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The ionic conductivity of a Nafion® 1100 series of proton-exchange membranes re-cast from butan-1-ol and propan-2-ol

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Abstract

The ionic conductivity of Nafion® 1100 extruded membranes re-cast from solutions of butan-1-ol and propan-2-ol is measured in 0.5 mol dm^{-3} H_2SO_4 at 295 K, using an immersed, four-electrode d.c. technique. The general trend is an increasing conductivity for the thicker membranes. Materials which were solution-cast from butan-1-ol yielded the highest conductivity while a series of membranes with lower conductivities (similar to those of an extruded Nafion® 1100 series of membranes) was found using propan-2-ol. The conductivity results indicate that membranes manufactured by extrusion and casting from various solvents might have different structures. Differences in the water content and conductivity of the membranes are considered to arise from the impact of processing conditions on the surface and bulk structure of the membranes.

Keywords: Area conductance; Butan-1-ol; Ion exchange membrane; Nafion® ionomer; Perfluorinated polymer; Proton exchange membrane; Propan-2-ol; Resistance; Solution-cast.

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1. Introduction

Polyfluorocarbon sulfonic acid based membranes, such as Nafion® (DuPont de Nemours), Aciplex® (Asahi Kasei) and Flemion® (Asahi Glass) have a wide range of applications due to their high chemical and electrochemical stability, reasonable mechanical strength, low permeability to non-ionic species, selective and high ionic conductivity and ability to provide electronic insulation [1]. Industrial applications of these ion exchange membranes include gas separation, gas sensors, electrodialysis, chlor-alkali cells, salt-splitting, supercapacitors, fuel cells and batteries [2-5].

Extruded membranes have traditionally been used in these applications due to their commercial availability and ease of use. Membranes cast from the ionomer resin dissolved in alcohols are, however, being commercialised by DuPont de Nemours [5], primarily for PEMFC applications where thin membranes of less than 30 μm are desired for their lower ionic resistance. It can be difficult to convert the extruded membranes to the acid form in the case of such thin materials.

Casting from polymer solutions is a common and reliable method of producing thin membranes and in the current development of PEMFCs, there is a major drive towards thin (<30 μm) solution-cast membranes [6, 7]. For such materials, the membrane resistivity, which exerts a large effect on PEMFC performance at intermediate current densities, is highly dependent on the solvent employed and is important to select a solvent that is reasonably slow-drying but which is completely removed from the dried membrane. Thin composite membranes for PEMFC applications have been manufactured by impregnating ionomer solutions into microporous supports such as PTFE [8-10], quartz sheets and high molecular weight

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polyethylene webs. Other microporous matrices, such as polysulfone and microglass fibre fleeces [11], have found use as membrane supports. In the PEMFC, the WL Gore composite membranes employing PTFE as the support have been widely adopted [8-10]. The composite structure combines mechanical strength with a tolerance to dimensional change during hydration and adequate conductivity at thicknesses below 30 μm.

Cast membranes have also been used in the production of self-humidifying membranes, where hygroscopic oxides, such as SiO_2 [12] TiO_2 [13], silicotungstic acid (STA) [14] and SiO_2 + TiO_2 + nanocrystallites of Pt [15], have been incorporated into the polymer matrix. The platinum provides a catalytic site for the combination of H_2 and O_2 while the water produced is retained by the hygroscopic oxides, providing a low electrical resistance and reduced crossover. This results in a simple cell with a rapid response time and a high power output [15] although the heat from the recombination reaction is a concern for membrane durability. Cast membrane films have been used to study polymer morphology using scanning force microscopy [16] and transmission electron microscopy [17, 18], where thin sample films of less than 10 μm were required.

To prepare cast membranes, the ionomer is typically supplied as an alcoholic or aqueous colloidal solution. Membranes are readily obtained by pouring the 'as-received' solutions into casting dishes and allowing the solvents to evaporate [15-19]. In some cases, however, the solvent composition has been modified, prior to casting materials as thin films or incorporating them into microporous supports [8, 16, 20]. Hybrid inorganic/organic polymer electrolyte membranes have also been prepared by

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a centrifugal casting process using sulfonated polyetheretherketone (SPEEK) and polyethoxysiloxane (PEOS) in dimethylacetamide. The morphology of the films was controlled by the segregation process determined by the rate of evaporation of the solvent and by the transformation of PEOS into SiO_2 particles using a catalyst. In the humid state the conductivities of the membranes were comparable to commercial Nafion® 115 membranes [21].

For Nafion® ionomers, large differences in structure have been observed between the Nafion® species dissolved in solution and those existing in the solid state. In the solvent, the fluorocarbon phase exists as micelles surrounded by ionic groups while a continuous phase consists of ionic clusters distributed throughout the solid matrix in films. Details of structural changes in Nafion® related to the casting process remain unclear. In a recent review of the state of the understanding of Nafion®, Mauritz et al. [22] reported that water and ethanol solutions containing the ionomer are heterogeneous with rod-like particles forming cylindrical structures with the solvent-polymer contact at the surface of the charged particles in solution exhibiting similar electrostatic repulsion as in colloidal suspensions. The authors reported several studies in the literature in which Nafion® solutions contain large colloidal aggregates of anisotropic structure and a size greater than 15 nm. In the films formed by re-casting Nafion® solutions in ethanol-water at room temperature, the authors reported that cast films had different physical and chemical properties to the 'as-received' membranes. The cast films tended to be "mud-cracked", brittle, and soluble at room temperature in polar organic solvents, whereas the as-received Nafion membranes were flexible and insoluble in all solvents up to 200 °C. If high boiling point solvents were used in the casting procedure the films tend to reproduce the properties of the as-

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received Nafion® membranes at a temperature of 160 °C. It has been suggested [22] that the solid state structure of the cast films is a function of the macromolecular organization of the Nafion® chains during the evaporation of the solvent which implies a morphological difference between the re-cast and the 'as-received' films.

The present work considers the ionic conductivity of Nafion® membranes prepared by re-casting of extruded material from solutions of propan-1-ol and butan-2-ol. The membrane thicknesses produced were of the same order of magnitude as those of an extruded Nafion® series of materials [23]. The relationship between the ionic conductivities of the cast and extruded membranes and the effect of hot-pressing the membranes are considered as well as the performance differences associated with the method of membrane manufacture.

2. Experimental details

2.1 Materials

The commercially available extruded membranes Nafion® NE-112, 1135, 115 and 117 (of nominal equivalent weight 1100 and in the acid form) were obtained from DuPont de Nemours. Solution-cast membranes (550 cm^2 area) were prepared from 5 wt% solutions of the Nafion® ionomer (1100 EW, H^+ form) in butan-1-ol and propan-2-ol solvents. The Nafion® containing solutions were placed in casting trays and left *in vacuo* at 373 K for 3-4 hours until the solvent had evaporated. Three membranes of a given thickness were produced and characterised for each solvent system to establish reproducibility.

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To ensure membrane purity and to achieve full hydration, all membranes were pre-treated by heating to 353 K in 2 % vol H_2O_2 (Fisher Scientific, AnalaR grade) for 2 hours, followed by cooling and rinsing with doubly distilled water to remove all traces of H_2O_2. The membranes were then soaked in 0.5 mol dm^{-3} H_2SO_4 (Fisher Scientific, AnalaR grade) for 48 hours, rinsed in water and boiled in 0.02 mol dm^{-3} H_2SO_4 for 1 hour. Such a pre-treatment is important; membrane resistance is a strong function of the state of hydration [4, 24]. After a further water rinse to remove the final traces of acid, the membranes were stored in doubly distilled water until required. The conductivity of the water used for all experiments was measured before use to ensure it remained below 0.1 μS cm^{-1}.

2.2 Membrane thickness

Both the dry membrane thickness and the hydrated membrane thickness following immersion in 1 mol dm^{-3} H_2SO_4 at 295 K were measured (±1 μm) at 30 random points over the surface, using a digital micrometer (Mitutoyo, Digimatic Micrometer). The hydrated membranes were equilibrated in 1 mol dm^{-3} H_2SO_4 for a minimum of 24 hours at 295 K prior to thickness measurements in order to achieve the acid form of the membrane.

2.3 Proton conductivity

The proton conductivity of each membrane was measured at 298 K by a d.c. technique using a four-electrode cell incorporating twin reference electrodes in 1 mol dm^{-3} H_2SO_4. The cell is shown in Figure 1. By careful adjustment of the position of the closely matched saturated calomel reference electrodes (SCE, Radiometer Ref

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401, Radiometer Ltd. Crawley, UK), it was possible to measure the voltage drop across the membrane as the current density was linearly swept from 0 to 1000 then back to 0 mA cm^{-2} (to check for the absence of hysteresis) between two, outer platinum gauze electrodes, placed either side of the membrane. The potential difference between the SCEs was measured with a high impedance digital voltmeter (Thandar TM451) connected between the SCEs. The accuracy of the Luggin capillary positions was carefully checked by measuring the gap between the tip of the Luggin capillary and the membrane surface with a calibrated vernier gauge. The identical distance of 1.5 mm between the Luggin capillary tip and the membrane surface, with different thicknesses of membrane, was achieved by altering the thickness of the flange gaskets. Great care was taken to ensure the flange defined an active membrane area of 1 ± 0.025 cm^2 and that the gasket material did not impinge on the membrane in the open flange area. The voltage drop across the membrane was plotted as a function of current density and the membrane resistance was obtained from the gradient. Due to the difficulty in obtaining reliable measurements from different areas of the membrane, several measurements on a minimum of 5 samples were obtained to provide an average membrane resistance. All measurements were corrected for the uncompensated *IR* drop between the Luggin capillary tip and the membrane surface on each side of the membrane. Full details of the experimental procedure and a discussion of the problems associated with obtaining reliable measurements have been described elsewhere [23].

2.4 Ion-exchange capacity and equivalent weight

Sections of membrane were pre-treated as described in Section 2.1, weighed (ca. 1 ± 0.0010 g) then placed in 50 cm^3 of 0.1 mol dm^{-3} NaCl solution (BDH, AnalaR grade)

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for 24 hours at ambient temperature (295±2 K) to convert the membrane from the H^+ to the Na^+ form. The membrane samples were removed and dried over P_2O_5 (BDH, SLR grade) in a closed container at ambient temperature for 48 hours. The NaCl solution was titrated against 0.02 mol dm^{-3} NaOH (BDH, AnalaR grade) to a pH 7.0 end point using phenol red indicator (Aldrich). The volume of NaOH consumed was used to calculate the amount of H^+ in solution. Assuming complete conversion of the membrane to the Na^+ form, the ion-exchange capacity (IEC, mmol H^+ / g polymer) was calculated [4, 23, 25]:

$$IEC = \frac{V_{NaOH} \times c_{NaOH}}{w} \quad (1)$$

where c_{NaOH} is the concentration of the sodium hydroxide solution (mol cm^{-3}), V_{NaOH} is the volume of sodium hydroxide used (cm^3) and w is the mass of dried polymer (g). The equivalent weight, *EW* (g polymer / SO_3H group) was obtained as the reciprocal of the *IEC* value.

2.5 Water content

Samples of the membrane that did not increase their weight after been immersed in water were carefully blotted dry of all surface moisture and weighed (±0.0001 g). Membranes were then dried over excess P_2O_5 (BDH, SLR grade) at room temperature in a sealed container for 48 hours at ambient temperature (296 K) then re-weighed. The water content of the membranes, λ (mol H_2O / SO_3H group) was calculated using the expression:

For Peer Review

$$\lambda = EW \left[\frac{w_1 - w}{M_R(H_2O)\ w} \right] \quad (2)$$

where w_1 is the mass of the hydrated polymer, w is the mass of dried polymer and M_R (H_2O) is the relative molar mass of water.

3. Results and discussion

3.1 Treatment of the membrane potential difference data

Plots of the potential difference between the matched SCE reference electrodes versus the current, over a wide range of current density, obeyed Ohm's Law:

$$\Delta E_{ref} = I.R_{cell} \quad (3)$$

This allowed the average cell resistance to be determined from the slope of the line. The electrolyte resistance was then obtained by measuring the cell resistance in the absence of the membrane:

$$\Delta E_{ref} = I.R_{electrolyte} \quad (4)$$

The background electrolyte resistance was subtracted from the cell resistance to give the membrane resistance:

$$R_{mem} = R_{cell} - R_{electrolyte} \quad (5)$$

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This background electrolyte resistance accounted for some 60% to 80% of the cell resistance. This is a significant correction and is the major reason why great care is required to correct for the membrane resistance in these measurements. The membrane resistance was then used to calculate the area resistance:

$$R_A = R_{mem}.A \tag{6}$$

and the membrane resistivity:

$$\rho = R_A / L \tag{7}$$

3.2 Ion-exchange capacity, equivalent weight and water content

The ion-exchange capacity, equivalent weight and water content of all membranes are shown in Table 1. All of the cast membranes had *IEC*/*EW* values which are comparable to the extruded membranes and consistent with the nominal range specified by the manufacturer for the 'as-received' extruded membranes and the ionomer in the 5 wt% Nafion® solution (0.91 mmol H^+/g or and 1100 g polymer/SO_3H group, respectively). This confirms that the solvent exchange and coating procedures did not lower the proton concentration within the membranes.

While providing values which were consistent with the nominal IEC or EW, the prescribed titration procedure did not access all of the protons in the ionomer; *IECs* of 0.93 to 0.99 and *EWs* of 1000 to 1050 are typical. Deviations in the measurements can be attributed to limitations in the weighing and calculation procedures used to determine the content of polymer in the casting solution.

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Table 2 shows the water content (λ) of the membranes following immersion in water and in 1 mol dm^{-3} H_2SO_4 at 298 K. The data show that all of the extruded membranes were close to full hydration, which is important in any study of hydrated membrane resistance; it has been shown that a λ value of 22 in pure water represents a fully hydrated, extruded Nafion® membrane [26-30]. A decrease in hydration number is seen when the hydrating solution is changed to 1 mol dm^{-3} H_2SO_4 with the membrane water content decreasing by 3-5 mol water per sulphonic acid group. This probably reflects the effect of H_2SO_4 present in the membrane reducing the water activity in the membrane and decreasing activity of external water, these effects having been reported previously in the literature [29] and [31], respectively.

For solution-cast membranes, Table 2 generally shows that the solution-cast membranes have a significantly higher water take-up compared to the extruded membranes, indicating their greater tendency to hydrate following the re-adsorption of water. In water, for example, the membranes cast from butan-1-ol show λ values from 27 to 30 and those cast from propan-2-ol λ values of 25 to 48. In 1 mol dm^{-3} H_2SO_4, the λ values are much closer to those in the extruded membranes. This suggests that the solution-cast membranes have a higher acid content or that a lower water-sorption isotherm occurs for membranes cast in butan-1-ol.

Table 2 also lists the dry and hydrated membrane thickness in 1 mol dm^{-3} H_2SO_4 together with the increase in membrane thickness compared to the dry condition. In all cases, the membrane thickness increases on hydration, due to the swelling caused by the water take-up. Figures 2 and 3 show the relationship between the thickness increase and the water take-up of the membranes in 1 mol dm^{-3} mol dm^{-3} H_2SO_4 for a

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range of hydrated membrane thicknesses. The extruded membranes show a similar increase in thickness of approximately 20 % over the thickness range (Figure 2), which is consistent with the high water take-ups of 15.5 to 22.1 (Figure 3).

For the solution-cast membranes, the behaviour is very dependent on the solvent. With butan-1-ol cast membranes, the thickness increase and the water take-up for the thicker membranes is comparable to those for the extruded membranes. At a thickness of 90 μm, however, the membrane shows a thickness increase of 65.5% (Figure 2) that cannot be associated with the typical water take-up of 17.8 (Figure 3). This suggests that the membranes cast from butan-1-ol may undergo an internal polymer reorganisation on hydration, which is more pronounced for the thinnest membranes. Thinner membranes tend to be more resistive [23], possibly due to a larger relative contribution of surface resistance to the overall behaviour. A restructuring of the membrane on casting would reorientate the ion domains present in the dry membrane into connected networks of polymer rods when fully hydrated [27].

For re-cast membranes from propan-2-ol, the relationship between the thickness increase of the membrane and the water take-up is more straightforward, over a range of membrane thicknesses, as shown in Figures 2 and 3. At thicknesses below 100 μm, the dimensional changes (Figure 2) and the water take-up (Figure 3) are consistent with the behaviour of extruded membranes. For the thickest membrane, the increase of 69% in membrane thickness can be associated with a high water take-up of 27.7 mol of H_2O per SO_3H^- group (Figure 3). Assuming that the thickness of the membrane is uniform, this indicates that the polymer is more hydrophilic in nature at higher membrane volumes. Such behaviour must be related to the casting solvent and

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further work is required to understand these effects. Although propan-2-ol has a lower boiling point than butan-1-ol, and would be expected to be more easily removed from the polymer, it is a smaller molecule, more hydrophilic and also an excellent wetting agent. It is likely that propan-2-ol is being trapped in the polymer during casting and, since it is hygroscopic, it attracts more water into the bulk of the polymer. Some evidence for this is provided by the very high water take-up of 48 in water (Table 2). This value is much higher than the value of 22 expected for full membrane humidification, suggesting that the membrane is over- hydrated.

3.2 Resistance and conductivity measurements

The calculated membrane area resistance for the three different series of materials is shown as a function of the hydrated membrane thickness in Figure 4. The membranes exhibited the expected trend of increasing resistance with increasing membrane thickness within all ranges. For the extruded Nafion® membranes, the observed non-linearity of the membrane resistance with membrane thickness may be related to an alteration in the membrane surface during the manufacturing processes. During production, thinner extruded membranes require a higher roller pressure, resulting in increased local temperatures and an increased melt flow of the surface layers. This would result in some closing of ion and water channels due to a reduction in their size and/or an increase in their tortuosity, leading to an increased area resistance [23].

For the solution-cast membranes, the data in Figure 4 show that casting from butan-1-ol produces lower resistance materials than those manufactured by extrusion or casting from propan-2-ol. The latter cast membranes show similar resistance trends to

For Peer Review

the extruded materials, with the exception of the thinnest membrane, which has a reduced resistance similar to the membranes produced from butan-1-ol.

Figure 5 presents a plot of the resistivity *vs.* thickness. This clearly shows that neither the extruded nor the cast membranes behaved as model, ohmic conductors, since the resistivity is not independent of the membrane thickness. From the three membrane types shown, it is the membranes cast from butan-1-ol which are closest to 'model' ohmic behaviour. Membranes cast from propan-2-ol, show similar behaviour at thicknesses above 100 μm to extruded membranes but at lower thickness the resistivity is similar to that of the butan-1-ol cast membranes. This suggests that, as in the case of extruded membranes, the surface composition is different to that of the bulk. In this case, however, the surface material may be more conductive.

These results clearly show that not only the method of manufacture but also the casting solvent has a large effect on the resistivity and structure of the resultant membranes. The resistivity data suggest that membranes cast from butan-1-ol appear to have a more regular structure which does not change with thickness. Butan-1-ol has higher viscosity, boiling point and vapour pressure than propan-2-ol and will, therefore, evaporate at a lower rate, which might allow formation of a more organised structure. Butan-1-ol is partly miscible with water, whereas propan-2-ol is completely soluble. Butan-1-ol also has less hydrogen bonding than propan-2-ol. As casting occurs, the rod like Nafion® particles in solution are more likely to be kept in position during solvent evaporation, thus forming a more regular structure in the dry membrane. Following hydration, a much more even polymer matrix might be formed, resulting in relatively small changes in resistivity as the thickness increases.

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In the case of membranes cast from propan-2-ol, the presence of trapped solvent in the material, assisted by hydrogen bonding, might explain the non-ohmic behaviour. For the thinnest membrane, the presence of the alcohol is not detrimental and the cast membrane shows a typical water take-up of 21.2 and a thickness increase of 11.5% in 1 mol dm^{-3} H_2SO_4. The resistivity is lower than in the case of extruded membranes and is comparable to the values found for butan-1-ol cast materials (Figure 4) reflecting the typical surface and bulk structure of the butan-1-ol membranes. As the membrane thickness increases, the propan-2-ol trapped in the phase-inverted ionic clusters might have a significant effect on the swelling of the ionic clusters, resulting in a substantial increase in water content and reducing the interfacial tension between the fluoropolymer- backbone and the aqueous phase. This could result in blocking of the ion channels and the proton hopping sites; high water content has been ascribed to increased resistivity due to dilution of the ionic groups. Consequently, the resistivity of the thicker propan-2-ol cast membranes is close to that of the extruded membranes, as shown in Figure 4.

A small angle x-ray scattering study of re-cast Nafion membranes from dimethylacetammide solvent has also indicated the importance of casting conditions on the ionic conductivity and structure of proton exchange membranes [32]. The authors found that a larger distance between the water pools embedded in the polymer matrix and a larger diameter of the water clusters compared to corresponding, off-the-shelf Nafion NE-115 membranes were found. The ionic conductivity of ion exchange membranes for PEM fuel cells is known to depend on the fabrication conditions, pre-treatment (including solvent re-casting) and operational conditions. Vayenas and co-workers have attempted the prediction of ionic conductivity using a first principles

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model [33]. The model considers proton tunnelling as a charge transfer mechanism and indicates that changes in molecular structure (which can be a consequence of re-casting conditions in the present case) can exert a strong influence on the observed proton conductivity. The authors consider that the conductivity of fully hydrated membranes is largely dictated by surface proton-transfer rather than by ohmic proton transport. In the present case, the use of different solvents may give rise to differences in the surface structure which result in the modification of proton transfer rates.

The selection of a slow-drying solvent that can be removed from the dried membrane determines the resistivity of thin membranes (< 30 μm). Annealing the dried membrane increases the charge density and improves the physical and mechanical stabilities and the resistance to flow [34. 35]. This is necessary to achieve suitable materials properties to facilitate handling and processing of the membrane during subsequent MEA fabrication and durability of the cast membranes in PEMFC stacks. There is a requirement to extend these studies to encompass lower *EW* membranes and solution-cast composite membranes; both of these materials are being increasingly used in PEMFCs to improve durability and performance. The impact of ionomer in the catalyst layer of MEAs is also critical and this subject area demands increasing attention for the industrial development of cast membranes.

4. Conclusions

1. Nafion® membranes manufactured by the casting of Nafion® polymer from solutions of butan-1-ol and propan-2-ol have shown a trend of decreasing resistivity with increasing membrane thickness. Despite the broadly similar

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physical properties of the two solvents used for casting significant differences were seen in membrane resistivity.

2. Membranes re-cast from butan-1-ol exhibited the best performance, which was closest to that expected of a homogeneous ohmic conductor. Membranes cast from propan-2-ol showed performance trends which were similar to those observed for the extruded series of membranes.

3. The polymer structures formed by casting membranes are highly dependent upon the solvent used. Selection of a solvent that is slow-drying is beneficial for membrane conductivity. Solvent trapped within the bulk of the membrane influences the swelling and conductivity of the membrane. Solvent effects could be causing different polymer structures to be formed in the cast membrane with regard to the orientation of ionic clusters.

4. Further studies on structure-property relationships for membranes re-cast under controlled solvent conditions are important to an improved understanding of membrane conductivity as a function of processing conditions.

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Nomenclature

EW	Equivalent weight (g polymer / SO_3H group)
ΔE_{ref}	Potential difference across the membrane, between matched Reference electrodes (V)
G_A	Membrane area conductance (S cm^2)
I	Current (A)
j	Current density (A cm^2)
R_{cell}	Cell resistance (ohm)
R_{mem}	Membrane resistance (ohm)
$R_{electrolyte}$	Electrolyte resistance between luggin capillaries (ohm)
R_A	Membrane area resistance (ohm cm^2)
A	Membrane area (cm^2)
L	Hydrated membrane thickness (cm)
IEC	Ion exchange capacity (mmol H^+/g polymer)
IX	Ion exchange (g polymer/SO_3H group)
w_1	Hydrated membrane weight (g)
W	Dry membrane weight (g)
V_{NaOH}	Volume of NaOH (cm^3)
c_{NaOH}	Molar concentration of NaOH (mol dm^{-3})
$M_R(H_2O)$	Relative molar mass of water

Greek

κ	Membrane conductivity (S cm^{-1})
λ	Water content (mol H_2O / mol SO_3H)
ρ	Membrane resistivity (ohm cm)

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Figure captions

Figure 1. The glass, four-electrode cell used to measure the membrane resistance of a circular sample (1 cm^2) using a steady state, d.c. linear sweep galvanodynamic technique. The resistance value was corrected by measuring the uncompensated *IR* drop resistance between the two Luggin capillaries fitted with a SCE reference electrode in the absence of a membrane [23].

Figure 2. Hydration thickness increase of membranes immersed in 1 mol dm^{-3} H_2SO_4 electrolyte at 295 K. ● extruded, □ re-cast from butan-1-ol and △ re-cast from propan-2-ol.

Figure 3. Variation in water take-up of membranes immersed in 1 mol dm^{-3} H_2SO_4 electrolyte at 295 K. ● extruded, □ re-cast from butan-1-ol and △ re-cast from propan-2-ol.

Figure 4. The variation in area resistance of the extruded Nafion® 1100 EW, solution re-cast from butan-1-ol and solution cast from propan-2-ol series of membranes as a function of hydrated membrane thickness in 1 mol dm^{-3} H_2SO_4 electrolyte at 298 K: ● extruded, □ re-cast from butan-1-ol and △ re-cast from propan-2-ol.

Figure 5. The variation in ionic resistivity of the extruded Nafion® 1100 EW, solution re-cast from butan-1-ol or from propan-2-ol series of membranes as a function of hydrated membrane thickness in 1 mol dm^{-3} H_2SO_4 electrolyte at 298 K. ● extruded, □ re-cast from butan-1-ol and △ re-cast from propan-2-ol.

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Table 1: Membrane ion-exchange capacities (*IEC* ≈ 1) and equivalent weights (*EW* ≈ 1100) of extruded and re-cast membranes

Membrane designation	Manufacturing method	*IEC* / mmol H^+ per g	*EW* / g polymer per SO_3H group
N112	Extrusion	0.98	1026
N1135	Extrusion	0.98	1021
N115	Extrusion	0.99	1012
N117	Extrusion	0.93	1071
NCB321	Re-casting from butan-1-ol	0.95	1055
NCB319	Re-casting from butan-1-ol	0.91	1102
NCB331	Re-casting from butan-1-ol	0.96	1046
NCP335	Re-casting from propan-2-ol	0.98	1020
NCP323	Re-casting from propan-2-ol	1.01	992
NCP340	Re-casting from propan-2-ol	0.94	1061

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Table 2: Membrane water content together with dry and hydrated thicknesses. The values are shown as a mean together with the limits of variation for typically 10 measurements.

Membrane designation	Manufacturing method	Dry film thickness / μm	Hydrated film thickness (1M H_2SO_4), *L* / μm	% Increase in the hydrated thickness compared to the dry film	Water content, λ in H_2O / mol H_2O per SO_3H group	Water content, λ in 1M H_2SO_4 / mol H_2O per SO_3H group
N112	Extruded	51 ± 2	64 ± 2	25	21 ± 1	15 ± 1
N1135	Extruded	91 ± 2	110 ± 2	21	21 ± 1	18 ± 1
N115	Extruded	136 ± 2	157 ± 2	15	22 ± 1	19 ± 1
N117	Extruded	186 ± 4	223 ± 8	20	23 ± 1	19 ± 1
NCBP321	Re-cast from butan-1-ol	55 ± 6	91 ± 11	65	27 ± 1	18 ± 1
NCB319	Re-cast from butan-1-ol	114 ± 13	140 ± 12	23	30 ± 1	22 ± 1
NCB331	Re-cast from butan-1-ol	177 ± 26	207 ± 15	17	27 ± 1	18 ± 1
NCP335	Re-cast from propan-2-ol	69 ± 14	77 ± 11	11	25 ± 1	21 ± 2
NCP323	Re-cast from propan-2-ol	81 ± 10	100 ± 8	23	27 ± 1	20 ± 1
NCP340	Re-cast from propan-2-ol	151 ± 18	255 ± 13	69	48 ± 4	28 ± 1

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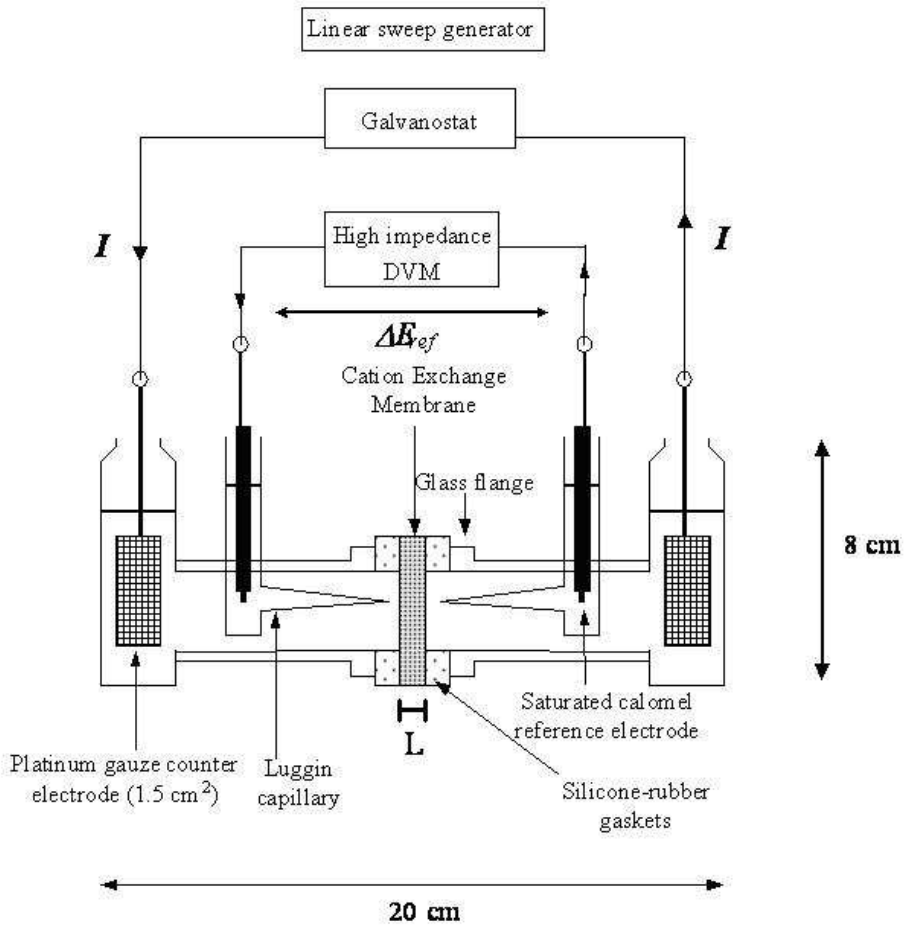

Figure 1. The glass, four-electrode cell used to measure the membrane resistance of a circular sample (1 cm2) using a steady state, d.c. linear sweep galvanodynamic technique. The resistance value was corrected by measuring the uncompensated IR drop resistance between the two Luggin capillaries fitted with a SCE reference electrode in the absence of a membrane [23].
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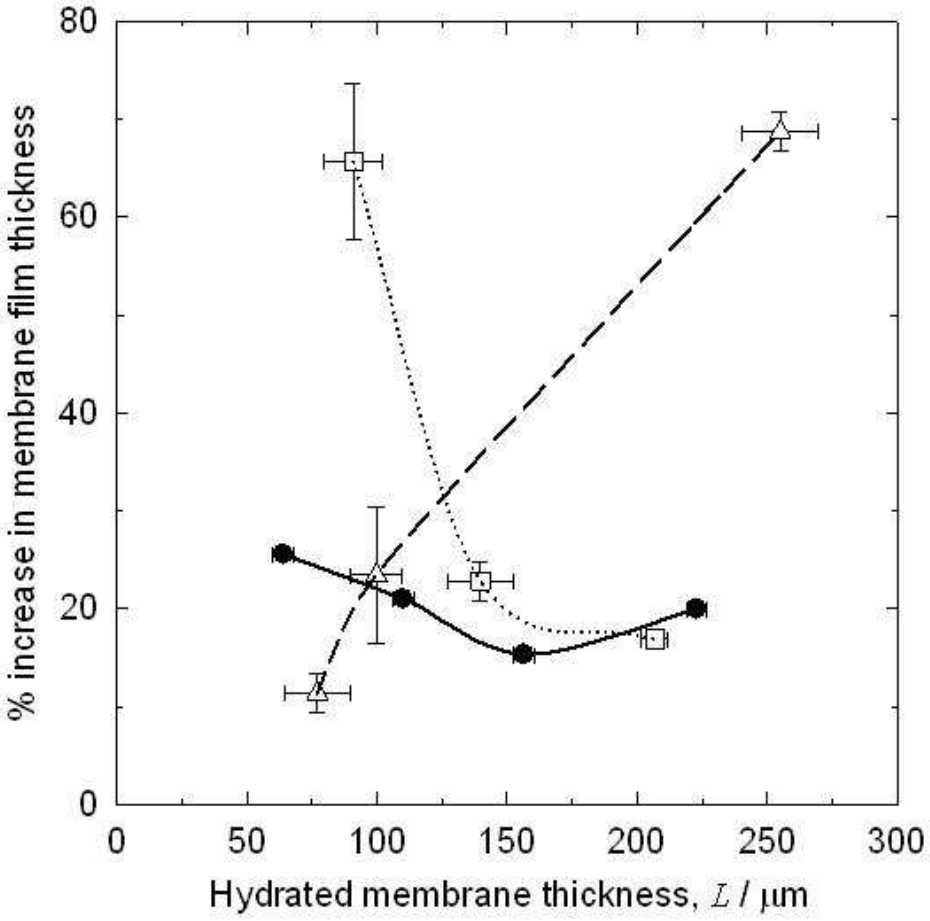

Figure 2. Hydration thickness increase of membranes immersed in 1 mol dm-3 H2SO4 electrolyte at 295 K. • extruded, ≧ re-cast from butan-1-ol and Δ *re-cast from propan-2-ol.*
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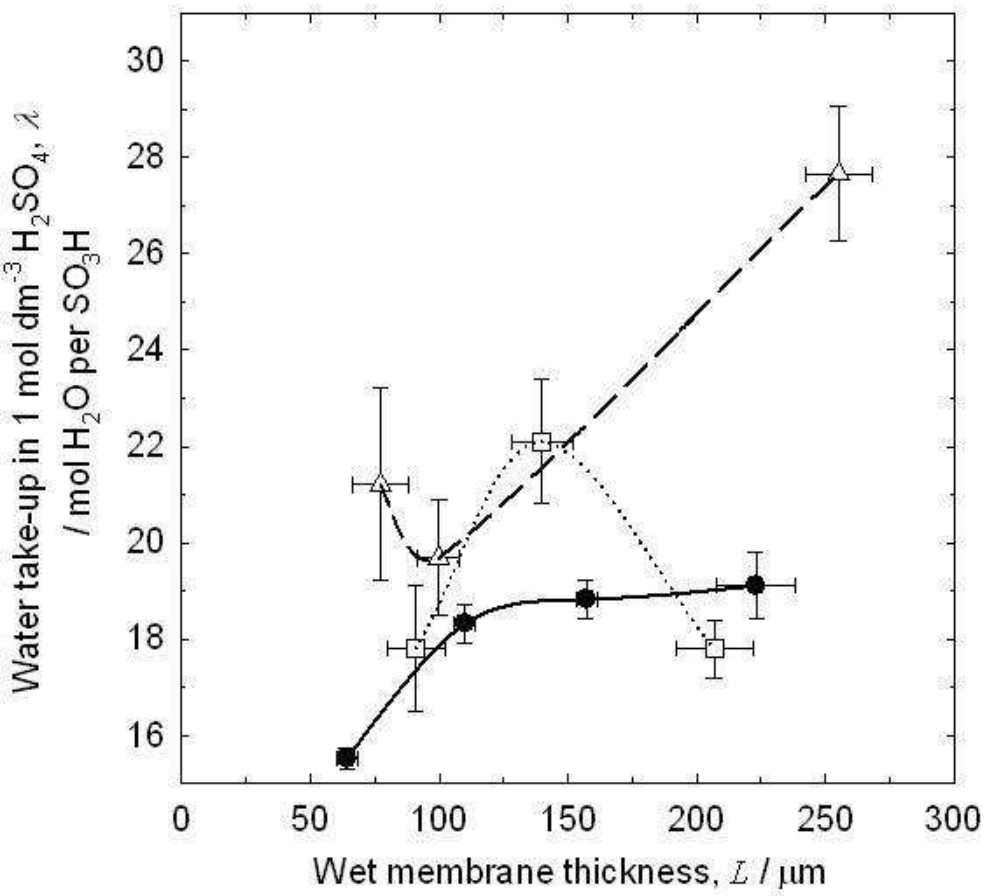
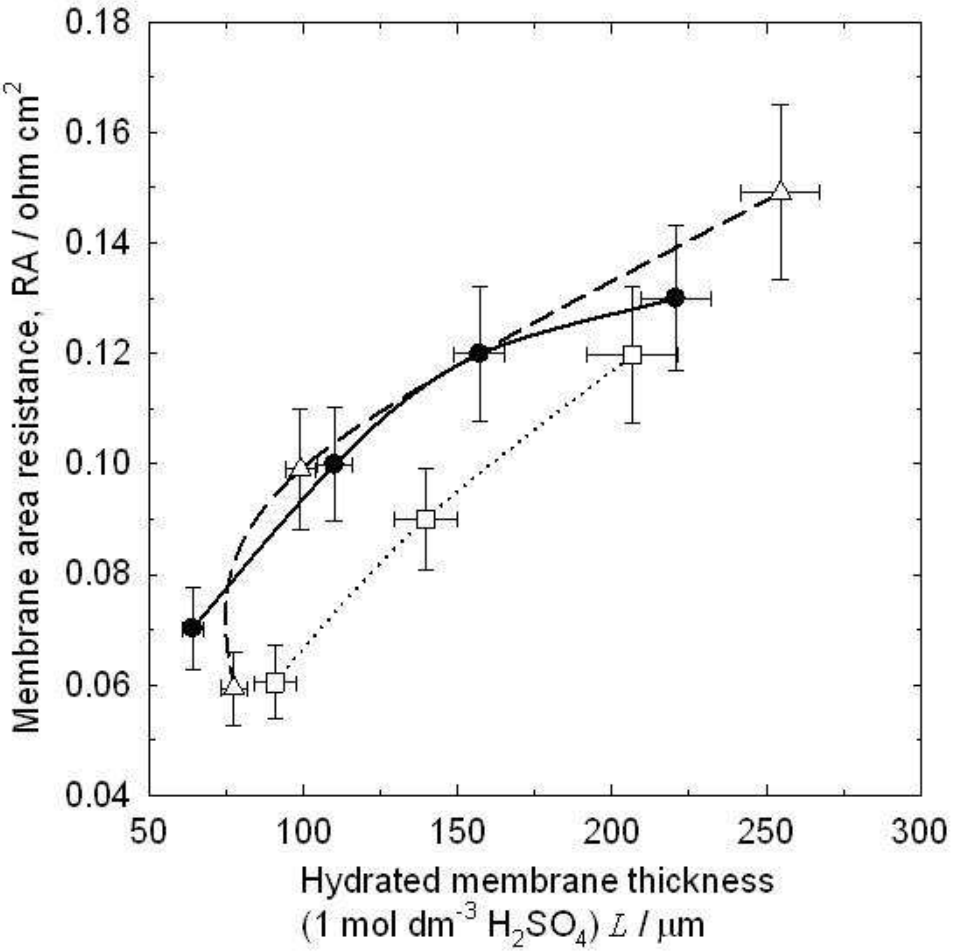


Figure 3. Variation in water take-up of membranes immersed in 1 mol dm-3 H2SO4 electrolyte at 295 K. ● extruded, ≧ re-cast from butan-1-ol and Δ re-cast from propan-2-ol.
151x163mm (96 x 96 DPI)



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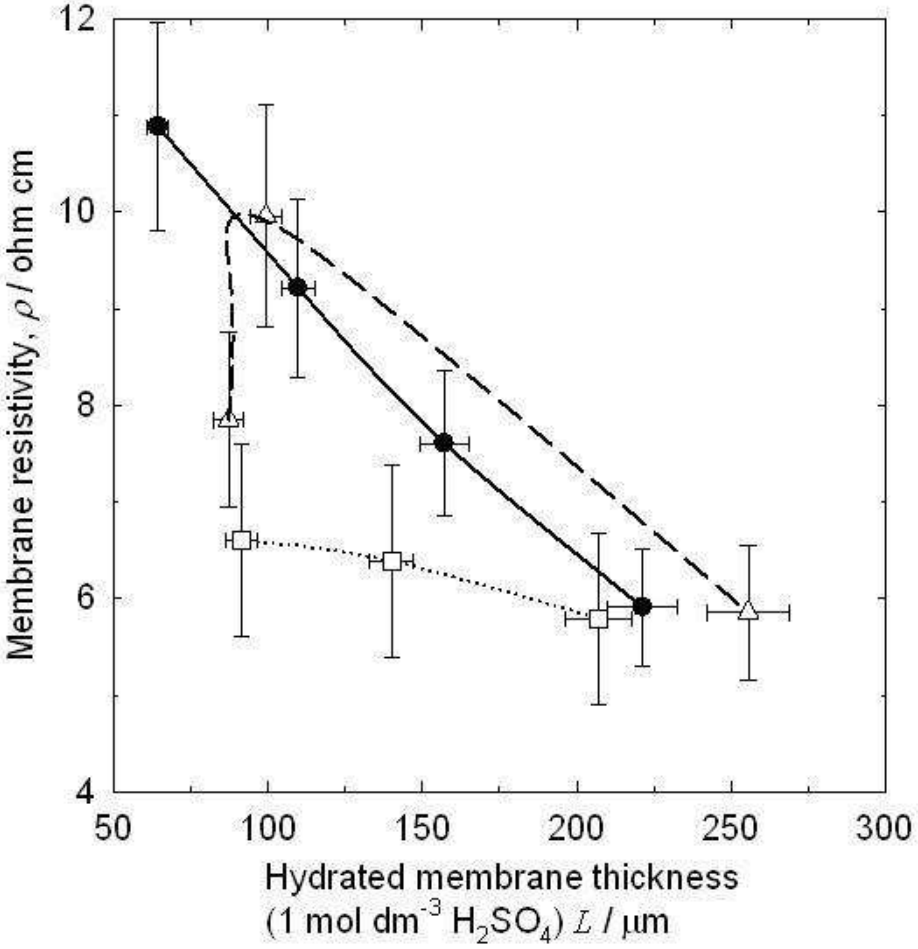

Figure 5. The variation in ionic resistivity of the extruded Nafion® 1100 EW, solution re-cast from butan-1-ol or from propan-2-ol series of membranes as a function of hydrated membrane thickness in 1 mol dm-3 H2SO4 electrolyte at 298 K. ● extruded, ≦ re-cast from butan-1-ol and Δ re-cast from propan-2-ol.
151x163mm (96 x 96 DPI)