INFLUENCE OF AMMONIUM ON NAFION_117 MEMBRANES
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ABSTRACT

The ion exchange equilibrium of ammonium between an aqueous phase and Na_.on_117 were measured at 10.0, 25.0, 40.0, and 60.0 °C by equilibrating the membrane in 0.1000 M chloride electrolytes of known cation composition. The water content in the membrane phase was found to decrease linearly with the cation fraction of ammonium in the membrane phase (y_{NH+4}) from ε_{H2O}=21.2 (moles of water per mole sulfonic acid groups) in proton form Na_.on_ in pure water to ε_{H2O}=13.2 in ammonium form Na_.on_ in a 0.1 M chloride solution. The conductivity was measured by impedance in a two-electrode set-up using a stack of membranes. The conductivity was also found to decrease linearly with y_{NH+4} from 97 mS/cm to 25 mS/cm at 25.0 °C. The temperature dependence of the conductivity was measured, and the fitted activation energy in an Arrhenius-type equation was found to depend on membrane composition, \text{E}_a=10.3+4.2 \cdot y_{NH+4}[kJ/mole].

INTRODUCTION

As research on low temperature Polymer Electrolyte Membrane Fuel Cells (PEMFC) has progressed, increasing focus has been put on how gaseous contaminants, and carbon monoxide in particular, influence the fuel cell performance, and how these effects may be alleviated. Less work has been published on other contaminants present in fuel and air streams, ammonia being one of these components. Ammonia may be formed in fuel reforming processes at levels up to 150 ppm (1) especially if the reforming involves homogeneous precombustion or the fuel itself contains nitrogen containing components (2). Ammonia may also be present as a trace component if ammonia is used as feedstock for hydrogen production by thermal splitting (3) and references therein), or in ambient air as such. Earlier work by Szymanski et al. (4) on Phosphoric Acid Fuel Cells has shown that ammonia has an effect on fuel cell performance and cathode performance in particular.

Since ammonia is alkaline, it is expected that it will be readily absorbed by the acidic membranes used in PEM fuel cells forming ammonium in the membrane phase. An important factor determining the performance of PEM fuel cells, is the ionic
conductivity. Ammonium reduces the conductivity of Nafion® as pointed out by Uribe et al. (5). Reduced conductivity can be important both as a bulk effect increasing the Ohmic drop in the cell, as well as in the active layer(s) on either anode or cathode. Based on High Frequency Resistance (HFR) and other data collected from a fuel cell operating with 13 and 130 ppm ammonia in the fuel, Uribe et al. (5) concluded that the most important effect in the short term is reduced conductivity in the anode catalyst layer. When operating the fuel cell for longer times, bulk conductivity, as measured by HFR, was also affected.

The aim of this work is to quantify the ion exchange equilibrium between Nafion® 117 in an aqueous electrolyte containing different cation fractions of ammonium, xNH+, and the corresponding membrane phase composition, yNH+. The influence of composition and temperature on membrane conductivity, Kmem, water content in the membrane, λH2O, as well as swelling effects are studied. An aqueous phase is used since it is easier to control the membrane phase composition indirectly through an aqueous phase rather than through a vapor phase by addition of ammonia. It should be kept in mind that the parameters studied here (swelling, conductivity, and water content) may be differently influenced when Nafion® is in equilibrium with a vapor phase rather than a liquid electrolyte, and that other effects, such as catalyst poisoning, may also be important factors influencing PEM fuel cell performance.

EXPERIMENTAL

Preparation of membranes and solutions. Nafion® 117 membranes were purchased from IonPower Inc., and pretreated at 85 °C in purified water produced in a MilliPore Academic purifying system, thereafter in 5% aqueous H2O2(Merck p.a.), then again in purified water, then twice in 0.05 M H2SO4(Merck p.a.), and then finally four times in purified water (6). Membrane disks (20.35 mm 0) were then punched out for conductivity measurements, and these disks were again purified using the same procedure. Samples used for equilibrium measurements were cut in a rectangular shape (approximately 25 by 30 mm and 0.2 to 0.3 g dry) prior to membrane pretreatment. All samples were stored in purified water at least over night and until used in further experiments.

Equilibration of membrane samples. Standard solutions of known molality were prepared using HCl and NH4Cl (Merck p.a.) and purified water. The required amounts of these solutions were weighed into measuring flasks to yield the desired cation compositions with a total chloride concentrations of 0.1000 M. All solutions were prepared in glassware calibrated with purified water. The membrane samples were equilibrated with the solutions of interest in water baths at the temperatures of interest (10, 25, 40 and 60 °C) within ±0.1 °C. The equilibrating solutions were changed at least four times during a minimum of six days.

Water content. The weights of wet membranes were determined by quickly wiping off excess liquid with a lint-free paper, and then weighing the membrane

1Nafion® is a DuPont registered trademark for its brand of perfluorinated polymer products, made and sold only by E. I. du Pont de Nemours and Company.
samples. The samples were then held in the solution again for at least 30 seconds to re-equilibrate the membrane with water. This procedure was repeated until at least three readings identical to within 0.0005 g had been obtained. Zawodzinski et al. (7) found that rehydration of even completely dry membranes is rapid; in about 15 seconds the membrane is hydrated to 90% of its equilibrium hydration level.

The membrane samples used for measurements at 25 °C were dried in their protic form under vacuum at room temperature for 24 hours, and then transferred to a dessicator containing Merck SicaPent dessicant (P2O5). The membranes were not exposed to elevated temperatures during the drying process as that has been shown to affect the membrane properties (7, 8). After four to five days the membrane samples were weighed in a glove box (<5 ppm water vapor) and the dry weights determined. The dry weights of the membrane samples used at other temperatures were estimated from the wet weights at 25 °C assuming the same relative water content in these samples as in those that were dried.

Swelling properties. A slide caliper was used to measure the diameter of the samples used in conductivity measurements to determine changes in dimensions of the membranes due to swelling. Membrane thicknesses were measured using a micrometer screw. Dimensional measurements were only performed on membranes equilibrated at 25.0 °C since the sample dimensions had to be measured at room temperature (approximately 23 ± 2 °C).

Equilibrium isotherm measurements. The membranes were taken out of the equilibrating solutions, and weighed as described previously to determine the water content at a given temperature and external ammonium cation fraction. The samples were then transferred to flasks containing known volumes of 0.1 M pure hydrochloric acid to ion-exchange ammonium from the membranes. The membranes were kept in these solutions for seven to ten days at room temperature before the samples were transferred to a fresh hydrochloric acid solution for further ion-exchange. The concentrations of ammonium in the exchange solutions were determined by using an Ion Selective Electrode (NH4ISE25 from RadioMeter). The results were compared to analysis performed using Kjeldahl’s method, and there was very good agreement between the two methods.

Conductivity measurements. The apparatus used to measure the conductivity is shown in Figure 1, and uses the same principle as used by Ottøy (9) and Halim et al. (10). The conductivity cell is made out of glass whereas the electrode pistons are made out of PTFE. The cell was thermostated from the same water bath as the membrane samples were kept in. The platinum electrodes were platinumized prior to use, and stored short-circuited in 0.1 M HCl between measurements. In our experiments, four membranes were stacked between the two electrodes at the time, and loads added to ensure good contact. The cell was filled with the equilibrating electrolyte. The High Frequency Resistance (HFR) was measured using a Solartron 1287/1255B set-up (25 mV AC amplitude applied and the imaginary part of the impedance was zero at 2 to 6 kHz). The HFR as function of the number of membranes in the stack recorded. The coefficients of determination of the fitted straight lines, $R^2$, were larger than 0.9998 in all cases.
The ohmic components in the membrane stack can be represented by the network of resistors shown in Figure 2. The total resistance, $R_{tot}$, is found from the slope of the HFR vs. number of membranes (the total resistance of all elements contained within the square brackets in Figure 2), and contains contributions from liquid layers between the membranes, $R_{lay}$, and resistance due to incomplete filling of the cross section in the conductivity cell, $R_{gap}$. Ottøy (9) showed by using electrolytes of different strengths that the liquid layer contribution, $R_{lay}$, is negligible. The conductivity of the membranes may also be affected by ingress of chloride into the membrane phase as discussed further later.

As shown later, the diameter of the membrane samples was found to depend on $y_{NH^+}$. The membranes were cut out from Nafton® in the protonic form, and hence contracted when exposed to ammonium containing external electrolytes. To correct for this we assume that the contraction is a linear function of $y_{NH^+}$, see Figure 5 for
justification of this, and that the conductivity in the aqueous phase \( \kappa_{\text{elec}} \) is a linear function of the composition, i.e. \( \kappa_{\text{elec}} = x_{H^+}\kappa_{HCl}^0 + x_{NH_4^+}\kappa_{NH_4^+}^0 \). The conductivity of pure 0.1000 M HCl and 0.1000 M NH\(_4\)Cl is 39.11 and 12.88 mS/cm respectively at 25 °C (11). The resistance due to the membrane, \( R_{\text{mem}} \) is then calculated from

\[
\frac{1}{R_{\text{mem}}} = \frac{1}{R_{\text{tot}}} - \frac{1}{R_{\text{gap}}} = \frac{1}{R_{\text{tot}}} - \kappa_{\text{elec}} (A_{\text{tot}} - A_{\text{mem}}) / l_{\text{mem}}
\]

where \( A_{\text{mem}} \) is the actual area of the membrane, \( l_{\text{mem}} \) is the actual thickness of the membrane, and \( A_{\text{tot}} \) is the total cross sectional area of the conductivity cell.

Calculating the membrane conductivity \( \kappa_{\text{mem}} \) is then straightforward:

\[
\kappa_{\text{mem}} = l_{\text{mem}} / (A_{\text{mem}} R_{\text{mem}})
\]

### RESULTS AND DISCUSSION

**Equilibrium between Nafion® and aqueous electrolytes**

**Membrane equivalent weight.** The equivalent weight was found to be 1100 ± 40 g/mole SO\(_3^−\) based on addition of 20 ml aliquots 0.05 M sodium hydroxide to membrane samples that were in equilibrium with purified water and back titration with hydrochloric acid using Bromothymol Blue as indicator.

Based on analysis of Nafion® 117 membranes in equilibrium with 0.1000 M ammonium chloride, we found that the equivalent weight was 1056 ± 20 g/mole SO\(_3^−\). A possible explanation of the observed difference is absorption of chloride into the membrane phase. Jones et al. (12) report that the content of chloride in Nafion® 117 in equilibrium with a 0.1 M NaCl solution is about \( \lambda_{Cl^-} = 0.05 \) (moles chloride per mole sulfonic acid group). The difference in the equivalent weights reported here corresponds to \( \lambda_{Cl^-} = 0.04 \).

The equivalent weight of 1100 g/mole SO\(_3^−\) is used in further calculations on water content since the reported \( \lambda_{H_2O} \) values are based on the number of sulfonic acid groups in the membrane. Equilibrium isotherms and membrane compositions are based on the total amount of ammonium in the membrane phase, i.e. including ammonium found as ammonium chloride in the membrane phase.

**Equilibrium isotherms.** Equilibrium isotherms at 10.0, 25.0, 40.0, and 60.0 °C were measured in Nafion® 117 in equilibrium with solutions with total chloride concentrations of 0.1000 M. Only the 25.0 °C isotherm is shown here in Figure 3.

**Water content in Nafion®.** The water content in Nafion® 117 was determined at room temperature (23 ± 2 °C), and was found to be \( \lambda_{H_2O} = 21.2 ± 0.4 \) mole water per equivalent of sulfonic acid groups in the membrane two days after preparation. This is in good agreement with other results reported (\( \lambda_{H_2O} = 21 – 23 \) (7, 10, 13-15)).

If the membranes were left in water for additional time, the water content decreased from 21.2 ± 0.4 to 20.5 ± 0.4 as shown in Figure 4a. The water content
Figure 3: Ion exchange equilibrium between proton and ammonium at 25.0 ± 0.1 °C for Nafion® 117. The line $x_{NH_4^+} = y_{NH_4^+}$ is also shown.

of Nafion® was slightly dependent on the temperature, and was also lower when in equilibrium with 0.1000 M hydrochloric acid as compared to pure water, see Figure 4a. However, none of these observations are statistically significant at the 95% level.

The water content was found to vary significantly with the ammonium content of the membrane phase as shown in Figure 4b. We observed that the water content in pure ammonium form Nafion® is reduced to $\lambda_{H_2O} = 13.2$ at 25.0 °C. Xie and Okada (13) studied the water content in different alkaline and alkaline earth ionic forms of Nafion® in equilibrium with 0.03 M chloride solutions, and found that the water content of sodium form Nafion® 117 was $\lambda_{H_2O} = 16.5$ whereas the potassium form had $\lambda_{H_2O} = 10.8$ at 25.0 °C.

Dimensions of Nafion® at various membrane composition. The diameters and thicknesses of membrane samples equilibrated at 25.0 ± 0.1 °C were measured at room temperature (23 ± 2 °C). The absolute values when in equilibrium with 0.1000 M HCl were 20.33 ± 0.05 mm and 207 ± 10 µm for diameter and thickness respectively. In Figure 5 the relative changes in diameter and thickness are shown as function of membrane composition. If we assume that 1) the total volume of Nafion® is the sum of the partial volumes of Nafion® and water, 2) the swelling is isotropic, and 3) that the density of both proton and ammonium form dry Nafion® is 2.05 g/cm³ (16), we estimate that the relative dimensions in ammonium form Nafion® should be 95.2% of those in proton form Nafion®. This is in good agreement with our findings for the diameter, see Figure 5a, but less good for the thickness. Morris and Sun (16) found that the thickness changed about two times more relatively to the diameter of Nafion® 117 when in equilibrium with different vapor pressures of water. Datasheets for Nafion® provided by Du Pont (17) states that the swelling is nearly equal in all directions. In our measurements the uncertainty for the determination of membrane thicknesses was much larger than for the diameter determinations, and even though the observed thicknesses change less than the diameter, this difference is not statistically significant.
Figure 4: Water content in Nafion® 117 at a) different temperatures in pure water and 0.1000 M hydrochloric acid (error bars shown are only one standard deviation, data are averages of 4 to 8 observations) and b) at different ammonium contents in the membrane phase \( y_{NH^+} \). The regression lines for the different temperatures are also shown in b). The water content in Nafion® in 0.1000 M at 25.0 °C is estimated by regression to be \( \lambda_{H_2O} = 20.6 \pm 0.2 \).

Figure 5: a) Relative diameter, and b) relative thickness of Nafion® 117 at 23 ± 2 °C. Also shown is the least square fits with the constraint that the lines shall go through (0,100). The fitted lines were a) \( 100 - (4.47 \pm 0.20) y_{NH^+} \) and b) \( 100 - (3.69 \pm 1.10) y_{NH^+} \). The measured diameter of proton form Nafion® was 20.33 ± 0.05 mm and the thickness 207 ± 10 \( \mu \)m.
Conductivity of Nafion® 117

The conductivity of Nafion® 117 in equilibrium with different electrolytes containing ammonium and protons was measured at 25.0 ± 0.1 °C. The results were corrected for the fact that the membrane diameter and thickness changed in different electrolytes (Equations 1 and 2). In pure proton and ammonium forms of Nafion® 117 the conductivities were found to be 97 mS/cm and 25 mS/cm respectively. The results are plotted in Figure 6 a) and b), and as seen from this figure, there is a linear relationship between membrane cation fraction of ammonium, $y_{NH^+}$, and conductivity, $\kappa_{mem}$. This is in accordance with the findings of Logette et al. (18), and indicates that the ionic mobilities of protons and ammonium are independent of membrane composition. This is somewhat surprising taking into account that the membrane is a rather concentrated solution. However, in situations involving di- and trivalent cations, the situation has been shown to be more complicated (14, 18–20).

![Figure 6: Conductivity at 25.0 ± 0.1 °C in Nafion® 117 plotted against a) ammonium content in the aqueous phase ($x_{NH^+}$), and b) ammonium content in the membrane phase ($y_{NH^+}$). The linear interpolation between the pure proton and the pure ammonium form Nafion® 117 conductivity is also shown in both plots.](image)

The measured conductivity may be influenced by presence of chloride in the membrane phase. As discussed earlier, Jones et al. (12) report that the content of chloride in a 0.1 M NaCl solution in equilibrium with Nafion® 117 is about $\lambda_{Cl^-} = 0.05$. However, the mobility of the anions is probably low due to the structure of Nafion®, and there are indications that anions are transported in the hydrophobic regions of the membrane (21) which significantly reduces the mobility of the anions. However, the presence of chloride naturally also increases the amount of mobile cations in the membrane which increases the conductivity.
We used three different ensembles of membranes cut out of the same sheet of Nafion®. However, we measured differences in membrane conductivity between the different ensembles. The differences between the ensembles were within 2%. When the conductivity measurements at 25 °C and at different compositions were finished, the membranes were transferred back to their protonic form by ion exchange, and the conductivity measured again. It was noted that the conductivity in the pure protonic form had dropped by about 2% during the experiments. This was not recoverable even when the membranes were treated in hydrogen peroxide and dilute, hot sulfuric acid as described in the preparation procedures. We have not been able to identify the reason for this irreversible reduction of conductivity.

Comparison with available literature data. Using basically the same cell as in Figure 1, Ottøy (9) found the conductivity of proton form Nafion® 117 to be 93 mS/cm at 25 °C. Halim et al. (10) found the conductivity to be 90 mS/cm also using a membrane stack. Zawodzinski et al. (22), using in-plane conductivity measurements, found the conductivity to be 101 mS/cm. Datasheets from Du Pont (17) reports the conductivity to be 83 mS/cm. Okada et al. (13, 14, 20) reports the conductivity of proton form Nafion® 117 to be 160 to 200 mS/cm when measuring in a cell similar to the one described by Zawodzinski et al. (22). However, Okada et al. filled the voids of the cell with the equilibrating solution, hence, part of the current carried through the cell flowed through the aqueous electrolyte resulting in a higher observed conductivity. Logette et al. (18) found a conductivity of 62 mS/cm, but no detailed description of the conductivity cell employed was given in the paper.

Most data reported in literature are in good agreement with our findings (97 mS/cm). We see this both as a confirmation of the accuracy of the method and an indication that the conductivity in Nafion® is isotropic. In contrast, Gardner and Anantaraman (23, 24) found that the tangential component is three times larger than the normal component of the conductivity (85.6 vs 23.9 mS/cm). We have found no other literature data showing that the conductivity is anisotropic.

We found that ammonium reduces the conductivity by a factor of 3.8 (Table 1) to 3.9 (Figure 6) relative to pure H-form Nafion® 117 at 25.0 °C which is in good agreement with the findings of Uribe et al. (5) who found that the conductivity of Nafion® 1035 decreased from 133 to 32-33 mS/cm or by a factor of 4.0 to 4.2.

The ratio of conductivities, \( \frac{\kappa_{HCl}}{\kappa_{NH4Cl}} \), in 1.0 M aqueous electrolyte is about 3.10 (11). The higher relative conductivity in proton form Nafion® compared to an aqueous solution can possibly be explained by the fact that ammonium form Nafion® also contains less water thereby reducing the mobility of the ions within the membrane phase. It is well known that conductivity in Nafion® in equilibrium with water vapor depends strongly on water vapor activity and thus water content in the membrane (8, 16, 25). If we assume that the same correlation for conductivity as function of water content as used by Springer et al. (25) may be used in this case, we estimate that the conductivity ratio due to difference in water content should be 1.47. Multiplied with the relative conductivity ratio in 1.0 M aqueous solutions, a total conductivity ratio of 4.56 is estimated. This is slightly high suggesting that the effects of ionic form and water content on conductivity are not simply additive.
Temperature effect on conductivity. The conductivity of Nafion® 117 was also measured at various temperatures as summarized in Table 1. The same membranes were used as in previous measurements, and as noted above, the conductivities are slightly lower than the ones shown in Figure 6. From Table 1 we see that a linear relationship between membrane composition and conductivity still holds, and we are able to predict the conductivity at $x_{NH^+} = 0.5$ within 4%.

Table 1: Conductivity in Nafion® at different temperatures and ionic forms, equilibrium content of ammonium in membrane phase $y_{NH^+}$ at $x_{NH^+} = 0.5$, and estimated conductivity at $\kappa_{mem}^{est}$ at $x_{NH^+} = 0.5$ assuming that a linear combination of conductivity in the two pure membrane forms is valid. Conductivities reported in this table are not corrected for $R_{gap}$, see Equations 1 and 2. Further, it is assumed that the dimensions of the membranes are the same at all temperatures as at 25 °C.

| Temperature [°C] | $x_{NH^+} = 0$ [mS/cm] | $x_{NH^+} = 0.5$ [mS/cm] | $y_{NH^+}$ at $x_{NH^+} = 0.5$ [mS/cm] | $\kappa_{mem}^{est}$ at $x_{NH^+} = 0.5$ [mS/cm] |
|------------------|------------------------|------------------------|-----------------------------------|-----------------------------------|
| 10               | 73                     | 35                     | 18                                | 0.71                              | 34                               |
| 25               | 95                     | 47                     | 25                                | 0.69                              | 47                               |
| 40               | 117                    | 61                     | 34                                | 0.70                              | 59                               |
| 60               | 144                    | 79                     | 46                                | 0.70                              | 76                               |

The temperature effect is also shown in Figure 7. The data for each composition of Nafion® 117 were fitted to an Arrhenius type equation:

$$\ln \left( \frac{\kappa_{mem}(T)}{\kappa_{mem}(T_0)} \right) = k_1 \left( \frac{1}{T} - \frac{1}{T_0} \right)$$

(3)

The datum temperature, $T_0$, was taken to be 298.15 K. The parameter $k_1$, often denoted activation energy, $E_a = R \cdot k_1$, was found to vary with membrane composition as shown in the insert graph in Figure 7 and we used a linear relation to describe $k_1$, $k_1 = 1238 + 502 \cdot y_{NH^+}$ [K] or $E_a = 10.3 + 4.2 \cdot y_{NH^+}$ [kJ/mole]. The calculated temperature variation using this model is also shown in Figure 7. The deviation between experimentally measured conductivities and those calculated using the model given in Equation 3 is within ±5%.

The parameter $k_1$ for pure proton form Nafion® 117 based on regression results for proton form Nafion® only (i.e. not using the linear model for $k_1$) is 1256 K or an $E_a$ equivalent to 10.4 kJ/mole, in even better agreement with the findings of Springer et al. (25) who found $k_1$ to be 1268 K. Halim et al. (10) found $k_1$ to be 1024 K. Sone et al. (8) found a more complex relation between temperature and conductivity when measuring on samples in the vapor phase. Below 45 °C they did not measure any temperature dependence, whereas above 45 °C they found the activation energy to be less than 2 kJ/mole equivalent to a $k_1$ of 240 K.
The ion exchange equilibrium of ammonium between an aqueous phase and Nafion® 117 were measured at 10.0, 25.0, 40.0, and 60.0 °C. The water content in the membrane phase was found to decrease linearly with the cation fraction of ammonium in the membrane phase ($y_{NH^+}$) from $\lambda_{H_2O} = 21.2 \pm 0.4$ in proton form Nafion® in pure water to $\lambda_{H_2O} = 13.2$ in pure ammonium form Nafion® in a 0.1 M chloride solution. The conductivity was also found to decrease linearly with $y_{NH^+}$ from 97 mS/cm to 25 mS/cm at 25.0 °C. The relative conductivity ratio of proton form Nafion® compared to ammonium form Nafion® is higher than the relative conductivity ratio of pure aqueous 1.0 M HCl and 1.0 M NH₄Cl (a factor of 3.8 - 3.9 vs. 3.10). This difference may be explained by the additional effect of lower water content in the membrane phase when in the ammonium form resulting in a lower conductivity. The temperature dependence of the conductivity was measured, and the fitted activation energy was found to depend on membrane composition, $E_a = 10.3 + 4.2 \cdot y_{NH^+}$ [kJ/mole].

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