

# Low energy plasma treatment of Nafion<sup>®</sup> membranes for PEM fuel cells

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Received 13 October 2006; received in revised form 10 November 2006; accepted 18 November 2006

Available online 12 January 2007

## Abstract

Understanding the effects plasmas have on polymer electrolyte membranes such as Nafion is important if plasma technologies are to be employed in the fabrication of MEA components. An argon plasma has been used to treat the surface of Nafion membranes at several energy doses from 0 to 3.056 J cm<sup>-2</sup>. The effect of the treatment has been characterised using Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and X-ray Photoelectron Spectroscopy (XPS) as well as measuring water contact angles, proton conductivity and electrical performance. It was found that as energy dose is increased, hydrophobicity of the membrane decreases, as does proton conductivity. The water contact angle for untreated Nafion is around 120° while the surface treated with the maximum dose has a contact angle of 50°. Similarly the proton conductivity drops from above 200 to 35.8 mS cm<sup>-1</sup>. SEM and AFM results showed only a small change in the surface roughness of the treated samples while XPS results indicated a marked reduction in the concentration of fluorine at the surface of the membrane for increasing dose. Fuel cell electrical performance was also very poor for the treated membranes and this was attributed to the decrease in conductivity as well as an observed poor adherence between electrode and membrane in the pressed MEA.

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**Keywords:** Fuel cells; Nafion; Plasma modification

## 1. Introduction

The development of Proton Exchange Membrane (PEM) fuel cells is envisaged as providing a solution for small to medium size energy needs, moving away from fossil fuel sources. One of the main components of the PEM fuel cell is the proton conducting polymer membrane. The membrane used most widely today is Nafion which was developed over 50 years ago by Dupont, with only limited research in to finding alternate products [1]. Properties such as its proton conductivity, ‘hydrophobic’ outer surface and structural stability make it well suited to this application. Over the past few years, research into the control and manipulation of these properties, particularly at the interfacial boundary with the electrode has lead to increased

fuel cell performance [2–6]. The use of plasma based technology in the development of fuel cell electrodes as well as membranes has contributed to this increase while at the same time reducing production costs by lowering catalyst loadings [7–12].

Of particular importance is the interfacial boundary between membrane and electrode, the three-phase boundary where the electrochemical reaction of the fuel and oxidant occurs: the greater the contact surface-area between the membrane, catalyst and reactants, the greater the reaction rate. Cho et al. [6] reported that roughening the surface with ion bombardment increased the maximum power density of a single cell operating on hydrogen and oxygen. This was attributed to the larger contact area between the membrane, catalyst and reactants. Prasanna et al. [4] went further to show that higher fuel cell performance was possible with lower catalyst loadings when roughened membranes were used with hydrogen and air.

Understanding the effect plasmas can have on membrane surfaces is important as some new methods of polymer preparation

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involve the use Plasma Enhanced Chemical Vapour Deposition (PECVD). Mahdjoub et al. [9] have shown that plasma polymerisation of 1,3-butadiene and styrene mixtures result in proton conducting membranes suitable for PEMFC. They found that membranes produced in the afterglow of the plasma had a 10-fold increase in their proton conduction over membranes produced in the glow discharge suggesting that understanding the nature of the discharge and its effect is important in membrane development. However, these new polymers still have much lower proton conductivity than a traditional Nafion membrane.

Plasma effects on Nafion are also important when sputtering catalyst layers directly onto the Nafion surface. This has been attempted by Cha and Lee [13], O'Hayre et al. [7] and Haug et al. [14] with mixed results. Cha and Lee found that coating the Nafion first with a Nafion/carbon ink drastically improved performance. O'Hayre reported a peak performance of  $33 \text{ mW cm}^{-2}$  in an MEA with a thin sputtered film of platinum on the PEM while Haug reported a performance of  $65 \text{ mA cm}^{-2}$  at  $0.6 \text{ V}$  or  $39 \text{ mW cm}^{-2}$ . This increased to  $170 \text{ mA cm}^{-2}$  at  $0.6 \text{ V}$  when multiple and alternate layers of a Nafion-carbon ink was used. This is still considerably smaller than the  $500 \text{ mW cm}^{-2}$  that we report for a reference MEA in this paper. Neither of these studies delves into the effect the plasma has on the membrane during the sputtering process although Haug does test the response of Nafion 117 to vacuum and found it had little effect.

Water management is also of great importance in fuel cell operation and also one of its greatest challenges. Water needs to be present in sufficient quantities to hydrate the membrane for sufficient proton conduction [15], but also removed at a sufficient rate at the cathode so as not to choke the fuel cell. Fuel and oxidant are often humidified to provide water for the reaction while membrane and gas diffusion layers contain hydrophobic polymers to expel excess water. Poor water management in the cell can result in drop out of current. The membrane is of particular interest in water management because, despite its hydrophobic outer surface due to its perfluorinated backbone, it contains hydrophilic sulfonated groups that cluster within the membrane and are responsible for the transport of the protons via a hydronium ion [1,16,17].

In this work we look at the low energy treatment of Nafion using a low-pressure high-density radiofrequency argon plasma and the changes in the membrane properties and fuel cell performance. Water contact angle measurements, Scanning Electron Microscopy, Atomic Force Microscopy, X-ray Photoelectron Spectroscopy and proton conductivity have been used to characterise the membrane properties while current/voltage curves are used to evaluate performance. A better understanding of the effect plasmas have on Nafion membranes will help in the development of vacuum based fuel cell production systems.

## 2. Experimental

### 2.1. Nafion preparation

Nafion<sup>®</sup> 115 membranes was prepared prior to plasma treatment by cutting into  $1.5 \text{ cm} \times 4 \text{ cm}$  rectangles and  $5 \text{ cm} \times 5 \text{ cm}$

squares. Cleaning of Nafion was conducted in the conventional way and has been described previously [18,19]. It was placed in  $\text{H}_2\text{O}_2$  at  $60^\circ\text{C}$  for 60 min to remove organic impurities, washed in de-ionised water, placed in  $\text{H}_2\text{SO}_4$  at  $60^\circ\text{C}$  for 60 min to remove any metallic impurities, washed in de-ionised water and dried in an oven at  $100^\circ\text{C}$  for 24 h. XPS results however showed trace amounts of hydrocarbons still remained on the surface which were either remnants left after cleaning or more likely picked up sometime between the cleaning process and when the XPS was conducted. Rectangular membranes were placed in a holder exposing both sides of the membrane to the plasma over an area of  $1.5 \text{ cm} \times 2 \text{ cm}$  while the square membrane had an exposure area of about  $4.5 \text{ cm} \times 4.5 \text{ cm}$ . The rectangular membranes were used for contact angle, proton conductivity and AFM measurements while the square membranes were used in fuel cell tests.

### 2.2. Ar plasma treatment

The sample and holder were placed in a low-pressure argon plasma in the horizontal diffusion chamber of a 13.56 MHz helicon source reactor called 'Piglet', shown in Fig. 1. The reactor consists of a 20 cm long, 15 cm diameter glass source tube connected to a 28 cm long, 30 cm diameter aluminium diffusion chamber. Two solenoids surround both the source and diffusion chambers however the source solenoids are not used in this experiment. A current of 6 A is passed through the two diffusion coils producing a field of  $\sim 100 \text{ G}$ . An Alcatel (Pascal 2015 SD) rotary pump and an Alcatel turbo-molecular pump are used to pump the chamber down to a base pressure in the range of  $10^{-6} \text{ Torr}$  with an operating pressure of 2 mTorr achieved with an argon flow of 30 sccm. Nafion samples were exposed for 5, 10, 20, 60 and 120 s at a power of 50 W at position  $z = 27 \text{ cm}$ .

### 2.3. UV treatment

It is well known that UV light is emitted by the plasma, which also brings energy to the membrane surface, as well as the bulk material [20,21]. It is therefore necessary to understand the effect that UV light has on the surface separate from the ion dose. Samples of Nafion were treated under an i-line filtered mercury lamp (365 nm). The intensity of the light was measured both above and below the membrane and the sample was placed on a silicon wafer coated with a Backing Anti-Reflective Coating (BARC) that has near zero reflection at 365 nm. This was the reason the 365 nm mercury source was chosen. The samples were exposed for 6, 60, 600, 1800 and 6000 s.

### 2.4. Membrane characterisation

Contact angle measurements of the treated Nafion were conducted using a KSV Contact Angle Goniometer and CAM200 software using the sessile drop method. Repeatability of the measurement was verified over several cycles of increasing and decreasing the volume of the drop. The advancing contact angle was taken as the average contact angle between when the drop reached an equilibrium angle to the time the

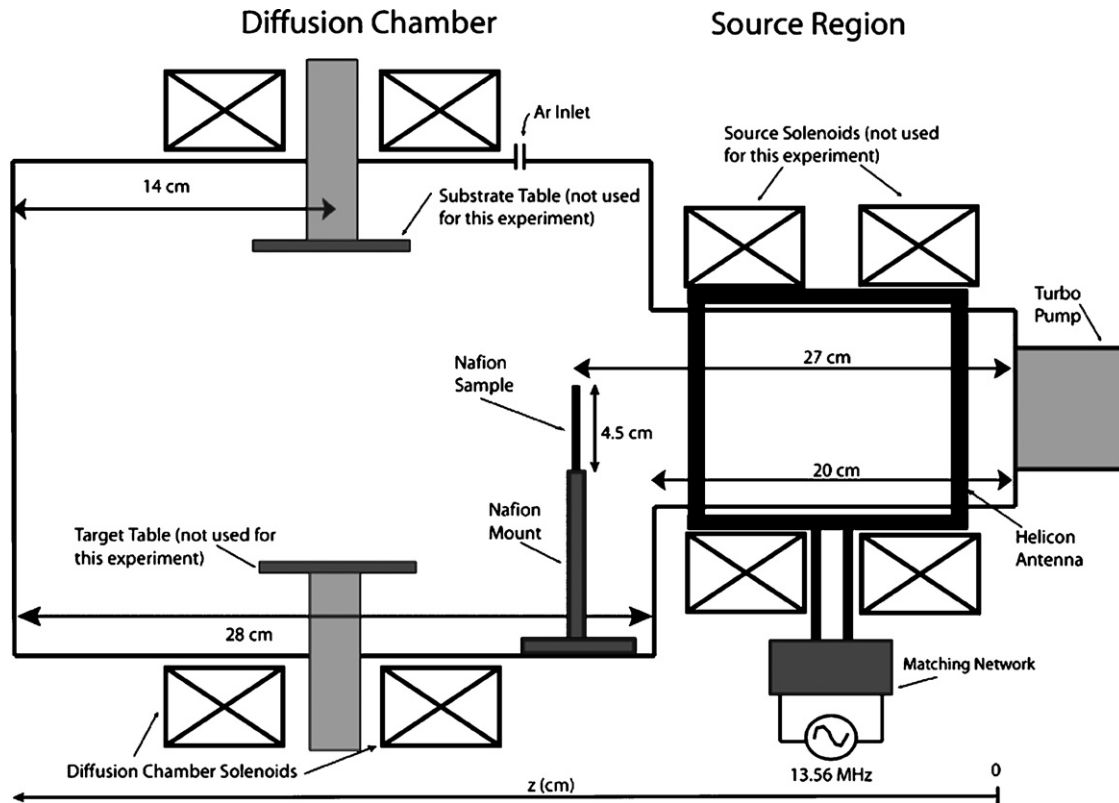


Fig. 1. Schematic of Piglet showing position of Nafion for plasma treatment.

volume was no longer increased, approximately 40 s. Receding contact angle measurements were also attempted however an equilibrium angle could not be established. Scanning Electron Microscopy (SEM) using a Hitachi S4500 Field Emission SEM was conducted to observe surface morphology. The samples were coated with a thin layer of platinum to aid in surface conductivity and reduce charging. Surface roughness was also measured with a Digital Instruments Nanoscope Multimode Atomic Force Microscope (AFM) carried out in tapping mode.

Surface elemental and chemical analysis was carried out by X-ray Photoelectron Spectroscopy (XPS) using an AXIS-His spectrometer (Kratos Analytical Inc., Manchester, UK) with a monochromated Al K $\alpha$  source at a power of 12 kV  $\times$  12 mA, a hemispherical analyser operating in the fixed analyser transmission mode and the standard aperture (1 mm  $\times$  0.5 mm). Each specimen was analysed at an emission angle of 0 $^\circ$  as measured from the surface normal. Assuming a value of approximately 3 nm for the electron attenuation length of relevant photoelectrons (e.g. C 1s, N 1s, O 1s, F 1s) in a polymeric matrix this translates into an approximate value for the XPS analysis depth (from which 95% of the detected signal originates) of less than 10 nm. All elements present were identified from survey spectra. The atomic concentrations of the detected elements were calculated using integral peak intensities and the sensitivity factors supplied by the manufacturer. To obtain more detailed information about chemical structure, high resolution spectra were recorded from individual peaks at 40 eV pass energy (yielding a typical peak width for polymers of 1.0 eV). This data were quantified using a minimisation algorithm in order to calculate

curve fits and thus to determine the contributions from specific functional groups.

Proton conductivity measurements were made using two-electrode transverse impedance measurements. The electrodes were circular, of 8 mm diameter, made of gold-plated copper and pressed together with a force of 22.2 N. This corresponds to a pressure of 442 kPa. Samples were conditioned by soaking in distilled water for at least 1 h, and were tested while immersed in distilled water at 26  $^\circ$ C. A sinusoidal voltage, of 10 mV amplitude, was applied over the frequency range ( $10^2$  to  $3.2 \times 10^7$  Hz) using a Solartron 1260 Frequency Response Analyzer (FRA). The measurement was repeated three times in different areas of the membrane and the results averaged.

## 2.5. MEA performance

The Nafion samples exposed in Piglet were pressed into Membrane Electrode Assemblies (MEAs) using E-Tek ELAT $^\circ$  electrodes with 5 mg cm $^{-2}$  platinum catalyst. Each electrode was coated with approximately 1.4 mg cm $^{-2}$  of Nafion from a 5% (w/v) DE521 Nafion solution using a pipet and allowed to dry at 50  $^\circ$ C for 1 h. The MEA was then pressed in a Rondol hydraulic bench-top press with 10 kN of force at 130  $^\circ$ C for 2 min. The MEA was placed in an Electrochem single stack 5 cm $^2$  fuel cell block and fed with a flow of 100 sccm of hydrated (100% RH) hydrogen and oxygen at 80  $^\circ$ C. The fuel cell itself was heated to 80  $^\circ$ C and pressurised to 3 bar. The load across the fuel cell was varied, the current and voltage measured and the gas flow and backpressure regulated using an Electrochem

MTS 150 and ECL 150 manual test station. Measurements were taken 10 min after the load had been increased to allow the fuel cell to come to equilibrium.

### 3. Results and discussion

#### 3.1. Energy dose from ion flux

The energy dose to the Nafion surface is given by the flux of ions multiplied by the energy of the ions and the exposure time:

$$E_{\text{ion}} (\text{J cm}^{-2}) = t e \mu_{\text{ion}} (V_p - V_f)$$

where  $t$  is the exposure time in seconds,  $e$  the electronic charge,  $V_p$  the plasma potential,  $V_f$  the floating potential and  $\mu_{\text{ion}}$  is the ion flux bombarding the surface [21]. As the floating potential is small (confirmed by Langmuir probe measurements) it can be ignored and the ion flux is simply the ion saturation current  $I_{\text{sat}}$  as measured by a Langmuir probe, multiplied by the electronic charge and divided by the area,  $A$ , of the probe, so:

$$E_{\text{ion}} (\text{J cm}^{-2}) = t V_p \frac{I_{\text{sat}}}{A}$$

The plasma potential was measured to be 30 V by calculating the second derivative of a Langmuir probe current/voltage trace and the ion saturation current was 0.12 mA. The ion energy dose to the membrane surface is therefore 0.127, 0.255, 0.509, 1.528 and 3.056 J cm<sup>-2</sup> for exposure times of 5, 10, 20, 60 and 120 s, respectively. The energy dose associated with the light emission from the plasma (mostly UV) is about three times less than that related to ion bombardment [20,21] so the associated UV dose is approximately 0.042, 0.085, 0.170, 0.509 and 1.019 J cm<sup>-2</sup>, respectively.

#### 3.2. Energy dose from UV light

The measured light intensity above the Nafion sample during mercury i-line irradiation was 1.5 mW cm<sup>-2</sup> and the intensity below the sample was 1.09 mW cm<sup>-2</sup>. Since the reflection below the sample is negligible due to the BARC, the power dose throughout the bulk of the material is 0.41 mW cm<sup>-2</sup>. The Nafion samples were exposed for 6, 60, 600, 1800 and 6000 s giving UV doses of 0.002, 0.025, 0.246, 0.738 and 2.460 J cm<sup>-2</sup>, respectively.

#### 3.3. Membrane characterisation

As a measure of hydrophobicity of the Nafion surface, water contact angle measurements were conducted for a reference samples and argon plasma treated samples with the result shown in Fig. 2. The reference angle is about 120° with increasing dose reducing the hydrophobicity of the sample eventually making it hydrophilic. The effect of the UV light from the plasma was determined to have no effect on the membrane in regards to hydrophobicity as the contact angle measured on the samples treated under the UV light source showed no change as also seen in Fig. 2. This suggests that any change in the membrane

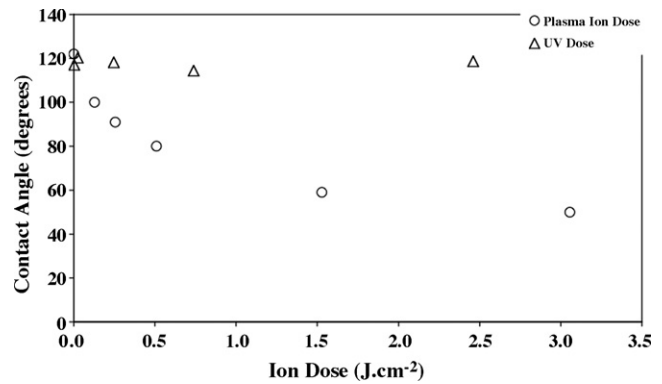


Fig. 2. Contact angles of Ar plasma treated and UV treated Nafion samples.

hydrophobicity is due only to the ion bombardment. This result is in agreement with work we have conducted previously [21].

Fig. 3a and b shows SEM images taken of an untreated reference samples and a 60 s Ar plasma treated sample, respectively. The second image show little difference from the first suggesting that there is effectively no change in the morphological characteristics at the scale shown. Fig. 4a–c shows three images of the Nafion surface taken by the AFM with the untreated Nafion having an RMS roughness of 0.651 nm, while the 10 s exposed

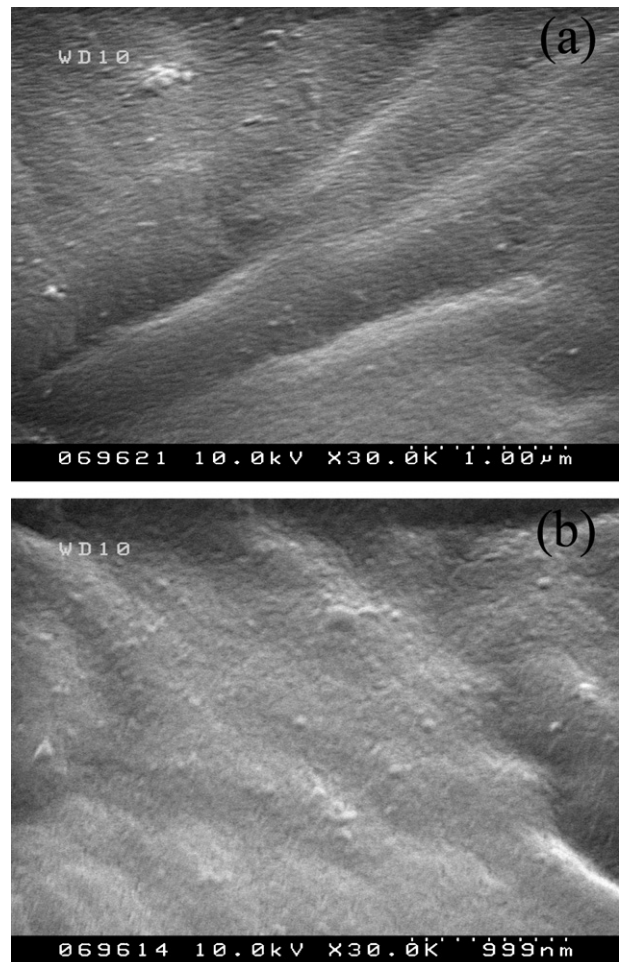


Fig. 3. SEM image of (a) untreated and (b) 60 s plasma treated Nafion.



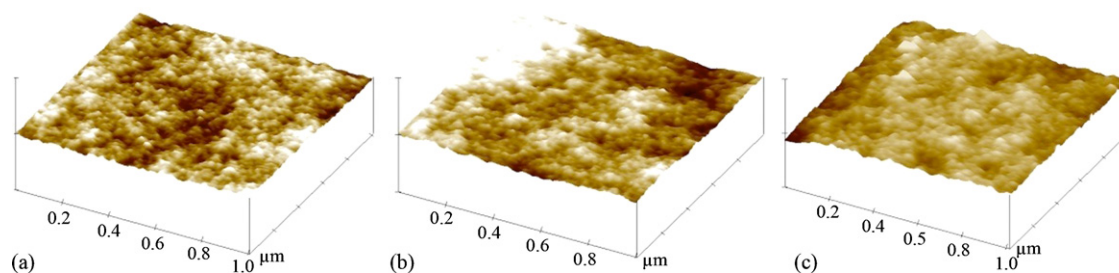


Fig. 4. AFM images of (a) untreated Nafion, (b) Nafion treated for 10 s and (c) Nafion treated for 60 s in an argon plasma corresponding to RMS roughness of 0.651, 0.579 and 0.476 nm, respectively.

sample has a roughness of 0.579 nm and the 60 s exposed sample has a roughness of 0.476 nm. There does appear to be a slight smoothing effect due to the plasma treatment, however this variation is very small, being only just above the error of the measurement. Hence the AFM results confirm that there is very little change in the surface morphology of the membrane.

XPS analysis was carried out in order to monitor the changes to the chemical structure of the Nafion membranes following Ar plasma treatment and the subsequent exposure to the atmosphere. Note that this study only presents preliminary results; because of its limitations (e.g. inability to detect hydrogen, poor spectral resolution) XPS would need to be supported by complementary surface analysis techniques such as Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR FTIR) and/or Time-of-Flight Secondary Ion Mass Spectrometry (TOF SIMS) in order to obtain a comprehensive characterisation of the membrane surface. This would also allow a more detailed interpretation of the XPS data such as a more complete assignment of individual spectral components used to fit the C 1 s and O 1 s high resolution spectra (see Fig. 5). However, this

is beyond the scope of the present report and will be the subject of further work/publications.

The XPS results are summarised in Table 1. Representative high resolution spectra (including curve fits) are shown in Fig. 5. The two major changes observed are dramatic reductions in the concentrations of fluorine and sulphur. After only 10 s of plasma treatment the F/C ratio is reduced by more than half, and after 120 s it has dropped to about 20% of the original value. The decrease in S concentration appears to be slower but after 120 s exposure to the Ar plasma S levels have also dropped to a small fraction of the original value indicating an almost complete loss of sulphonic groups within the top few nm of the membrane surface. These changes are not only observed as a reduction in intensity of the F 1 s and the S 2p spectra (not shown) but are also reflected in the C 1 s and O 1 s spectra (see Fig. 5). Most obvious is the drop in intensity of those spectral components that are associated with fluorocarbon segments (C 1 s peaks above 290 eV binding energy and O 1 s component at ca. 535.5 eV) confirming abstraction of fluorine to be one of the major processes occurring during plasma modification of the

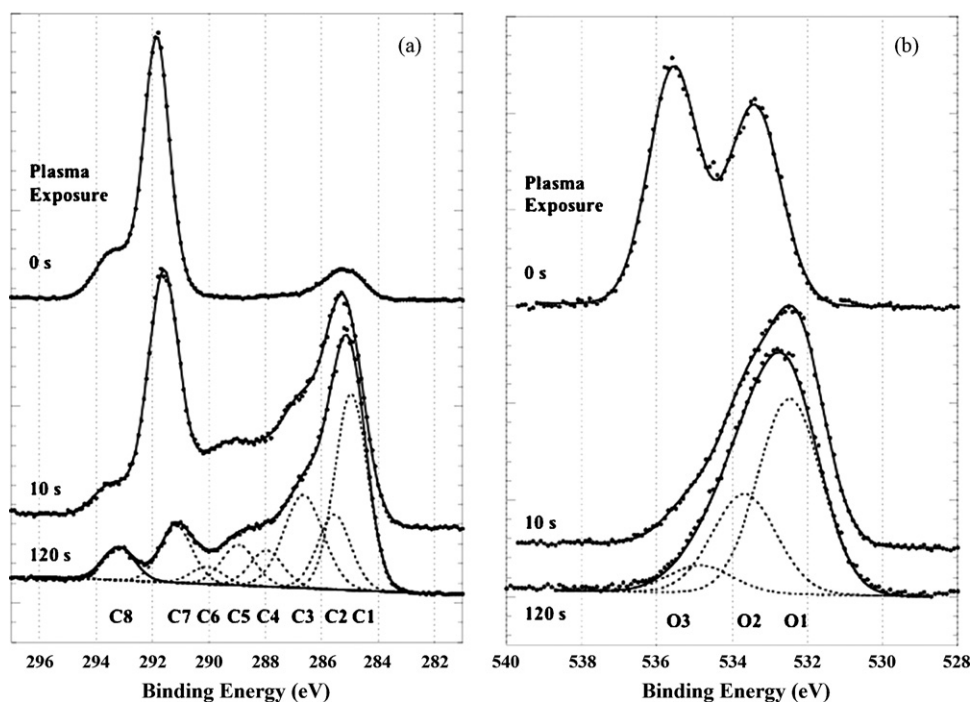


Fig. 5. Representative high resolution C 1 s (a) and O 1 s (b) XPS spectra with curve fits.

Table 1  
Atomic ratios of all detected elements relative to total carbon as measured by XPS

Element	Component	Untreated		10 s exposure		120 s exposure	
		Mean	S.D.	Mean	S.D.	Mean	S.D.
Fluorine	F	1.865	0.024	0.712	0.000	0.383	0.013
Carbon	C1–C5	0.138	0.009	0.603	0.005	0.809	0.008
	C6–C8	0.862	0.009	0.397	0.005	0.191	0.008
Oxygen	O1–O2	0.124	0.001	0.279	0.002	0.158	0.007
	O3	0.139	0.003	0.032	0.000	0.016	0.001
Sulphur	S	0.040	0.001	0.028	0.000	0.005	0.000
Nitrogen	N	0.000	0.000	0.042	0.002	0.020	0.001

See text for details.

surface. Simultaneously an increase in signal intensity and/or the appearance of additional peaks is observed at lower binding energy (C 1 s below 290 eV and O 1 s below 535 eV). In addition, nitrogen is incorporated into the membrane surface. As mentioned above, an unambiguous assignment of these peaks is not possible at this stage; the situation is further complicated by possible secondary shifts in binding energy, induced by fluorine. Nevertheless, we can interpret the observed changes as a consequence of the reaction of the plasma treated surface with the atmosphere. Free radicals created by the plasma via chain scission can either recombine to form crosslinks or, on exposure to the atmosphere, may react with oxygen, water vapour or (less likely) with nitrogen. These reactions have been well documented and usually are the beginning of autoxidative chain reactions which, via various metastable species, eventually lead to the formation of a range of more stable oxidative products [22]. It is the (mainly) carbon–oxygen functional groups within fluorine deficient polymer segments which give rise to the C 1 s and O 1 s peaks at lower binding energy values as shown in Fig. 5.

It is the reduction of fluorine at the surface that is the most likely cause for the decreasing hydrophobicity. Khayet [23] has shown that modifying the top surface of polymeric membranes with oligomeric fluropolymer macromolecules results in an increase in fluorine concentration from 0 to 14.3% and a concomitant increase in the water contact angle from 86.1° to 102.2°. There have also been other studies that show that change in fluorine concentration on surfaces have a direct effect on the measured contact angle [24,25]. On the other hand, Sangribsub et al. [26] have shown that immersion of Nafion in water can result in a decrease in contact angle by drawing the hydrophilic SO<sub>3</sub><sup>-</sup> group to the surface. This is however not the case here as the XPS results clearly show a reduction in both sulphur and fluorine.

The reduction in contact angle and unchanged surface roughness as a function of increasing energy dose is markedly different from the results obtained by Cho et al. [6]. They used significantly higher energy doses with ion fluxes ranging from 1 × 10<sup>15</sup> to 1 × 10<sup>17</sup> ions cm<sup>-2</sup> at 1 keV and found that measured contact angles actually increased with energy dose and gave a reference value of 80°. They also found that at these higher doses the impact of ions changed the surface morphology increasing the RMS roughness from 21 to 204 nm, which resulted in the increased contact angle. The discrepancy with our value for

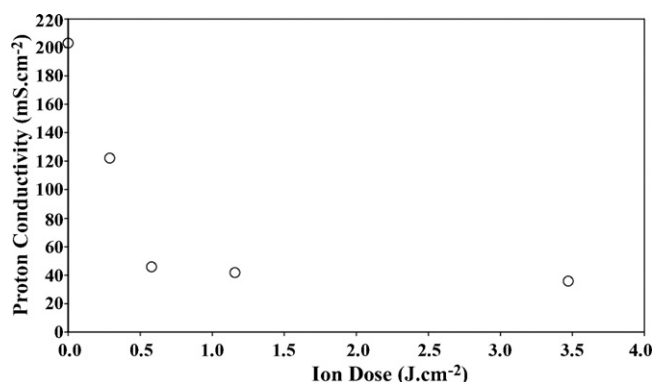


Fig. 6. Proton conductivity of Ar plasma treated Nafion treated.

untreated Nafion of about 120° cannot be accounted for, however it is well documented that Nafion is very hydrophobic meaning it has a contact angle with water that is greater than 90° [1,26,27]. The lack of roughening of our treated samples probably arises from the much lower energy of the ions impacting on the surface. At around 30 V, the ions in Piglet will have little sputtering effect on the surface while at 1 kV there is a much greater rate of sputtering leading to a roughening of the surface.

The results of proton conductivity measurements on treated Nafion samples are shown in Fig. 6 for plasma treated Nafion and Fig. 7 for UV treated Nafion. The Nafion conductivity shows a definite decrease with increasing energy dose while the UV treatment appears to have less of an effect. This is again at odds with the results of Cho et al. It has been shown in a previous study that heat-treatment of Nafion results in a lowering of the proton

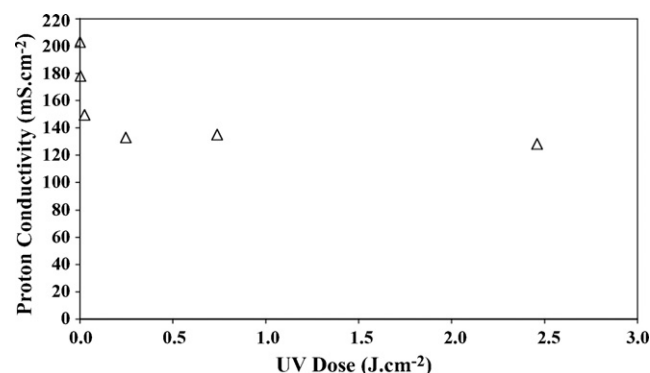


Fig. 7. Proton conductivity of UV treated Nafion samples.

Table 2

Proton conductivity of untreated, heat-treated and vacuum treated Nafion samples

	Conductivity ( $\text{mS cm}^{-1}$ )
Reference, uncleaned	186
Reference, cleaned, heat-treated	144
Reference, cleaned	203
Vacuum 1 h, not cleaned	179
Vacuum 1 h, cleaned, heat-treated	160
Vacuum 24 h, cleaned, heat-treated	139
Vacuum 24 h, not cleaned	174
Heat-treated, not cleaned	185

conductivity [18]. In this study Nafion was heat-treated at 80, 105 and 120 °C. There it was found that increased heat resulted in a decrease in the proton conductivity by almost an order of magnitude with untreated Nafion, although the difference in conductivity between the higher temperatures was very small. This was attributed to a change in the structure of the membrane and shrinking of the pores in the material as the glass transition temperature of Nafion is around 110–120 °C [18,28,29]. We tested this by heat-treating our own membranes at 100 °C as well as vacuum treating several membranes without plasma treatment to determine if the desiccation due to vacuum had any effect on proton conductivity. These results are summarised in Table 2. ‘Reference’ samples have not been vacuum treated while those that have been are designated 1 or 24 h in reference to the treatment time. ‘Cleaned’ refers to whether the samples underwent the cleaning process described earlier. There is a range of results from about 140 to 204  $\text{mS cm}^{-1}$  with three of the four heat-treated samples account for the lowest conductivity. It is likely that our plasma treatment heats the Nafion above its glass transition temperature or imparts a mechanical change to its structure causing the same changes shown in the heat-treatment above 100 °C.

### 3.4. MEA performance

Current/voltage measurements were conducted as a measure of performance using an untreated Nafion membrane as a reference (that had been cleaned and dried) and comparing this result with those from the treated samples. These current/voltage curves are shown in Fig. 8. It was found that the MEAs with plasma treated membranes performed extremely poorly. The 5 s treated sample performed best of the modified membranes while the 10, 20 and 60 s treated membranes performed much more poorly. No performance curve exists for the 120 s sample as a near zero current was detected for all loads. Two reasons exist for this poor performance. The first relates to the reduction in proton conductivity of the treated membranes. From Fig. 7, the 5 s treated sample still has a proton conductivity of about 120  $\text{mS cm}^{-1}$  resulting in its better performance. The remaining samples all drop to below 50  $\text{mS cm}^{-1}$  accounting for their much poorer performance. Secondly, when the MEAs were removed from the fuel cell block, the electrodes easily fell away from the membrane suggesting the adhesion after pressing was not as strong as with membranes that had not been treated. It was

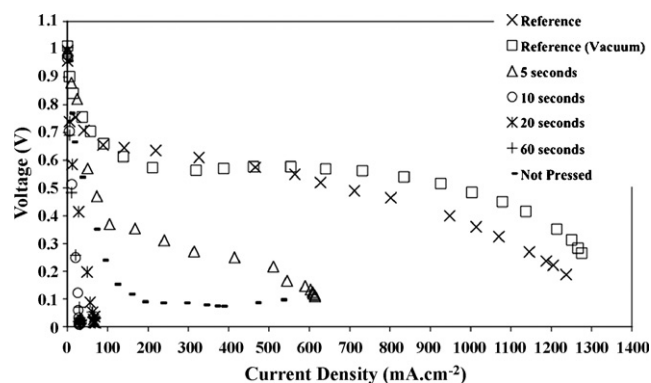


Fig. 8. Performance of plasma treated Nafion samples in MEAs treated for 5, 10, 20 and 60 s against two reference samples, one stored under vacuum for 24 h, and an MEA that was not hot pressed.

observed that for the membrane treated for 5 s, the electrode did not fall away as readily as for the longer treated membranes. To further investigate this, an MEA was created that was not hot pressed to determine the effects of poor bonding between electrode and membrane. A second Nafion membrane was placed under vacuum ( $\sim 1 \times 10^{-8}$  bar) for 24 h to isolate the plasma treatment as the sole cause of the poor adhesion. These results are also shown in Fig. 8. The Nafion membrane kept under vacuum performed just as well as the reference membrane, which confirms the result of Haug et al. [14] mentioned previously. Also, the membrane treated for 5 s performed better in an MEA than the MEA that was not hot-pressed indicating that there was some bonding between this membrane and the electrodes. It is clear that the poor performance of the remaining membranes occurs due to a combination of a reduced proton conductivity and poor adhesion between electrode and membrane and that this is due to the plasma treatment and not the preparation of the membrane or the result of storage under vacuum. These results are again different to Cho et al. [6] who found an increase from 300 to 620  $\text{mW cm}^{-2}$  when using ion bombarded Nafion in their MEAs. Our results could however explain the ‘drastic’ increase in performance Cha and Lee [13] observed when they first coated their Nafion membrane with a Nafion/carbon ink (NCI) prior to catalyst sputtering. The NCI would have formed a protective layer between the membrane and the plasma possibly preventing some of the detrimental effects we have seen. This could also explain the low peak power densities found by O’Hayre et al. [7] and Haug et al. [14] described earlier, as the effect of the plasma on the membrane has not been thoroughly considered in either work.

The poor adhesion we saw in the plasma treated Nafion could have something to do with the reduction of fluorine at the membrane surface or the reduction in pore size due to heating, however these reasons are just speculation at present and the authors will further investigate this phenomenon in future work.

## 4. Conclusion

Nafion 115 membranes have been treated in low energy argon plasmas and the effect on surface contact angle, surface morphology and elemental analysis, proton conductivity and MEA

performance has been analysed. It was found that the membrane becomes very hydrophilic as the ion dose to the surface increases but little change is seen in the surface morphology likely due to the low energy of the ions. It was also found that it is solely the ion dose and not the UV light incident on the surface that is responsible for the change. XPS results showed that the change in hydrophobicity could be attributed to a reduction in fluorine at the surface. The plasma treatment also had the effect of reducing the proton conductivity, which in turn resulted in poorly performing MEAs. The adhesion between electrode and membrane was much reduced in our plasma treated membranes, which would have reduced proton conduction from the electrode to the membrane, and added to the poor performance. It is clear that there is still much to be understood before plasma-processing techniques can be fully integrated with all parts of MEA production.

### Acknowledgements

The authors would like to thank Maryla Krolikowska for her assistance with the AFM measurements as well as the Australian Research Council through its Discovery program for funding this research.

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