Performance analysis of sulfonated PPTA polymers as potential fuel cell membranes

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Abstract

In this paper, preliminary fuel cell tests on sulfonated poly(p-phenylene terephthalamide)s (PPTAs) are reported. Two polymers with differing degrees of sulfonation were imbibed into a porous support matrix (Solupor® (DSM) with proton conductivities ranging from 10^{-3} to 10^{-2} S cm^{-1}. Under fuel cell conditions, the fully sulfonated PPTA demonstrated longer lifetime. Furthermore, the same polymer exhibited a higher open circuit voltage and constant current value under constant voltage conditions. The partially sulfonated PPTA failed after approximately 250 h. SEM analysis indicated a less uniform integration of the partially sulfonated PPTA into the Solupor® matrix, which could account for the premature failure of the membrane. Initial polarisation measurements showed slightly poorer performance for the partially sulfonated PPTA but after 230 h, the polarisation curves for the two membranes were very similar. Under similar conditions, Nafion® 112 is a far superior membrane. However, if the incomplete filling of the Solupor® with PPTA in the present materials is taken into consideration, the performance of the sulfonated PPTAs becomes more competitive.
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1. Introduction

Our ever-increasing energy demands are pushing natural resources to the limit, prompting the need for alternative energy sources to be considered. A hydrogen fuel cell provides a clean and efficient form of electricity that can be utilised in portable devices, such as laptops and mobile phones, as well as for vehicles and buildings. The performance of the fuel cell is largely dependent on the properties of the membrane electrode assembly (MEA), which consists of a polymer electrolyte membrane and carbon based electrodes. The role of the polymer membranes is three-fold [1]: it should separate the two electrodes and act as an electronic insulator, ensure that there is no mixing of the gases (hydrogen and oxygen), but also allow for efficient transport of protons between the two electrodes. The ideal polymer electrolyte membrane should also exhibit good mechanical, chemical and thermal stability, to ensure that the fuel cell can function for up to 5000 h [2]. For mid-range temperature fuel cells (60–100 °C), DuPont's Nafion® membranes are the benchmark materials. The perfluorinated hydrophobic backbone provides mechanical integrity while the sulfonated hydrophilic side chains appear to cluster to form proton-conducting channels [3–5]. When operating at 100% relative humidity, the proton conductivity is of the order of 10^{-1} S cm^{-1}, a value that has been difficult to surpass. However, a reduction in the water content upon exposure to lower relatively humidities results in a considerable decrease in the conductivity [6]. Furthermore, there are also concerns about electro-osmotic drag of water and methanol crossover (in the case of direct methanol fuel cells) influencing the overall cell efficiency [7–9]. Consequently, new proton conducting membranes that overcome the limitations of

Nafion® while maintaining excellent conductivities are being investigated.

For Nafion®, as well as many of the new materials that are being developed as fuel cell membranes, there is very little control over the polymer morphology. Therefore, proton transport is expected to follow a random path, which may lead to a reduction in fuel cell efficiency. Ideally, a membrane morphology that incorporates a linear path between the two electrodes should provide the most efficient means of proton transport. With this in mind, a series of polymers based on poly(p-phenylene terephthalamide) (PPTA) were developed in order to test this hypothesis [10–14]. The synthesis can be controlled such that the placement and degree of sulfonation can be varied. These polymers are water-soluble and show an increase in solubility for higher degrees of sulfonation. Solutions in water exhibit liquid crystalline characteristics as a result of aggregate formation. Furthermore, the nematic alignment observed in solution is imparted to the film upon drying, as demonstrated by X-ray analysis [14,15]. It is expected that this alignment of the aggregates and by analogy the polymer chains, could be controlled to obtain a fully ordered membrane with well-defined pathways for proton transport.

Proton conductivities of these sulfonated PPTA films range from 10^{-3} to 10^{-1} S cm^{-1}, depending on the degree of sulfonation. Furthermore, there is some evidence that the film structure does indeed affect the proton conductivity, with much higher values obtained for measurements performed parallel to the polymer alignment [14,15]. In this work, the fuel cell performance of two forms of sulfonated PPTA was tested. The position of the sulfonic acid group was the same for both polymers, but the degree of sulfonation differed. The proton conductivity is sensitive to the number of sulfonic acid groups and thus it was expected that the fuel cell performance should also reflect such differences. As it was not possible to form freestanding films of these materials, a porous support matrix, Solupor® (DSM), was used. By using this porous matrix, it is possible that the polymer alignment is affected. Although no steps were taken to optimise the polymer films or MEAs, by doing so could result in further improvement in the fuel cell performance.

2. Experimental

2.1. Materials

The sulfonated poly(p-phenylene terephthalamide) polymers (Scheme 1) were prepared as reported elsewhere [10,14]. Dimethylformamide (DMF, ≥99.8% from Merck) was used as received. A solution of 25 wt.% Nafion® in 1,2-propanediol was prepared by first evaporating the water from a 10 wt.% Nafion® dispersion in water (Dupont) and dissolving the solid material in 1,2-propanediol (for synthesis, Merck). The Solupor® film is a trademark product from DSM. Pt/C HiSpec® 9100 catalyst material (56 wt.% Pt on high surface area carbon) was obtained from AlfaAesar. SGL Carbon supplied the Sigracet® GDL 31 BC backing materials.

2.2. Membrane preparation

Two polymers with differing degrees of sulfonation were studied: a fully sulfonated diamine form where each diamine monomer contains a sulfonic acid group (Scheme 1a) and a partially sulfonated diamine form where two out of three diamine monomers are sulfonated (Scheme 1b). A porous material known as Solupor® was used as a support matrix, into which the PPTA polymers were imbibed. The Solupor® is 20 μm thick and 83% porous, with a mean flow pore size of 0.7 μm. Thus, for a film of 4.5 cm × 4.5 cm × 0.002 cm the pore volume is approximately 0.034 cm^3. Assuming the density of the PPTA polymers is 1.4 g cm^{-3}, 0.047 g of polymer are required to fill the pores. Solupor® is hydrophobic and is therefore unable to absorb water solutions of the polymers. Thus, the polymers were dissolved in dimethylformamide (DMF) and subsequently imbibed into the Solupor®. The fully sulfonated PPTA is readily soluble in DMF; the solubility limit of the partially sulfonated PPTA in DMF is 1 wt.%. Furthermore, only 2 ml of solution was required to cover the surface of the Solupor® film; greater volumes flowed off the surface. Consequently, the actual fraction of pores filled by the polymer is approximately 40%. The solutions were only exposed to one side of the Solupor® and the DMF was allowed to evaporate. From a macroscopic view, the fully sulfonated PPTA
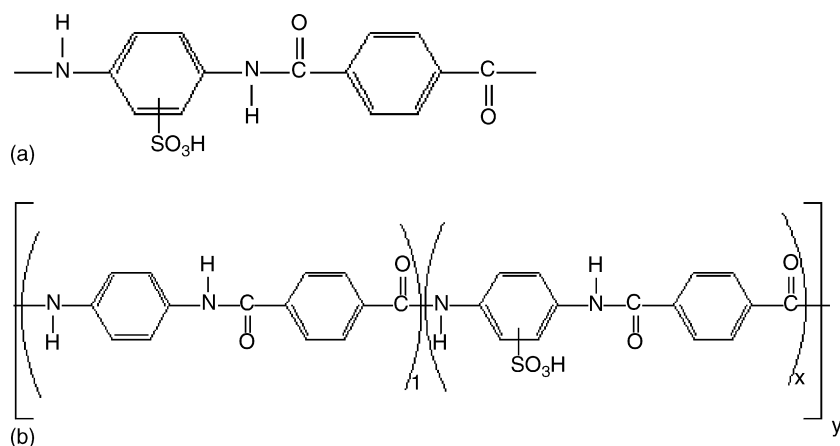
Scheme 1. Chemical structures of (a) the fully sulfonated diamine version of PPTA and (b) the partially sulfonated diamine version of PPTA. The value of x is 2.

appeared to be well imbibed within the sample; the partially sulfonated PPTA seemed to only coat the surface.

2.3. Conductivity measurements

Proton conductivities were measured with a Novacontrol Alpha Analyser dielectric response analyser. Measurements were performed on the Solupor® membranes imbibed with each polymer. A standard windowpane cell with indium electrodes was employed, allowing the samples to be exposed to an atmosphere of 100% relative humidity. The measurements were performed over a temperature range of 26–90 °C and a frequency range of 1 MHz–0.1 Hz.

2.4. MEA preparation

An electrode ink was prepared from Pt/C HiSpec® 9100 material and the Nafion® solution. This ink was applied on the Sigracet® GDL 31 BC backing material with a nominal platinum loading of 0.33 mg cm^{-2}. After evaporation of the solvent a small amount of Nafion® dispersion in water was applied to ensure good contact between the electrode and the membrane. The Nafion® to carbon ratio in the ink was 0.6 and the additional amount of Nafion® was 0.5 mg cm^{-2}. This formulation for the electrode was found to be optimal for cathodes on a Nafion® 112 membrane [16]. No re-optimisation for the present membranes was undertaken.

This electrode was used as both anode and cathode and the membrane was sandwiched between the electrodes. To avoid melting the Solupor® (mp ≈ 120 °C), the MEAs were pressed at 65 °C, at 4 bar for 90 s. The active surface area of the MEAs was 7 cm^2.

2.5. Fuel cell tests

The performance of the Solupor® MEAs was evaluated in a single cell setup at the Energy Research Centre of the Netherlands (ECN). Measurements were performed under fully humidified conditions at 65 °C with anode and cathode pressures of 1.5 bar (absolute). Gas temperatures were maintained at the same temperature as the cell. At the anode, the hydrogen stoichiometric ratio was 1.5, while at the cathode, the air stoichiometric ratio was 2. The cell voltage was set at 0.4 V and the first V–I curve measured after approximately 20 h. The cells were left at constant voltage, with the open circuit voltage (OCV) measured for 30 s every hour. V–I curves were recorded periodically. Impedance measurements were also conducted on the functioning fuel cell in order to determine the resistance of the cell. For this a Zahner IM6e was used with a PP200 power potentiostat over a frequency range of 100 kHz–0.1 Hz. Measurements were made at 550 and 350 mA cm^{-2} for the fully and partially sulfonated MEAs, respectively.

2.6. SEM analysis

Both pre-test and post-mortem analysis of the Solupor® film structures was observed using a Phillips scanning electron microscope (SEM XL 20) equipped with 15 kV electron source. Images were recorded for the unfilled Solupor® and contrasted with those of the imbibed films. Both sides of the imbibed films were examined in each case; cross-sectional analysis provided no useful information.

3. Results and discussion

3.1. Pre-test SEM analysis

From visual observation of the Solupor® films imbibed with the sulfonated PPTA polymers, the fully sulfonated PPTA appears to be well absorbed into the porous matrix while the partially sulfonated PPTA seems to mostly coat the surface of the exposed side of the Solupor®. In order to obtain a better indication of structure of these films prior to testing, SEM analysis was performed, with the results shown in Figs. 1 and 2. The unfilled Solupor® (Fig. 1) appears as matted strands of polymer with pores in between. The strands range from less than 1 μm to a few microns in diameter; the pore size is of similar dimensions. Upon imbibing the Solupor® with the PPTAs, the resulting structure is quite different (Fig. 2). From the top surface (the surface exposed to the PPTA solution), the fully sulfonated polymer seems to be well imbibed into the Solupor® matrix (Fig. 2a). For the partially sulfonated polymer however, most of the pores appeared to be filled, but the surface is also dotted with small particles, which could be the result of incomplete solubilisation of the polymer (Fig. 2c). Images from the bottom surface (that was *not* exposed to the polymer solution) show a reduced filling of the pores (Fig. 2b and d). This also seems to be more pronounced in the case of the partially sulfonated PPTA where more unfilled pores were observed. Therefore, it appears the impregnation of the partially sulfonated PPTA was less successful, which could be a direct consequence of the reduce solubility of this polymer. Such structural differences within the films could impact both the fuel cell performance and long-term stability of the MEAs.
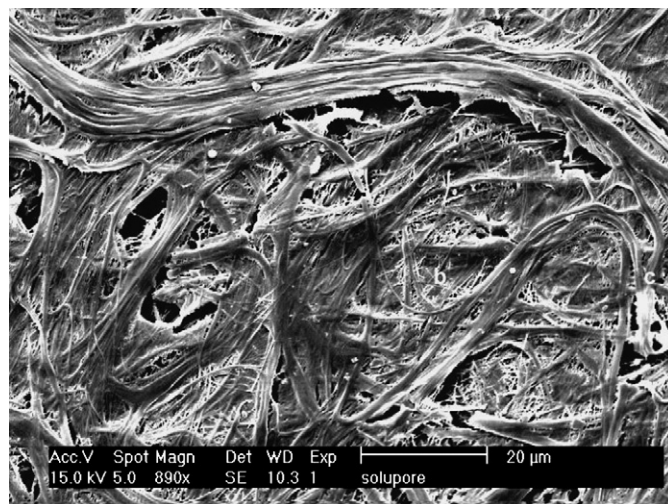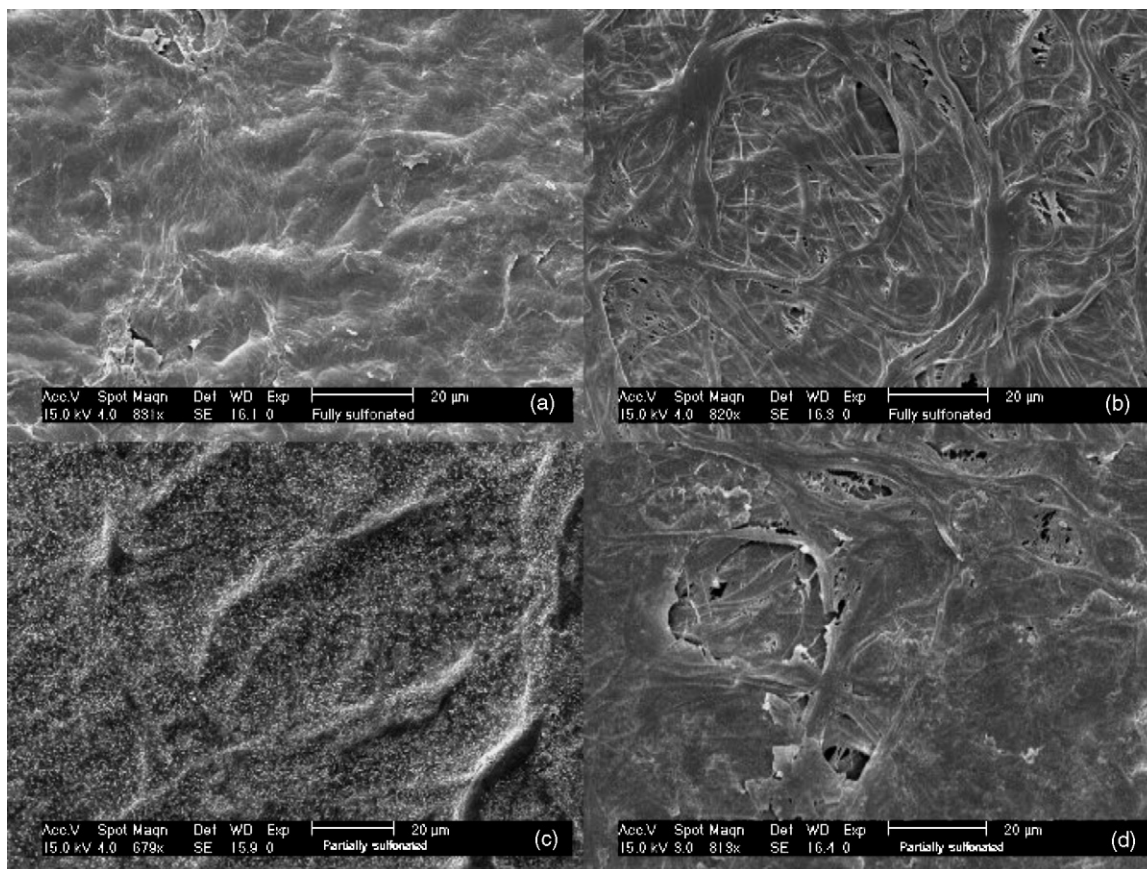

Fig. 1. SEM image of the unfilled Solupor® matrix.

Fig. 2. Pre-test SEM analysis of Solupor® imbibed with sulfonated PPTA. For the fully sulfonated PPTA, images (a and b) are from the top and bottom film surfaces, respectively. For the partially sulfonated PPTA, the same surfaces are shown in images (c and d).

3.2. Conductivity measurements

Proton conductivity measurements (Fig. 3) were performed as a function of temperature for the Solupor® films imbibed with both polymers. In both cases, the conductivity shows a steady
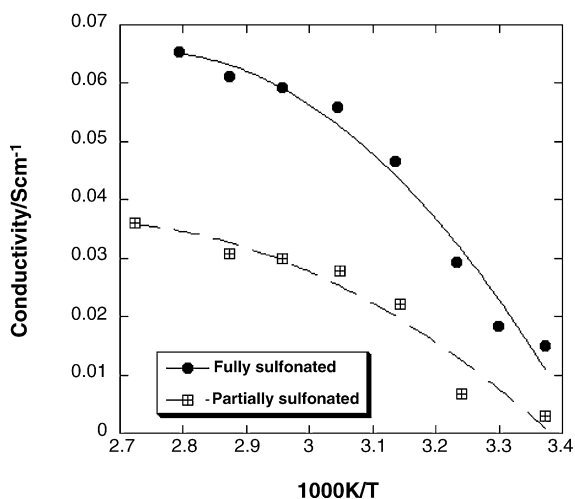

Fig. 3. Proton conductivity measurements as a function of reciprocal temperature for Solupor® films imbibed with the fully and partially sulfonated PPTA. Measurements performed at 100% relative humidity. Lines are to guide the eye only.

increase with increasing temperature with the values ranging from 10^{-3} to 10^{-2} S cm^{-1}. Furthermore, the fully sulfonated polymer exhibits conductivity values that are consistently double that of the partially sulfonated polymer. Given that the fully sulfonated polymer contains twice the number of sulfonic acid groups compared to the partially sulfonated polymer, these results directly reflect the degree of sulfonation. In contrast to other measurements on freestanding films of these polymers [14,15], it appears that the Solupor® does not restrict proton conduction. Thus, it is indeed an appropriate support matrix for assessing the performance of these sulfonated polymers.

3.3. Fuel cell analysis

Several fuel cell experiments were conducted in order to assess the performance of the MEAs. The cells were maintained at a constant voltage of 0.4 V and the corresponding current was measured, the results of which are shown in Fig. 4. Open circuit voltages were monitored for 30 s every hour and these results are shown in Fig. 5. The partially sulfonated polymer shows some increase in the current over time during most of the measurement period. Only after about 150 h does the current appear to stabilize at a current density value of 0.4 A cm^{-2}. The open circuit voltage also shows a steady increase over the same time period before reaching a maximum value of approximately 920 mV. After approximately 250 h, the MEA starts to degrade rapidly
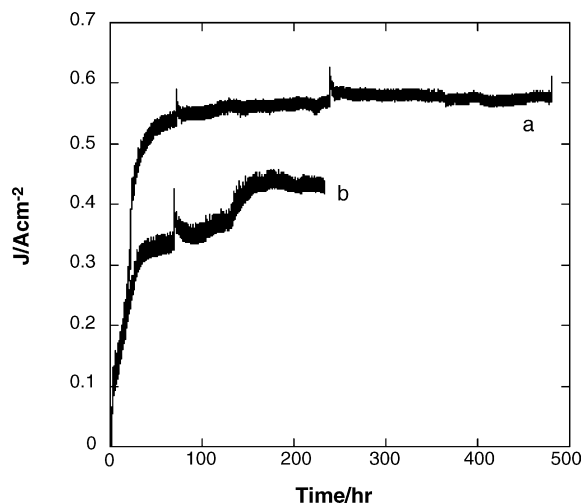
Fig. 4. Time dependent current response for fuel cells measured under a constant voltage of 0.4 V for a) the fully sulfonated membrane and b) the partially sulfonated membrane.

Fig. 6. Polarisation curves for the fully and partially sulfonated MEAs. Measurements were made after 20 and 230 h for both MEAs and in the case of the fully sulfonated membrane, after 480 h also.

(not shown), with the current density dropping to $0.06\,A\,cm^{-2}$ and the open circuit voltage to 760 mV. This sudden decline in performance was related to membrane failure, as confirmed after disassembling the cell.

The fully sulfonated polymer showed slightly different behaviour (Figs. 4 and 5), stabilizing after a considerably shorter time period (approximately 50 h). The current density reaches a value around $0.58\,A\,cm^{-2}$ and the open circuit voltage has a maximum value of 940 mV. Unlike the partially sulfonated polymer, the performance was maintained for almost 500 h and there was no evidence of cell degradation over this time.

For the two MEAs, polarisation curves were recorded after 20, 230 h and for the fully sulfonated polymer, another measurement was performed after 480 h (Fig. 6). In each case, there is some improvement in the fuel cell performance with time, which is mostly likely due to conditioning of the cell. While the partially sulfonated polymer deteriorated after 250 h, the fully sulfonated

polymer maintained the performance, even after 480 h. The difference between the measurements at 230 and 480 h is minimal.

In comparing the two MEAs, there are some clear differences in the fuel cell performance. Such differences can arise from several possible sources, i.e. the ohmic resistance of the MEA, the proton resistance in the electrodes, the gas transport in the electrodes and the utilisation of the platinum. Measurements of the ohmic resistance by impedance spectroscopy of the MEAs showed no significant variation in time. The values were $0.02\,\Omega$ ($0.14\,\Omega\,cm^2$) and $0.03\,\Omega$ ($0.21\,\Omega\,cm^2$) for the fully and partially sulfonated polymers, respectively (Fig. 7). For a Nafion® 112 membrane in an otherwise similar MEA and testing rig, the resistance was $0.08\,\Omega\,cm^2$ [16]. These data reflect the differences found in the conductivity measurements (Fig. 3). Moreover, it is clear that the ohmic resistance of these MEAs has only a limited effect on the V–I curves shown in Fig. 6. The improvement observed between 20 and 230 h is mostly due to
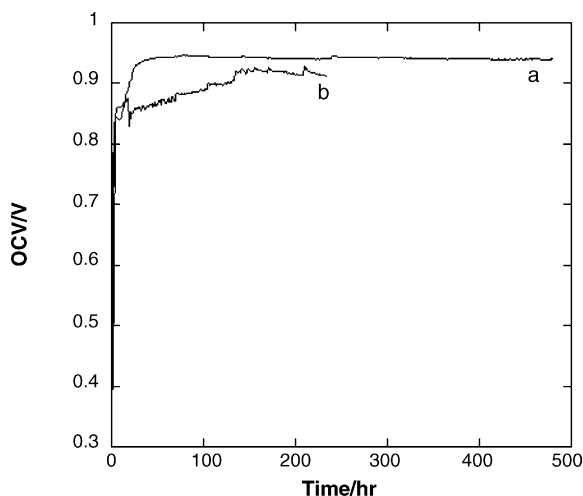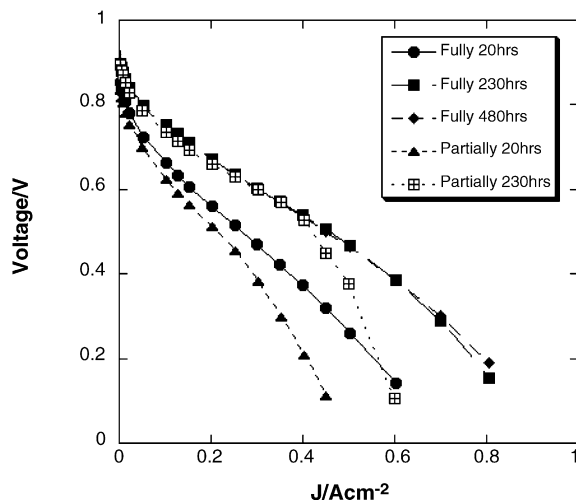

Fig. 5. Open circuit voltages (OCV) measured as a function of time for a) the fully sulfonated membrane and (b) the partially sulfonated membrane.
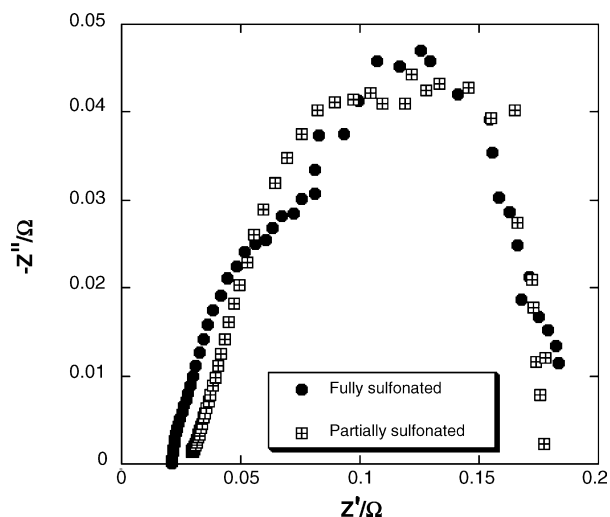

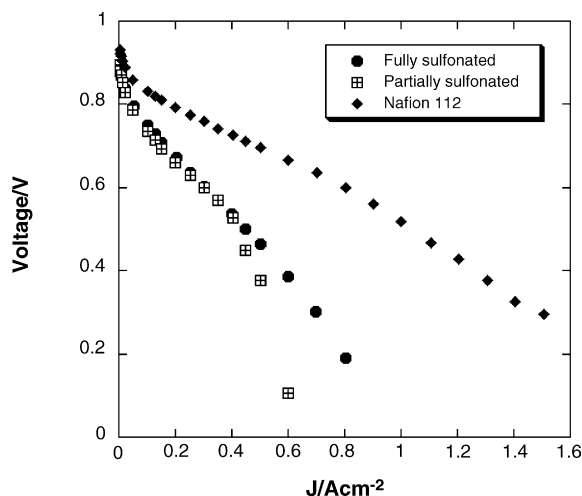Fig. 7. Impedance analysis of the functioning fuel cells to determine the cell resistance.

Fig. 8. A comparison of the fuel cell performance of the sulfonated PPTAs and Nafion® 112. The Nafion® results are also reported in reference [16].

electrode effects, i.e. mass transport effects or improved utilisation of the platinum. Better water distribution may have been the reason for such improvements resulting most of all in a lower proton resistance in the electrodes.

In Fig. 8, the fuel cell performance of these sulfonated PPTA MEAs is compared to that of Nafion® 112 (Nafion® results from reference [16]). For the Nafion® membrane, same electrode and

backing materials were used, but the gas pressures were 1 bar instead of 1.5 bar. Operation at 1.5 bar would have resulted in lower oxygen transport losses, i.e. better performance. Although the Nafion® membrane is considerably thicker (approximately 50 μm compared to 20 μm for the Solupor® films) the ohmic resistance of the MEA was much lower than that of the PPTA membranes (see above). This can be attributed to the higher intrinsic conductivity of the Nafion® at these conditions and to the use of composite membranes in the case of PPTA. Still, the difference between the V–I curves of Nafion® and the PPTAs cannot be explained by the ohmic resistance alone. The performance seems to be dominated by mass transport (proton and/or gas) effects and incomplete filling of the Solupor® membrane may be accountable for such behaviour. As was mentioned in Section 2.1, 20% of the volume is the Solupor® material itself, leaving 80% to be filled by the PPTA polymer. However, due to the limited solubility of the sulfonated PPTAs, only 40% of these pores could be filled. Thus, approximately 1/3 of the membrane consists of PPTA polymer. Furthermore, in the filling procedure, only one side of the membrane was exposed to the polymer solution. Despite the limited PPTA content within the Solupor® matrix, the measured OCV values strongly indicate that a gas-tight layer was formed. From this it can be inferred that the pores on the side exposed to the solution are filled, while on the other side, they are not. This implies that the Nafion®-PPTA contacts for proton transport at the
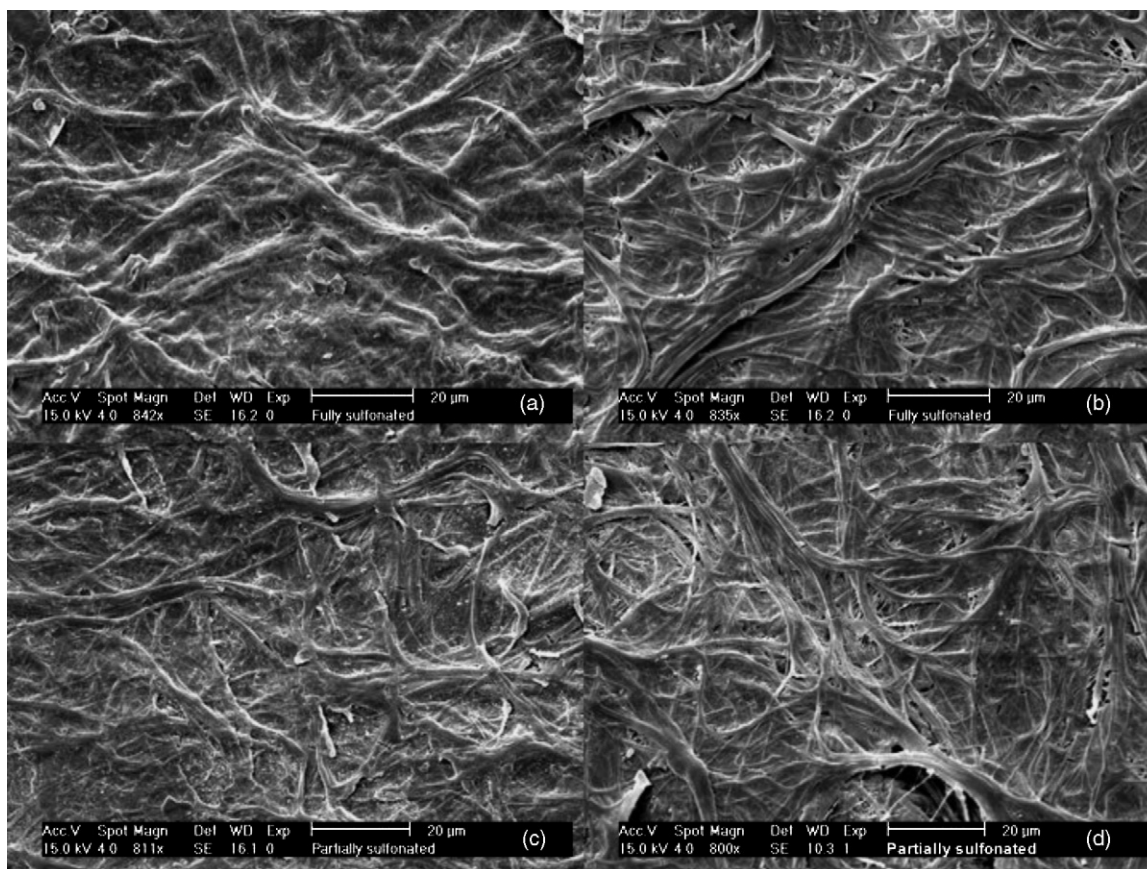

Fig. 9. Post-mortem SEM analysis of Solupor® imbibed with sulfonated PPTA. For the fully sulfonated PPTA, images a) and b) are from the top and bottom film surfaces, respectively. For the partially sulfonated PPTA, the same surfaces are shown in images (c and d).

electrode-membrane interface would have been especially poor for the relatively unfilled side of the Solupor®. This is consistent with the observation that mass transport is worse in the case of partially sulfonated PPTA. In Section 3.1, it was observed that the limited solubility of the partially sulfonated PPTA in DMF results in poor absorption into the Solupor® matrix. Consequently, improved filling of the Solupor® membrane may further improve the ohmic resistance, but also possibly reduce the substantial mass transport losses observed here in comparison to what is usually found with Nafion® membranes.

3.4. Post-mortem SEM analysis

It was somewhat surprising that the partially sulfonated PPTA MEA should fail while the fully sulfonated PPTA MEA did not. In order to investigate the cause of the failure, SEM images of the filled and unfilled Solupor® films were taken, as shown in Fig. 9. From the pre-test SEM analysis (Section 3.1 and Fig. 2), most of the pores in the Solupor® matrix are filled when imbibed with the fully sulfonated PPTA. The surface is quite smooth, although the Solupor® fibres can still be seen in some areas, which may indicate that some of the PPTA has dissolved during testing. However, even after testing, it still appears that the sulfonated PPTA is well integrated into the Solupor® structure. For the partially sulfonated PPTA, however, the pre-test and post-mortem SEM images are quite different (Figs. 2 and 9). The post-mortem film contains more porous sections, although in other regions, the polymer still seems to be well imbibed into the Solupor®. The precipitates that were seen in the pre-test film are still evident in the post-mortem, although possibly to a lesser extent. The post-mortem results clearly indicate a less uniform film. Consequently, it is envisaged that the presence of the unfilled pores and the inhomogeneous nature of the Solupor® film in this case could result in faster failure of the film. Furthermore, any polymer on the surface of the support could be more susceptible to dissolution, thus diminishing the ability to transport protons. It was mentioned earlier, however, that the partially sulfonate polymer has a reduced solubility compared to that of the fully sulfonated PPTA. Thus, one might expect the fully sulfonated PPTA to have dissolved more readily during testing. Consequently, it seems improved filling of the hydrophobic Solupor® support matrix plays a large role in stabilising the polymer against dissolution. However, given that these MEAs are not optimised in any way, it is difficult to draw any firm conclusions about the durability of the films.

4. Conclusions

Sulfonated polymers based on poly(*p*-phenylene terephthalamide) were imbibed in an inert porous matrix (Solupor®) and tested in a fuel cell. Two polymers were investigated with differing degrees of sulfonation. The conductivities of these films were measured using dielectric methods and found to be of the order of 10^{-3} to 10^{-2} S cm^{-1}. Lifetime analysis of the two cells showed some differences between the two polymers. At a constant voltage of 0.4 V, the partially sulfonated PPTA took longer to reach a steady state, only maintaining a constant current of approx-

imately 0.4 A cm^{-2} after 150 h. Similarly, it also took some time for the open circuit voltage to stabilise at the final value of 920 mV. The fully sulfonated membrane, however, showed much better stability, reaching a steady state early at values of 0.58 A cm^{-2} at 0.4 V and an open circuit voltage of 940 mV. Furthermore, the performance of the fully sulfonated polymer was maintained over a longer lifetime; the membrane showed no sign of deterioration after almost 500 h, while the partially sulfonated polymer failed after 230 h. The failure mechanism is thought to be the result of poor imbibition of the partially sulfonated PPTA in the Solupor® matrix. During the course of the fuel cell test, the polymer may dissolve thus limiting the means for effective proton transfer.

Differences were also observed in the polarisation response of the cells. Initial measurements indicated slightly poorer performance for the partially sulfonated PPTA as a result of the lower resistance and some limitations in the mass transport. However, over time, the performance of both membranes improved and the polarisation curves for each polymer were very similar after 230 h. Although the fully sulfonated polymer demonstrated a longer lifetime, there was no improvement in the polarisation behaviour after 250 h; the performance, however, was maintained. In comparison to Nafion® 112 under similar conditions, the PPTA polymers show poorer performance. This seems mostly due to incomplete filling of the Solupor® matrix, which seems to result in not only larger ohmic losses in the membrane but also in substantially larger proton transport losses in the MEA. Additional analyses, including impedance measurements, may shed more light on this. In spite of this shortcoming, it was shown that the materials presented here have potentially sufficient proton conductivity and can be used under fuel cell conditions.

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