance rechargeable batteries in the US$ 6 billion portable electronic devices market, based on the superior theoretical specific energy of methanol (6000 Wh kg^{-1}) compared with that of the best rechargeable battery (lithium-ion polymer: 600 Wh kg^{-1}) [3].

Perfluorosulfonic acid polymer-based membranes have been extensively used as electrolytes in PEMFCs because of their good chemical stability and proton conductivity [4,5]. Nafion has become the preferred electrolyte for DMFC applications due to enormous research efforts during the past 20 years that have produced valuable information about its chemical structure and the mechanisms of both ion and mass transport. Despite the complexity of the chemical structure of Nafion, it is widely accepted that there coexists hydrophilic regions (ion clusters that permit proton migration through the membrane) scattered amongst hydrophobic regions in the polymer backbone, which imparts structural integrity to the membrane and restricts fuel

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* Corresponding author. Tel.: +61 7 3365 6960; fax: +61 7 3365 4199.
  E-mail address: joedac@cheque.uq.edu.au (J.C.D. da Costa).

crossover. The magnitude of the proton conductivity in per-fluorinated membranes is influenced by the water content [2] and protons conduct via a Grotthuss mechanism. In the dry state, Nafion behaves like an insulator but when hydrated, the membrane exhibits proton conductivity.

One of the technical hurdles in DMFC development is the crossover of methanol from the anode to cathode via the membrane. This process has a severe negative impact on the overall performance of the cell because of a reduction in fuel efficiency by wasteful oxidation at the cathode side whilst seriously depolarising the electrode [1,6,7]. Several research groups have used various methods and strategies to decrease methanol crossover, e.g., operating a cell with relatively low methanol concentrations <2 M [3] and limiting temperatures below 70 °C. Another strategy is to carry out structural modifications of Nafion membranes. These includes: (i) grafting of styrene monomer [8]; (ii) pore-filling type PEM using Teflon as a substrate and acrylic acid-vinyl sulfonic acid copolymer as the proton conductive matrix [9]; (iii) modification with polyvinyl alcohol [10] or polypyrrole [11]; (iv) silicon dioxide–Nafion composites [12]. All these studies have achieved a considerable reduction of methanol permeation, but at the same time an undesirable decrease in proton conductivity.

Polyaniline has been investigated as a support for catalyst (platinum) particles in DMFC electrodes [13,14], and as a co-catalyst of platinum plates for methanol electro-oxidation [14,15]. These studies have resulted in an increase of the electro-catalytic efficiency of methanol. Tan and Belenger [16], carried out extensive characterization of composite Nafion/polyaniline films for proton conduction. The results showed that protonic transport is dependent on the amount of polyaniline disrupting the ionic pathways with potential application in fuel cell technology. Polyaniline is a well-known intrinsically conductive polymer. It can be easily obtained by chemical or electrochemical oxidation of the monomer aniline [17–19]. The electrical conduction in polyaniline may be ionic (charge carriers are ions), electronic (charge carriers are electrons) or mixed [20,21]. The ionic conductivity is explained on the basis of a percolation mechanism, where the mobile species are ions that are present inside the membrane phase between the polymer chains. In this work, we investigate the transport properties of polyaniline Nafion silica nanocomposite membranes for DMFC application. In particular, the structural properties of the membranes are studied whilst their conductivity, methanol crossover and fuel cell performance are assessed.

2. Experimental

2.1. Materials and sample preparations

Nitric acid 70%, ethanol 99.8%, methanol 99.8%, iron chloride, aniline 98%, and tetraethylorthosilicate (TEOS) 98%, were purchased from Aldrich, all were reagent grade and were used as-received. Nafion 117 membranes were purchased from DuPont and pre-treated by boiling in H_2O_2 (3%, v/v) for 1 h then in H_2SO_4 (0.5 M) for 1 h. The membrane was washed several times with distilled water until the washing solution became neutral.

Nafion 117 and Nafion/silica membranes were modified by an in situ polyaniline synthesis method. The Nafion/silica membrane was synthesized by in situ condensation of TEOS as described elsewhere [22] to yield a silica content of 3.8 wt%. In this technique, silica nanoparticles were embedded into the hydrophilic clusters of the perfluorinated membrane by means of a sol–gel process. Nafion 117 and the Nafion/silica composite membranes were modified with polyaniline by a redox polymerization process. The catalytic species were attached to the sulfonic functional groups of the membranes by immersion in a catalyst solution of iron chloride 0.1 M. The membranes were then immersed in a 0.2 M solution of aniline monomer in 0.8 M nitric acid for 10 min. The steps were repeated several times in order to obtain multi-layer coatings. The membranes are hereinafter identified as Nafio/PAni-X or Nafion/silica/PAni-X, where PAni stands for polyaniline and X represents the aniline solution immersion times. Once the aniline modification steps had been completed, the membranes were stored in acid media (0.1 M HNO_3) to ensure the complete exchange of ferric ions, then washed with de-ionised water at 60 °C for several times until the pH of the water became neutral. Polyaniline modification was evident because of the dark-green colouration of the emeraldine salt due to the protonation of polyaniline by the sulfonic groups of Nafion [23].

Water uptake was measured by initially drying a membrane in a vacuum oven at 80 °C for 4 h. The dried membrane was weighed and immersed in distilled water at 60 °C for 1 h and then re-weighed (hydrated). Methanol uptake was determined in a similar manner, by soaking vacuum-dried polymer membranes in methanol/water solutions of different concentrations, and re-weighing the sample after immersion in the respective solution for 1 h. Fourier transform infrared spectroscopy (FTIR-ATR) was carried out using a Perkin-Elmer 2000 instrument with a MCT detector cooled by liquid nitrogen. X-ray diffraction (XRD) data were collected on a Rigaku Miniflex X-ray diffractometer using a variable slit beam and Co Kα (1.79 Å) radiation. The scan rate was $2°\ min^{-1}$ from 2° to 60°. Differential scanning calorimetry (DSC) was performed on membranes equilibrated in water (i.e., hydrated condition) at a heating rate of $10\ °C\ min^{-1}$ using a TA Instruments 2920 Modulated instrument. Proton conductivities of the membranes were measured at different temperatures by a.c. impedance using a Solartron 1260 Impedance Analyser (frequency sweep 10 MHz to 1 Hz). The sample was placed in a cell between two gold electrodes each with $0.5\ cm^2$ area.

Testing of the membrane electrode assembly was performed using a $5\ cm^2$ single cell (ElectroChem), and tightened with 2 Nm of torque. Anode and cathode electrodes were purchased from Etek and the catalyst loading on each was $4\ mg\ cm^{-2}$. The catalyst used in the anode was 80 wt% Pt/Ru on carbon and Pt black was used as the cathode catalyst. All membranes were hot-pressed at 125 °C for 1 min without pressure and 2 min under 100 kg cm^{-2}. Methanol (2 M) and air were provided to the anode and the cathode, respectively. The corresponding flow rates were 12.4 and 75 ml min^{-1}. A Solartron 1480 Multistat was used as electric loading to control the fuel cell. The methanol crossover was further tested by purging the cathode with nitro-

gen and following procedure published by Qi and Kaufman [24]. In this testing procedure, methanol is fed via the anode but is catalysed at the cathode. The current is inversed and the proton diffuses back to the anode side of the PEM. Hence, the current generated by the fuel cell is due to the methanol crossover only.

3. Results and discussion

3.1. Characterization

After in situ modification with polyaniline (PAni), all modified membranes became dark-green due to the interaction of sulfonic and amine groups. The intensity of the green colour increased with the number of immersions of the membrane into the aniline solution. The membrane colour did not appear to result in any observable change in the Nafion/silica/PAni composite, irrespective of the number of immersions. This may be attributed to Nafion's cluster space being mainly occupied by silica, thus reducing polyaniline's interaction with sulfonic groups. This point is further substantiated in that during the preparation of Nafion/silica/PAni, the washing solution turned light green during the final washing process, which clearly indicates that polyaniline was liberated from the Nafion/silica membrane surface due to poor interaction with the ionic cluster.

The FT-IR spectra of Nafion 117, Nafion/PAni-5, and Nafion/silica/PAni-5 are shown in Fig. 1, and the characteristic bands of chemical bonding absorption and their assignments are listed in Table 1. The quinoid and benzenoid stretching modes can be found at around 1584 and 1493 cm^{-1}, respectively, in both Nafion/PAni-5 and Nafion/silica/PAni-5 membranes. The relative intensities of these bands are indicative of the proportion of quinoid and benzoid units [16]. The Nafion/PAni-5 sample shows a higher amount of polyaniline on its surface. This confirms a stronger entanglement than in the Nafion/Silica/PAni membrane. In the Nafion/silica/PAni-5 IR-spectrum, shoulders appear at 1047 and 780 cm^{-1} (Si–O–Si) and 960 cm^{-1} (Si–OH) near the Nafion's C–F stretching and C–S stretching frequencies, which provides evidence of hydrophilic Si–OH networks in the Nafion clusters.

The characteristic bands of water and hydronium ion (H_3O^+) indicate different concentrations in Nafion and the Nafion/PAni-5 membrane. The hydroxy group (–OH) at 3500 cm^{-1} in the case of the Nafion/silica/Pani-5 membrane is large and broad, which suggests strong bonding of water on the surface of silicon oxide.

Table 1
FTIR characteristic bands

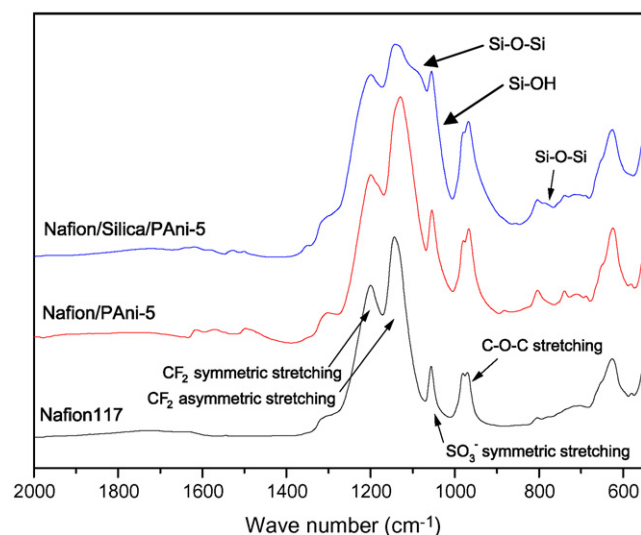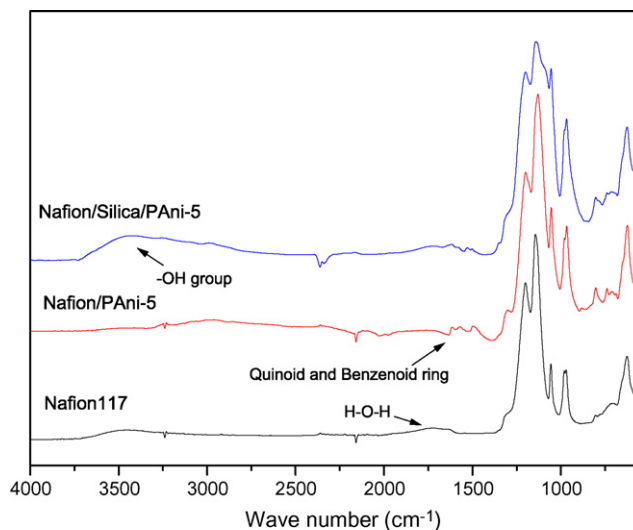| Wave number (cm^{-1})	Assignment
1500–2050	Hydrated H_3O^+
1199	CF_2 asymmetric stretching
1144	CF_2 symmetric stretching
1057	$SO_3{}^-$ symmetric stretching
1050	Si–O–Si asymmetric
960	Si–OH stretching
981 and 966	C–O–C stretching
804	C–S stretching

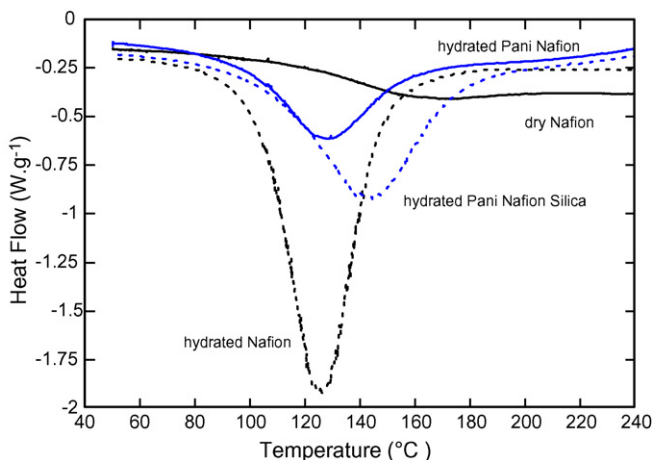Fig. 1. IR spectra of Nafion and Nafion/PAni composite membranes.

Fig. 2. Differential scanning calorimetry profiles for Nafion and Nafion/PAni composite membranes.
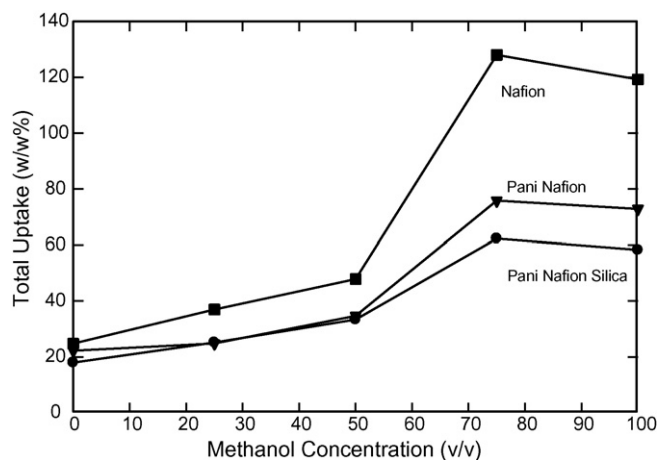
Fig. 3. Solvent uptake of Nafion and Nafion/PAni composite membranes.

The H_3O^+ peak at 1500–2050 cm^{-1} is present in all membranes including untreated Nafion, which demonstrates strong bonding between the water molecules and acid groups in the membranes. The DSC spectra in Fig. 2 also display the same trend in Nafion and the modified membranes. The endothermic peaks at 100–200 °C are indicative of water evaporation. The peak area and maximum peak temperature position are related to the water content in each membrane and its bonding or strength of interaction with the ionic cluster environment. The Nafion/PAni-5 membrane shows the lowest water content according to the peak area. This is attributed to the lower hydrophilic polyaniline surface layer and its interaction with sulfonic groups that prevent most of water from diffusing into the membrane matrix. On the other hand, the water evaporation peak becomes broader and shifts to a higher temperature for the Nafion/silica/PAni-5 membrane. This result further supports the IR results, as described above, and suggests that due to the hydrophilic silica surface (i.e., silanol groups at 960 cm^{-1}), water molecules are trapped on the silica surface nanoparticles embedded in the polymeric matrix.

The results obtained from methanol/water uptake experiments are given in Fig. 3. At zero methanol concentration or 100% water concentration, all membranes have similar total uptakes of around 20 wt%. As the concentration of methanol increases and the concentration of water decreases, the total uptake increases to a maximum at 75 vol.%. Methanol shows preferential solubility into all membranes over water, in particular for Nafion. As the DMFC conventionally operates at low methanol concentrations, it is noteworthy to observe that the total uptake in the membranes for low concentrations of methanol is very small, in particular for the modified polyaniline membranes. At a concentration of 25 vol.% methanol in water, the total uptake in modified membranes is around 10 wt% below that of untreated Nafion.

It is interesting to note the peak of the uptake on Nafion and composite membranes at high levels of methanol concentration (75%, v/v). This behaviour agrees with the findings of Rivin et al. [25], who suggested that the solubility of alcohols in Nafion was due to interaction between the functional groups of Nafion. All the uptake results indicate that the polyaniline layer on

the Nafion surface reduces water absorption (less hydrophilic), which prevents the methanol from diffusing into the bulk of the Nafion structure. For Nafion/silica membranes, the data suggest that the silica nanoparticles provide structural stability to Nafion, but no further benefits.

The XRD patterns of Nafion measured dry and after immersion in methanol/water solutions of different methanol concentrations are presented in Fig. 4. These show that the crystallinity of the Nafion Teflon backbone drops dramatically when immersed in methanol solution, and the backbone character peak almost disappears in 50 vol.% methanol solution. Accordingly, the Nafion backbone almost collapses in higher methanol concentrations and thereby, looses its crystalline properties. Comparing the XRD of Nafion and Nafion/Pani-5, the crystallinity of the backbone matrix in the Nafion/Pani-5 is maintained even when exposed to different methanol concentrations. The XRD data give strong evidence to suggest that the low hydrophilic polyaniline layer provides a barrier on the Nafion and therefore prevents to a large degree methanol diffusion through the membrane whilst maintaining the integrity and crystalline structure of the Nafion. Nafion membranes swell with higher methanol uptake (Fig. 4). These results suggest that
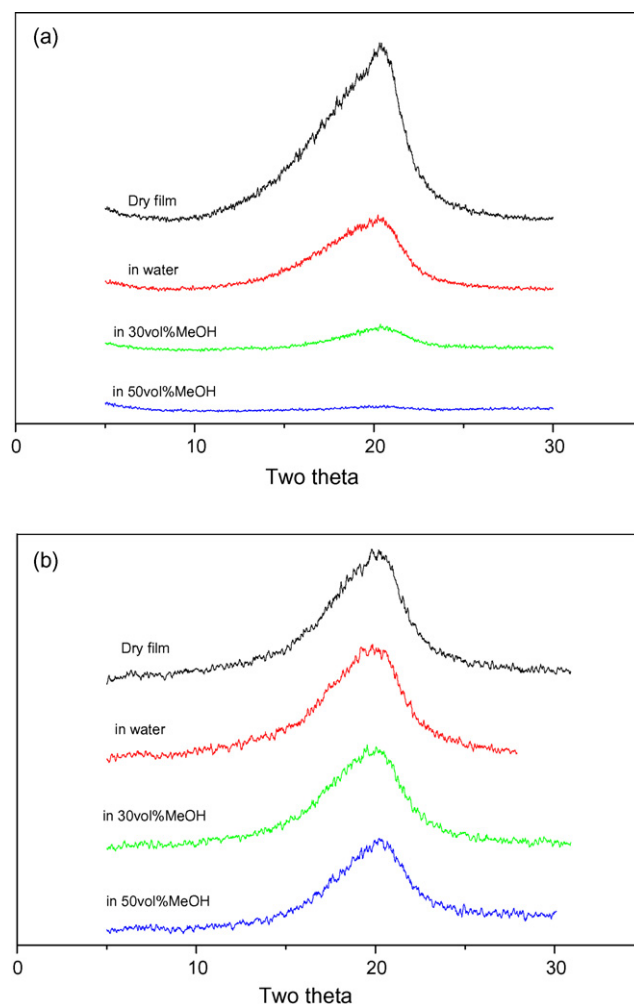

Fig. 4. X-ray diffraction patterns of (a) Nafion and (b) Nafion/Pani-5 composite membranes measured after immersion in different methanol concentrations.
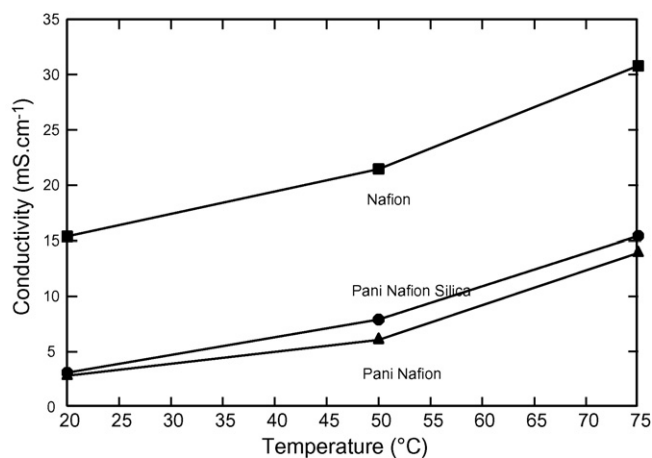
Fig. 5. Proton conductivity of Nafion and Nafion/PAni composite membranes measured at different temperatures.

Fig. 6. Polarization curves of DMFCS with Nafion or Nafion/PAni composite membranes at 20 °C.

the polyaniline modification layer restrains Nafion swelling, and thus reduces methanol uptake.

The influence of temperature on proton conductivity for all membranes tested in a fully hydrated condition is given in Fig. 5. Both polyaniline modified membranes show conductivities 3–5-fold below that of Nafion. The low the proton conductivity values are probably the result of two effects. First, the polyaniline molecules have a strong interaction (chemical bond) with Nafion, via the positive charged imine/amine groups and the negatively charged sulfonic groups [25,26], thus interfering with essential elements of the proton transport mechanisms. The second cause for the reduction of proton conductivity of Nafion is the lower hydrophilic properties of the polyaniline layer. The relationship between water content and conductivity in Nafion is fundamental as the Grothhus or proton hoping mechanism is believed to dominate proton conduction in this material. The polyaniline layers therefore restrict not only methanol diffusion but also water permeability into the membrane and thereby result in low conductivities. To investigate further the effect of polyaniline modification, Nafion and Nafion silica membranes were immersed for up to five times in aniline solution and tested for proton conduction, as shown in Table 2. The results clearly show that a high number of immersions decrease proton conductivity. On the other hand, reducing the number of immersions in aniline solution leads to acceptable conductivity values though conductivity loss also occurs due to the amount of polyaniline layer.

For cell testing, all MEAs were prepared under the same conditions, i.e., the same process was used to hot press the MEAs with the same commercially available electrodes. All membrane samples were housed in a single-cell DMFC testing unit to determine the performance curves. The polarization curves in 2 M methanol solution and air operation mode are shown in Fig. 6. The open-circuit voltage (OCV) values and MEA high frequency resistance (R_{HFR}) results at various temperatures determined from Nyquist plots are listed in Table 3. It is observed that polyaniline modified membranes have higher OCV values but lower polarization curves compared with Nafion 117. The HFR resistance at open-circuit is comprised of three components, namely: bulk membrane resistance (R_m), electrical resistance of wires and contact (R_e), and membrane electrode interface resistance (R_{in}). The electrical and contact resistance may be assumed to be similar in all cases, as the MEAs were pressed under same conditions, assembled with same torque value, and tested under similar operating conditions. Hence, any differences in the resistance between MEAs assembled with Nafion or polyaniline/Nafion must stem from the interface of the membrane and electrode. The results strongly suggest that the large interfacial resistance value in polyaniline modified Nafion membranes provides the possible reason for low performance output. Furthermore, it is observed in Fig. 7 that the performance curve of the Nafion/silica/PAni-2 composite membrane is similar to the Nafion/PAni-2 membrane, although the latter gives slightly better performance at current densities above 35 mA cm^{-2}. Nevertheless, the performance curve for the Nafion membrane is higher than those for the modified membranes. The performance

Table 2

Resistance analysis of Nafion and Nafion/PAni composite membranes under different wetting conditions

Conductivity	Bulk membrane resistance	
	Nafion	Nafion/PAni5
100RH%	2.4E−2	9.1E−3
52RH%-30 min	1.8E−2	5.8E−3
52RH%-18 h	1.3E−3	3.5E−4
Immersion in H$_2$O for 30 min	2.6E−2	1.2E−2

Table 3

MEA resistance of Nafion and Nafion/PAni composite membranes

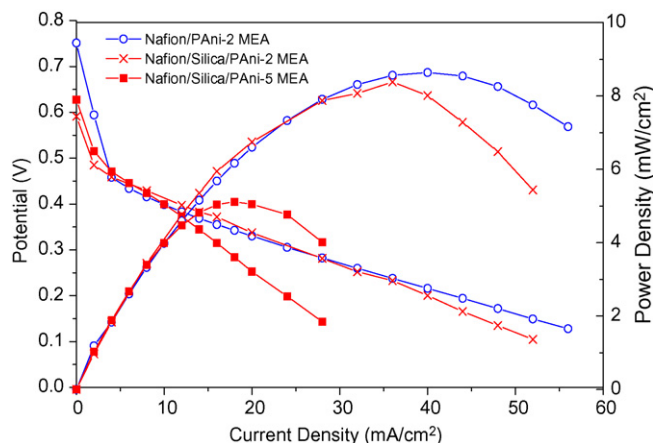| MEA samples	Open-circuit voltage (V)	MEA high frequency resistance (Ω cm^2)
Nafion	0.60	1.25
Nafion/PAni2	0.75	1.28
Nafion/PAni5	0.47	2.5
Nafion/silica/PAni2	0.59	1.5
Nafion/silica/PAni5	0.63	1.7

Fig. 7. Polarization curves of DMFCS with Nafion/silica/PAni composite membranes in different coating times (40 °C).

using Nafion/silica/PAni is further limited by increasing the number of aniline solution immersions from 2 to 5 (see Fig. 6). These observations clearly justify the findings discussed above in that polyaniline adds lower hydrophilic properties to the composite membrane whilst also having a strong interaction with the sulfonic groups.

The methanol limiting current method for investigating the real methanol crossover in a MEA was applied in this study, as shown in Fig. 8. The polyaniline modified membrane displays, lower permeability compared with Nafion. As the number of polyaniline dipping times increases (i.e., 5 for PAni/Nafion), methanol crossover decreases by over two orders of magnitude. The polarization curves for the MEAs and the methanol crossover limiting currents show that polyaniline modified Nafion membranes may be useful in DMFC application. The methanol crossover is reduced successfully by using in situ polyaniline modification, but there is an increased interface resistance and a lowered MEA performance.

In this work, polyaniline was intended to be located on the surface of Nafion in order to improve its interaction with the catalyst layers on the MEA by an efficient conduction of the electrons
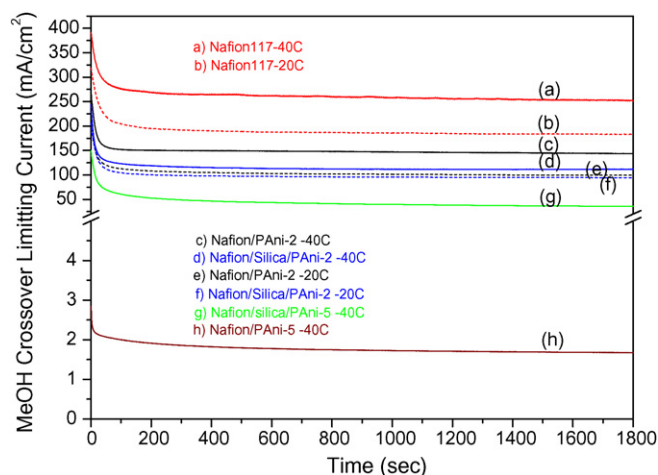
produced at the anode. Although polyaniline has an electron conductivity as high as $18,800\,\mathrm{ms\,cm^{-1}}$ in acid media [27], the results presented here suggest that the membranes are not short-circuited, despite the low values of proton conductivity for the polyaniline modified membranes as compared with Nafion. This suggests that the polyaniline occupies parts of the Nafion structure that is intended for proton transport. As a result, the interaction of aniline with the sulfonic groups of Nafion causes a restriction of protonic pathways. In addition, the polyaniline hydrophilicity is low, and further impedes proton transport via the Grotthus mechanism. The higher resistance on the surface can therefore be attributed to a very thin capacitance layer. On a positive note, methanol crossover is reduced. The low aqueous methanol concentration currently used to fuel in DMFCs limits their use in high-energy applications. This work may indicate that DMFCs could operate with higher methanol concentrations when using polyaniline modified membranes, with a potential to deliver higher specific energy. Ultimately, this becomes an optimization problem, as there are trade-offs to be made between the number of polyaniline coatings (i.e., immersion times) and the MEA performance at high methanol concentrations.

4. Conclusions

Modification of Nafion with polyaniline is found to reduce methanol uptake and decrease methanol crossover in a DMFC. Compared with Nafion, which loses its crystallinity, the polyaniline modified membrane largely retains its crystallinity on exposure to methanol and water. Modification of Nafion and polyaniline/Nafion by incorporation of silica nanoparticles into the polymer matrix provides no major advantages. Polyaniline modification does, however, reduce the proton conductivity of the membranes by a factor of 3–5, and increases the hydrophobicity of the Nafion. This is believed to be due to interaction of aniline with the sulfonic groups of Nafion.

On a positive note, methanol crossover of the polyaniline modified membranes is reduced by over two orders of magnitude, as verified by crossover limiting current analysis. The MEA performance using commercial catalysts and polyaniline modified membranes reaches $8\,\mathrm{mW\,cm^{-2}}$ at 40 °C in a cell operating on 2 M methanol solution and air. This performance is about two-fold lower than for MEAs with Nafion, which substantiates the proton conduction results. Nevertheless, the polyaniline membrane modification may allow operation at high methanol concentrations, an important aspect to attain high specific energy in DMFC applications.

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Fig. 8. Methanol crossover limiting current analysis of Nafion and Nafion/PAni composite membranes.

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