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Short communication

Studies on ion-exchange membranes. II. Measurement of the anisotropic conductance of Nafion®

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Abstract

Measurements of the conductivity of Nafion®117 in the tangential and the normal directions are reported in this paper. These measurements were made using the coaxial probe method described in an earlier paper. The tangential component of the conductivity of the swollen membrane at 100% humidification was 8.56×10^{-2} S cm^{-1}, while the normal component of the membrane under the same conditions was 2.4×10^{-2} S cm^{-1}. This anisotropy is examined in the light of current knowledge of the morphology and structure of swollen Nafion®. The normal component of the conductivity depends strongly on the pressure applied on the membrane, and therefore must be corrected to zero pressure. Our experiments show that the membrane resistance is linear with regard to the applied pressure. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

In previous papers [1,2], we have described the use of a coaxial probe technique for the measurement of the specific conductance of ionic membranes. This method is simple and it allows measurements to be made quickly. Control of physical parameters, such as water content, is achieved relatively easily using this method, as access is required only to one side of the membrane. Conductance measurements of ionic membranes have considered, almost exclusively, only the normal components [3,4]. One exception is that of Fontanella et al. [5], who measured the tangential component of the specific conductance by attaching electrodes to a strip of membrane.

The value of 6.61×10^{-2} S cm^{-1} that we obtained for the tangential component of the specific conductance using the coaxial probe method was in reasonable agreement with the results of Fontanella et al. [5], who reported a value of 6.1×10^{-2} S cm^{-1} for the specific conductance of Nafion®117 in the plane of the surface of the sample, under the same conditions. This value was considerably higher, however, than the value of 2.2×10^{-2} S cm^{-1} reported by Pourcelly et al. [4] for the conductance normal to the membrane surface, using a mercury cell. These results suggested that the conductance of Nafion®117 might be anisotropic.

To investigate this further [1], a cap was made to fit on to the end of the coaxial probe and the membrane sample was cut the same size as the inner conductor so that the conductance normal to the membrane could be measured. The measured value of 2.4×10^{-2} S cm^{-1} was in good agreement with Pourcelly's value. These results were further indication that the tangential component of the conductance is higher than the normal component.

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The question of the anisotropy of the conductance in Nafion® membranes has not been specifically addressed in the literature, perhaps in view of the fact that, from an operational standpoint, the conductance in the normal direction is of most concern. Nonetheless, the degree of isotropy of membranes may have a significant effect on the performance characteristics of fuel cells and electrolyzers. For instance, a high degree of anisotropy within the membrane may lead to low resistance paths in certain directions, and give rise to losses along those directions (directions other than normal).

To address these concerns, a systematic study of the conductance of Nafion®117, both in the normal and tangential directions, was undertaken. Two factors affect the accuracy of normal measurements: (a) compression of the test membrane, and (b) low values of normal resistance. The paper has addressed these factors by making measurements at different values of membrane compressions, and by the use of small probes of different cross sections, respectively.

2. Experimental

2.1. Membrane pretreatment

Nafion®117, purchased from Aldrich (Milwaukee, WI), with a reported equivalent molar mass of 1100 g mol^{-1}, was used in all experiments. The membrane was subjected to a pretreatment procedure using the following sequence, boiling in 30% nitric acid for 30 min, followed by rinsing and washing in distilled water, and finally, boiling in distilled water for 30 min. Membranes are then stored in deionized, distilled water until use.

2.2. Characterization of the membrane

Membrane thickness was measured with a micrometer at various points on the membrane surface. In order to obtain the dry weight, pretreated membrane samples were dried in a vacuum oven at 105°C for 2 h and weighed. Heating was continued at 105°C for a further 30 min, until a constant weight was recorded.

The ion-exchange capacity of the membrane was determined by titration. Three samples of the membrane in protonic form, approximately 0.5 g each, were accurately weighed and immersed in 100-ml aliquots of 0.1 M NaCl for 6 h, with occasional stirring. The solution was then titrated with 0.05 M NaOH to pH 7. $8.85 \pm 0.05 \times 10^{-4}$ g of H^+ g^{-1} of dry membrane was found as compared to 9.09×10^{-4} g based on the reported equivalent molar mass.

2.3. Impedance measurements

2.3.1. Measurement system

A computer-controlled Hewlett Packard 8753B network analyzer was used to measure the input reflection coefficient of the probe terminated with a sample of the membrane being studied. The network analyzer was interfaced to a computer for data collection.

2.3.2. Measurement of tangential component of the specific conductance of Nafion®117

The coaxial probe used in this work consisted of a short section of an open-ended 50Ω coaxial transmission line. The probe used was a custom-built air-filled line having an outer radius of 25 mm. An N-type connector was used at the end of the probe. The surface of both the inner and outer conductors was gold plated to avoid corrosion problems when the probe was in contact with the acidic membrane. Although the reference plane for the open-ended coaxial probe is at the end of the probe, calibration at this plane is difficult. In our measurements, the network analyzer was calibrated at the probe-connector plane and the measured reflection coefficients were corrected for the phase shift caused by the additional length of the probe. Measurements were made over the frequency range from 300 kHz to 200 MHz.

The membrane resistance is determined from the intercept of the impedance semicircle as described in [1]. The conductance of the membrane, σ_{tan}, can then be related to the measured resistance, R_T, by the expression [1]:

$$\sigma_{tan} = (2\pi R_T h)^{-1} \ln(b/a) \quad (1)$$

where h is the thickness of the membrane, and a and b are the radii of the inner and outer conductors, respectively, of the coaxial probe. When the coaxial gap is large compared to the thickness of the membrane, then the current distribution across the membrane can be assumed uniform and Eq. (1) is strictly valid.

Measurements in triplicate were made on four different membrane samples in order to obtain a good statistical sampling. Prior to measurement, the surface water was removed by wiping the sample with a paper tissue.

2.3.3. Measurement of normal component of the specific conductance of Nafion®117

Conductance measurements in the normal direction required changes in experimental design and procedure, in order to achieve internally consistent results. Because of the thin conduction path, the measured resistance is small and hence likely to show large variations in measured values. Another factor that significantly affects normal measurements, is the pressure applied on the membrane during measurements.

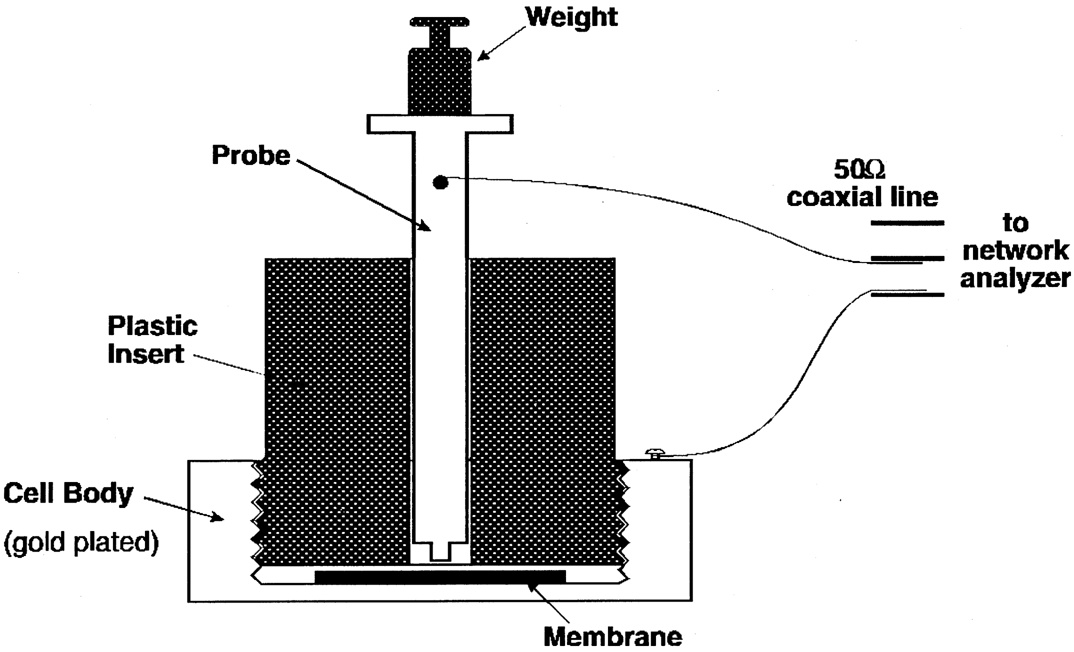

Fig. 1. Cell for the measurement of normal conductance.

In our previous measurements [1], a cap was made to fit on to the end of the coaxial probe and a sample of the membrane was cut slightly larger than the size of the inner conductor which had a diameter of 7 mm. The same calibration procedure was used. Measurements were made over the frequency range from 300 kHz to 200 MHz.

A slightly different experimental design was used for the normal component measurements with small probes. In order to increase the measured resistance, a modified cell was built that allowed a quick and easy change of the inner conductor of the co-axial probe. Special centre probes having diameters of 1,2 and 3 mm were machined precisely and gold-plated. The cell and the test arrangement, are shown in Fig. 1. As before, a Hewlett Packard 8753B network analyzer was used for impedance measurements, in the frequency range, 300 kHz to 20 MHz. The leads connecting the cell to the network analyzer cables contribute an inductive component to the measured impedance. This effect can be seen in the Nyquist plot shown in Fig. 2. The membrane resistance, R_N, was determined from the point where the curve crosses the real axis.

Preliminary measurements showed that the resistance depended strongly on the pressure that was applied to the probe. To correct for this, the cell design was modified so that a constant pressure could be applied by placing known weights on the top of the centre probe. Conductance measurements were made using four membrane samples and four different probe sizes having diameters of 1, 2, 3 and 7 mm. For each membrane/probe combination, several different weights were used so that the effects of pressure could be determined.

3. Results and discussion

3.1. The tangential component of the specific conductance of Nafion®117

Membrane resistance was determined graphically by extending the impedance semicircle to obtain the intercept with the real axis as described in [1,2]. The tangential component of the conductance of the membrane can then be determined from these resistance values,

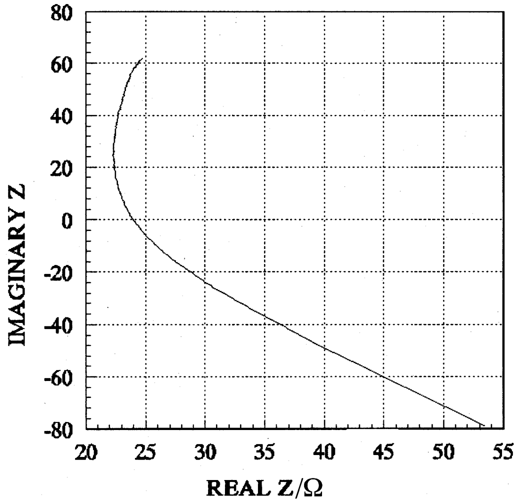

Fig. 2. A typical impedance plot.

Table 1
Measurements of the tangential component of the specific conductance

Sample							
1		2		3		4	
R_T/Ω	$10^{-2}\ \sigma_{\mathrm{tan}}/\mathrm{S\ cm^{-1}}$	R_T/Ω	$10^{-2}\ \sigma_{\mathrm{tan}}/\mathrm{S\ cm^{-1}}$	R_T/Ω	$10^{-2}\ \sigma_{\mathrm{tan}}/\mathrm{S\ cm^{-1}}$	R_T/Ω	$10^{-2}\ \sigma_{\mathrm{tan}}/\mathrm{S\ cm^{-1}}$
70.5	8.51	71.5	8.39	68.0	8.82	71.0	8.45
72.0	8.33	71.0	8.45	70.0	8.57	70.0	8.57
70.0	8.57	70.0	8.57	68.0	8.82	69.0	8.69

using equation (1). The results of the measurements on the four membrane samples are given in Table 1.

From the data given in Table 1, the tangential component of the conductance is determined to be $8.56 \pm 0.15 \times 10^{-2}$ S cm^{-1}. This value is about 20% higher than the value of 6.61×10^{-2} S cm^{-1} measured previously [1]. This discrepancy may partly be inherent in the polymer batch processing methods, and partly due to membrane morphology, particularly in the hydrated state. Furthermore, the earlier data was obtained on samples from a different batch of Nafion®, about 3 years old, when Nafion® was in an earlier stage of application in fuel cells.

3.2. The normal component of the specific conductance of Nafion®117

3.2.1. Effect of probe pressure on membrane resistance

As noted earlier, it was observed that the measured resistance of the membrane was very sensitive to applied pressure presumably because of deformation and thinning of the membrane under the surface of the probe. To correct for this, resistance measurements were made for several different pressures and the results extrapolated back to zero pressure to determine the resistance of the uncompressed membrane. Results for the 3-mm probe are shown in Fig. 3. Data for all four membrane samples are included. A linear regression was used to determine the x-intercept and its standard deviation. This data is included in Table 2.

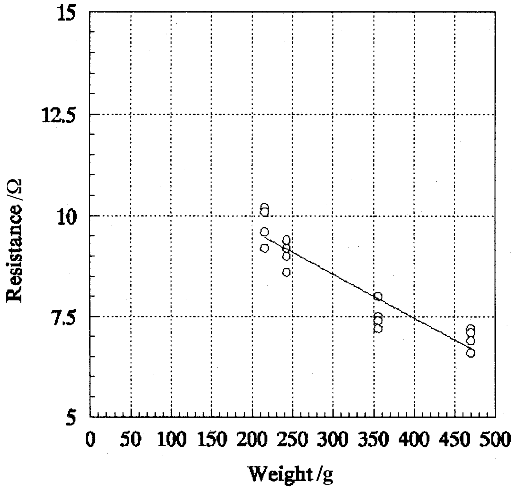

Fig. 3. Effect of pressure on membrane resistance.

3.2.2. Calculation of membrane conductance from the measured resistance

To determine the conductance of the membrane from the measurement of the total resistance, R_N, we use the duality that exists [6] between current density, $\vec{J}$, and displacement flux density, $\vec{D}$, in linear, isotropic materials. Provided the conducting boundaries remain the same and the dielectric medium is replaced by a conductive medium then

$$RC = \varepsilon/\sigma \tag{2}$$

where R is the resistance of the conducting structure with conductivity σ and C is the capacitance of the dielectric structure with dielectric constant ε.

If the probe diameter is much larger than the thickness of the membrane, the effects of the fringing fields can be neglected and the conductance can be determined from the parallel plate capacitance

$$C = \varepsilon(\pi r^2/h) \tag{3}$$

where r is the radius.

Then, from Eq. (2), the conductance, σ, becomes

$$\sigma_{\mathrm{norm}} = \pi r^2/R_N h \tag{4}$$

When the diameter of the probe is small, however, the fringing fields result in a significant lowering of the measured resistance. This factor needs to be taken into account to determine the conductance correctly. To do this, the capacitance of the axially symmetric structure shown in Fig. 4 was calculated using the finite element method[1]. Note that the structure has been doubled with

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[1] The commercial finite element package QuickField®, was used to make these calculations. To determine the capacitance of the structure, a charge of known value is placed on the centre conductor and its potential calculated using the finite element. The capacitance is obtained from the equation $C = q/U$, where q is the electric charge on the centre conductor and U is its potential.

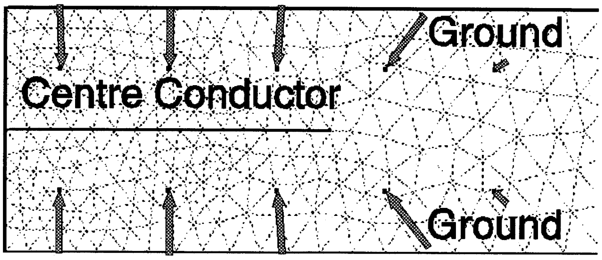

Fig. 4. Finite element model of conductance cell.

the centre conductor placed between two ground planes. The capacitance of this structure is twice that required. Fig. 5 shows the correction factor by which the measured resistance must be multiplied in order to obtain R_N, from which the normal component of the conductance of the membrane can be calculated using Eq. (4). The results of these calculations are included in Table 2. Note that, while the correction for the effect of the fringing fields is large for the 1-mm probe, it is small for the 7-mm probe.

The average value for the normal component of the conductance of Nafion®117 is 2.39×10^{-2} S cm^{-1}. This is in agreement with the value of 2.4×10^{-2} S cm^{-1} obtained earlier [1].

3.2.3. Comparison of the normal and tangential conductance of Nafion®117

Our results show that the specific conductance of Nafion®117 is anisotropic. The tangential conductance is almost 3.6 times as high as the normal conductance. These results may have practical implications in the use of such membranes in high current polymer electrolyte fuel cells or electrolyzers where the internal resistance of the cells is of major concern.

Nafion® belongs to a class of ion exchange polymers with a perfluoroethylene backbone and a side group containing the sulphonic acid group. The microstructure of the polymer has been extensively studied in the past decade, yet there is debate on this matter. It is well known that the conductance of Nafion® depends on the water content within the membrane. The variation of membrane conductance has two possible origins. The first is a change in the rate constant of the elementary ion transfer reaction due to the interactions between mobile ions and the fixed sites which depend on their hydration states (interparticle). The second originates from the microstructural changes within the membrane (intraparticle).

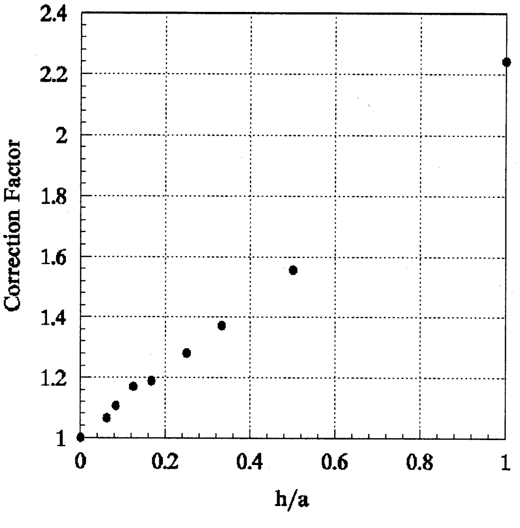

Fig. 5. Correction factor for probe size.

Ion clustering in hydrated Nafion® has been studied by a number of methods such as small angle X-ray scattering [7], electron microscopy [8], nuclear magnetic resonance [9] and other transport methods [10,11]. Gierke et al. [12] have used wide and small angle X-ray diffraction to determine the morphology of Nafion®. They conclude that the membrane consists of crystalline and amorphous regions, and that the hydrated clusters are located in the amorphous regions. Ion clusters do exist in the dry polymer, but as the polymer absorbs water, the cluster diameter, exchange sites per cluster and water molecules per exchange site, all increase [13]. Mauritz and Hopfinger [14] have proposed an empirical model for the dynamics of cluster formation in Nafion®. While these studies provide strong evidence of ion clustering in Nafion®, the detailed geometry and arrangement of these clusters and their orientation within the membrane are still being debated [15].

Our experiments provide the first direct evidence of conductance anisotropy in hydrated Nafion®117. Studies of low angle X-ray scattering and other physical properties by Yeo and Eisenberg [7] and Gierke et al. [12] suggest that hydrated Nafion® behaves like a two phase system, consisting of hydrated clusters of ions embedded in the surrounding fluorocarbon medium. Infra red studies of water in Nafion® by Falk [16] support the view that most of the water in hydrated Nafion® is in the clusters. Based on these conclusions, it is possible that the observed anisotropy results from the ionic clusters being oriented near the interface and away from the amorphous hydrophobic phase. Alternatively, the fluorocarbon backbone of the macromolecule may orient itself preferentially during extrusion of the membrane.

Table 2
Measurements of the normal component of the specific conductance

Probe/mm	R_N/Ω	$10^{-2}\,\sigma_{\mathrm{norm}}$ /S cm^{-1}
7	2.06 ± 0.20	2.57 ± 0.23
3	11.82 ± 1.18	2.22 ± 0.20
2	27.16 ± 3.98	2.06 ± 0.26
1	70.32 ± 9.00	2.69 ± 0.31

There is considerable debate regarding the geometry and dynamics of the ionic clusters, although most modeling studies have assumed spherical clusters with uniform pores. Detailed analysis of the conductance under different states of hydration can provide valuable information on this matter.

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