Effect of ammonium ion distribution on Nafion® conductivity

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ABSTRACT

Nafion® conductivity in a proton exchange membrane fuel cell (PEMFC) with the fuel stream containing ammonia is mainly affected by the ammonium ion composition and operating conditions. In this study, the effect of ammonium ion distribution on Nafion conductivity was investigated for the first time. The conductivities of two kinds of contaminated membranes having uniform and non-uniform ammonium ion distributions were studied. To simulate a membrane with a well-defined ammonium ion concentration profile, three individual Nafion membranes containing known amounts of ammonium ions were physically stacked together. The uniform and non-uniform cases represented membranes having three layers with the same $y_{NH_4^+}$ or step changes in concentration, respectively. Under fuel cell operations, the conductivities of non-uniformly poisoned membranes were ca. 1.07–1.86 times larger than those of uniformly poisoned membranes, depending on humidity, contamination level, and ammonium ion distribution. Consequently, the performance prediction of a cationic-poisoned PEMFC needs to consider any concentration gradients that may exist in MEA. The liquid-phase conductivities of composite membranes were also studied and the results show that conductivity measurements performed in deionized water are not representative of what exists under fuel cell conditions due to rapid redistribution of ions in the Nafion via the liquid phase.

1. Introduction

With worldwide energy demand increasing significantly, efforts have been made to limit the amounts of greenhouse gases emitted, especially of carbon dioxide (CO_2). Among the approaches proposed, use of proton exchange membrane fuel cells (PEMFCs) is believed to be a promising energy conversion technology for both portable and stationary applications due to their high efficiency, high power output, quick start-up, fast response to load changes, low operating temperature (60–90 °C), and zero polluting emissions [1–5]. However, low tolerance to impurities in the fuel or air streams to PEMFCs is one of the major barriers for fuel cell adoption.

Poly(perfluorosulfonic acid) polymers, such as Nafion®, are popularly used as the membrane and proton transport agent for the cathode and anode catalysts in a PEMFC [6,7]. It is known that residual impurities in the fuel and oxidant streams can affect the Nafion conductivity. One of the most harmful contaminants present in a H_2 fuel stream, ammonia, significantly decreases proton conductivity of Nafion components (membrane and ionomer layers) [8–11]. However, to date, fundamental investigations into the effect of ammonia on Nafion conductivity, especially under conditions similar to fuel cell operation, have been limited. It has been found previously that the conductivities of Nafion membranes decrease with an increase in ammonium ion composition in them [8–10]. This is because the conductivity in the Nafion involves the transport of protons (H^+) and any proton-containing molecules (such as H_3O^+, H_2O, and NH_4^+), but the ionic mobility of NH_4^+ ions is lower than that of protons by ca. 75% [10,12,13].

Since ammonia, if present, is in the H_2 fuel stream at the anode, ammonia initially adsorbs on Nafion at the contacted interface before it penetrates into the bulk membrane. However, as the fuel cell operates, transport of ammonium ions from the anode to cathode can occur, causing a change in the non-uniformity of ammonium ion distribution in the membrane and catalyst layers. The kinetics of ammonium ion diffusion through a membrane mainly depend on the operating conditions (temperature and relative humidity, current density, etc.), quality of feed streams (concentrations of impurities (e.g., ammonia)) [14,15], membrane properties (i.e., membrane type, thickness, equivalent weight, preparation method, thermal history, water content, etc.), and the rate of ammonia removal at the cathode. It is certainly true that initially, and potentially throughout its operation, NH_4^+ ions may be non-uniformly distributed throughout the membrane, especially since adsorption of ammonia on Nafion is essentially irreversible. So far, no studies have been published addressing the effect of ammonium ion distribution on Nafion conductivity.

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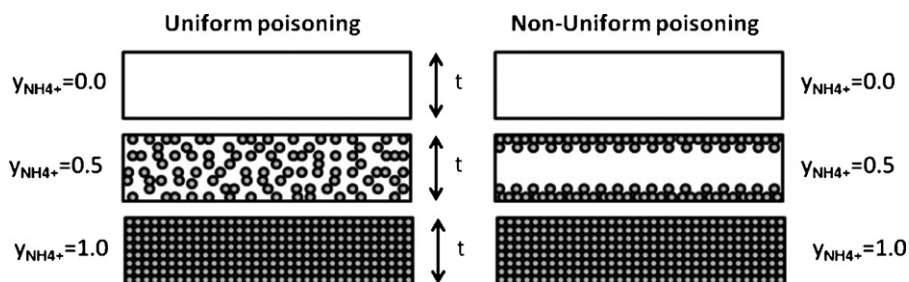E-mail address: jgoodwi@clemson.edu (J.G. Goodwin Jr.).

Fig. 1. Schematic of uniformly and non-uniformly ammonium ion-poisoned Nafion® membranes: where t is the membrane thickness.

In our previous study, the influence of gas-phase ammonia on the conductivities of the protonated form of Nafion® membranes (N-211) and the conductivities of pre-poisoned membranes with known ammonium ion fractions (where $y_{NH_4^+}$ is the ratio of sulfonic sites neutralized by ammonium ions and initial total sulfonic sites) at various conditions in a humidified He stream were investigated [12]. For gas-phase ammonia poisoned membranes, the N-211 membranes in the H⁺-form were exposed in situ to a He gas phase containing ppm levels of ammonia. Consequently, ammonia distributed non-uniformly in the membrane because ammonia first adsorbed on sites in the outer layers (being limited by the low concentration in the gas phase), and only later, after filling the more external sites, was able to diffuse in the gas phase further into the membrane. Pre-contaminated membranes, on the other hand, were prepared by ion-exchange with solutions having known concentrations of NH₄Cl and the ammonium ions in the membranes were homogeneously distributed. Fig. 1 presents schematic representations of ammonia poisoning during uniform/liquid-phase poisoning vs. non-uniform/gas-phase poisoning (with ppm concentrations of NH₃ on both sides of the membrane). Preliminary results suggested proton conductivity in a Nafion membrane is affected not only by ammonium ion concentration ($y_{NH_4^+}$) but also by its distribution. The conductivities as a function of $y_{NH_4^+}$ at 50%RH and 80 °C for uniformly and non-uniformly poisoned Nafion membranes are replotted in Fig. 2. It can be seen that the conductivity of a non-uniformly ammonium ion-poisoned membrane is different from that of a uniformly poisoned membrane, even though the membranes contain the same amounts of ammonium ions (overall values of $y_{NH_4^+}$ being the same). This is true over a wide range of conditions (30–100%RH at 80 °C) [16]. This observation implies that the distribution of foreign cationic ions (i.e., NH₄⁺ in this case) could have a significant effect on Nafion con-

ductivity. Especially, at low humidities (<50%RH) and moderate ammonium ion concentrations ($0.2 < y_{NH_4^+} < 0.8$), the conductivity of the non-uniformly poisoned membrane can be greater by 1.04–4 times than that of the uniformly poisoned membrane [16]. However, the ammonium ion distribution was not able to be quantitatively determined during those studies.

The objective of this work was to quantitatively investigate the influence of ammonium ion distribution on the conductivity of a Nafion membrane in a humidified gas stream at typical fuel cell conditions and in deionized (DI) water for comparison. The information derived in this study should be applicable qualitatively when other contaminated cations (i.e., Ca^{2+}, Ni^{2+}, Fe^{2+}, Fe^{3+}, etc.) are present in the membrane that originate from corrosion in a fuel cell, impurities in the H_2 and air streams, and/or fuel cell fabrication. This is because these metal cations neutralize sulfonic sites ($-SO_3^-$) in the Nafion ionomer in a similar manner and affected the conductivity within a comparable order of magnitude of NH_4^+ ions [17]. The quantitative results presented in this paper should be useful in future modeling of the performance of a cationic-poisoned PEMFC.

2. Experimental

2.1. Membrane modifications

Commercial Nafion® 211 membranes (N-211, 1100 EW, 25 μm thick) were purchased from DuPont. In order to obtain the H⁺-form of the N-211 membranes, rectangular samples of membranes (5.5 cm × 1 cm) were boiled separately in 3% H_2O_2, 0.5 M H_2SO_4, and deionized (DI) water for 1 h each. After that, the membranes were rinsed several times, immersed in DI water at room temperature (∼25 °C), and kept in the dark prior to an experiment.

In order to be able to investigate Nafion membranes with well defined and determined distributions, 3-layer composite membranes having various ammonium ion distributions were prepared by physically stacking together three membranes with known ammonium ion compositions (given by $y_{NH_4^+}$ which is the fraction of sulfonic sites ($-SO_3^-$) neutralized by ammonium ions). Each individual membrane was prepared by ion-exchanging the H⁺-form of N-211 in standard solutions containing known concentrations of NH₄Cl and HCl at room temperature under constant shaking at 250 rpm for at least 7 days [10,12]. The equilibrium isotherm for ammonium ion composition between an exchange solution ($x_{NH_4^+}$) and a contaminated membrane ($y_{NH_4^+}$) is given in Ref. [12]. All exchange solutions contained 0.1 M Cl⁻ and were changed periodically during equilibration to avoid any effect from differences in Cl⁻ concentration.

Single membranes having different ammonium ion compositions in two separate longitudinal regions were also prepared by immersing each end of the membranes in separate exchange solutions contained in a two-compartment Petri dish. The solutions in each compartment were also changed periodically, and the membranes were allowed to exchange in these static solutions at room temperature for at least 7 days.
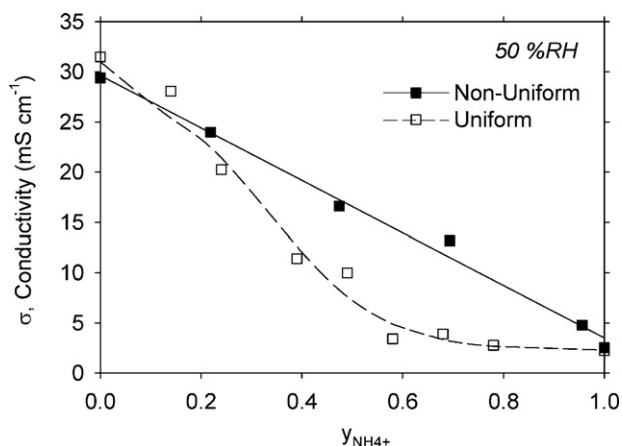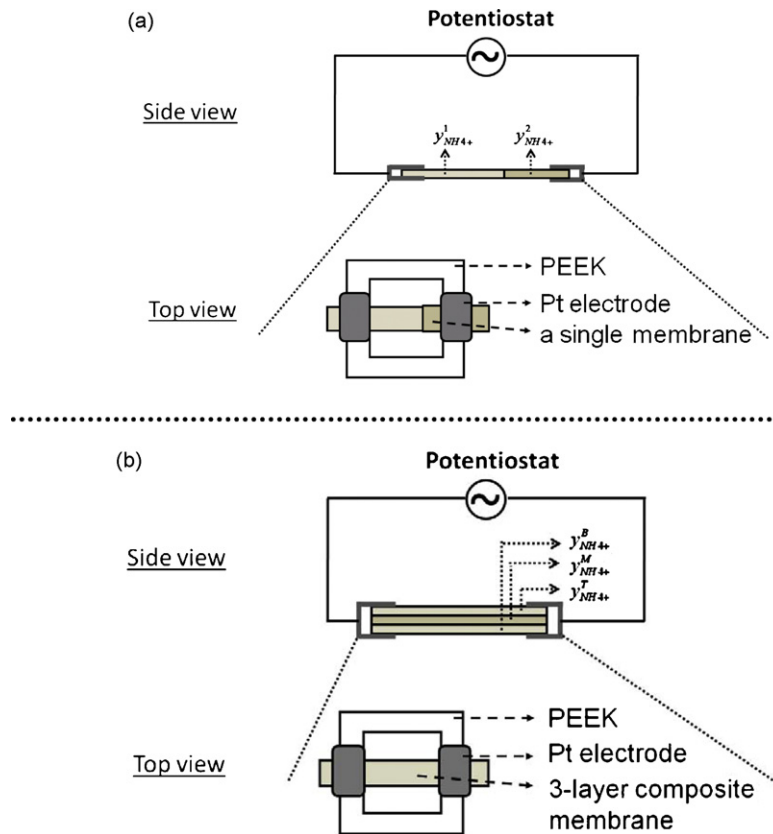

Fig. 2. The conductivity at 50%RH and 80 °C of single N-211 membranes containing different ammonium ion compositions with either uniform or non-uniform distributions. Replotted from Refs. [12,16].

Fig. 3. Schematic of conductivity measurements for: (a) a single membrane and (b) a 3-layer composite membrane.

2.2. Membrane pretreatment prior to conductivity measurements

Prior to conductivity measurements, each membrane sample having a given ammonium ion composition was taken out from the solution and rinsed several times with DI water to remove the excess exchange solution in the membrane. The membrane was then treated individually in a flow of 130 sccm He (UHP, National Specialty Gases) at 30%RH and 80 °C for 10 h in order to get rid of any weakly bound NH_4^+ ions in the Nafion clusters.

For conductivity measurements in the gas phase of single membranes having different ammonium ion compositions in two separate regions (Fig. 3(a)) or of 3-layer composite membranes (Fig. 3(b)) with known ammonium ion distribution, the membrane was allowed to equilibrate in the impedance chamber (ID = 16 cm, H = 25 cm) at a given humidity and temperature for 4 h and the conductivity was measured. Each measurement took ca. 15 min. Composite membranes with $y_{NH_4^+}^T$, $y_{NH_4^+}^M$, $y_{NH_4^+}^B$ (where $y_{NH_4^+}^T$, $y_{NH_4^+}^M$, and $y_{NH_4^+}^B$ are the ammonium ion concentrations of the top, middle, and bottom layers of the composite membrane) were prepared by physically stacking three membranes together.

For conductivity measurement in DI water, each membrane (5.5 cm × 1 cm) was re-equilibrated in DI water for 15 min before the conductivity was performed. Each measurement took ca. 5 min. Then, the three membranes with $y_{NH_4^+}^T$, $y_{NH_4^+}^M$, $y_{NH_4^+}^B$ were physically stacked together and allowed to equilibrate in DI water for 15 min prior to conductivity measurement in DI water.

2.3. Conductivity measurements

2.3.1. Conductivity in gas-phase He at 80 °C

The details of the measurement procedures are described elsewhere [12]. Basically, the ionic conductivity was analyzed using a two-probe ac technique. A potentiostat (Gamry Potentiostat Reference 600) was used for measuring the impedance of the membrane. Each measurement took ca. 15 min. The conductivity was calculated as follows:

$$\sigma = \frac{l}{RA} \qquad (2)$$

where σ is the conductivity (S cm^{-1}); l is the distance between the electrodes (2.5 cm); R is the resistance of the membrane (Ω); A is the cross-sectional area of the membrane.

Two sets of conductivity measurements were carried out in the gas phase:

- *Increasing humidity study*: For uniform ammonium ion poisoning (a 3-layer composite membrane with $y_{NH_4^+}^T = y_{NH_4^+}^M = y_{NH_4^+}^B$), the conductivity at 30%RH of a composite membrane was measured until it was constant. After that, the humidity was increased in increments from 30%RH to 100%RH, and the conductivity was measured after equilibration at each humidity. It required ca. 3 h for the impedance chamber to stabilize at each new humidity. The dimensions of a composite membrane were determined at the end of the experiment.
- *Constant humidity experiments*: For non-uniform ammonium ion poisoning (a single membrane with different ammonium ion concentrations at each end or a 3-layer composite membrane with $y_{NH_4^+}$, 0, $y_{NH_4^+}$), the conductivity at a specific humidity of a membrane was measured. Then, the experiment was stopped and the dimensions of the single or the composite membrane were measured. After that, conductivity measurements at other humidities were made following the same procedure.

Table 1
Parameters for ionic conductivity of an ammonium ion-poisoned Nafion® membrane (N-211) at 80 °C. These parameters are based on a 2nd order polynomial fit of experiment data in Fig. 4, using Eq. (3) in the text.

RH (%)	A_1	A_2	A_3	R^2
30	6.069	−14.334	8.427	0.9938
40	9.566	−25.595	16.779	0.9925
50	13.046	−39.388	28.618	0.9920
60	16.527	−55.314	44.262	0.9918
70	20.530	−73.167	63.987	0.9918
80	26.154	−93.013	88.046	0.9919
90	35.163	−115.24	116.67	0.9919
100	50.049	−140.63	150.07	0.9916

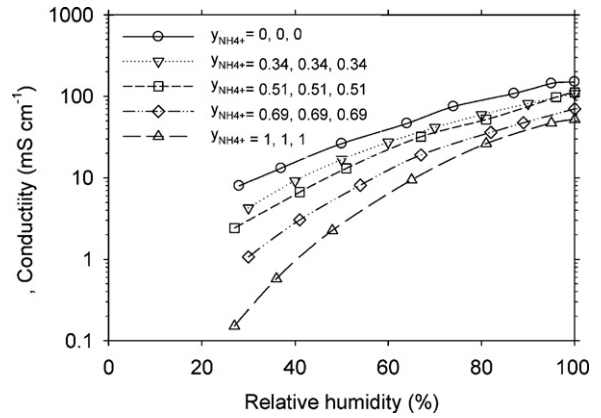### 2.3.2. Conductivity in DI water at room temperature (∼25 °C)

The ionic conductivities of 3-layer composite membranes were analyzed in DI water at room temperature and the dimensions of the composite membrane were measured at the end of each experiment. A typical conductivity measurement took ca. 5 min.

2.4. Ion-exchange capacity (IEC)

The ion-exchange capacity of proton sites of the N-211 membrane was determined by titration. Samples (5.5 cm × 1 cm, ∼30 mg) of the original H⁺-form of N-211 were immersed in 0.005 M NaOH (Acros Organics) at room temperature under constant shaking at 250 rpm for 2 days. Then, the membranes were taken out and the liquid aliquot back-titrated with 0.005 M HCl (Acros Organics) using phenolphthalein as an indicator. The end point of titration determined by pH meter was at pH 7.

2.5. Ammonium ion concentration

The ammonium ion compositions in each fraction of a single membrane and in each layer of a 3-layer composite membrane were investigated both prior to and after the conductivity measurements. For a single membrane with different ammonium ion compositions in two separate regions, the membrane was cut into fractions (one-third and two-thirds matching the sizes of the regions prepared) immediately after the conductivity measurement. For a 3-layer composite membrane, each layer was separated immediately after the conductivity measurements. Each fraction or layer was weighed and allowed to ion-exchange with 0.05 M


Fig. 4. Gas-phase conductivity of uniformly ammonium ion-contaminated composite membranes at various humidities and 80 °C.

HCl (Acros Organics) separately under constant shaking at room temperature for 10 days. After that, the membrane was removed from the liquid and the concentration of ammonium ions in the remaining solution was determined by an ion-selective electrode (ammonia electrode Thermo Scientific 9512 and Orion 4 Star pH benchtop meter).

3. Results and discussion

3.1. Gas-phase Nafion conductivity of uniformly ammonium ion-poisoned composite Nafion membranes vs. uniformly poisoned single membranes

Fig. 4 presents the conductivities at different humidities and 80 °C of homogeneously ammonium ion-poisoned composite membranes. The explanations for the effect of ammonium ions on Nafion conductivity have already been discussed in more detail elsewhere [12]. As expected, under the same conditions and the same ammonium ion compositions, the conductivities of single (data not shown) and 3-layer composite membranes taken from the same batch of Nafion membranes were identical within experimental error. The results were slightly higher (<10%) than those of a single membrane from the previous batch reported in our previous work [12]. This is likely due to small variations in physical
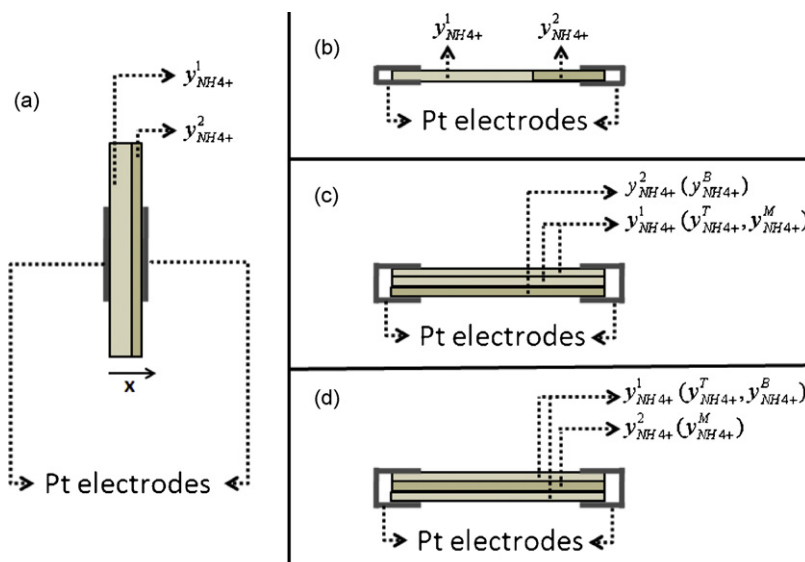
Fig. 5. Side-view of the different sample arrangements for membrane conductivity measurements.

properties of different batches of commercial Nafion membranes. The similarity of the conductivity results of single and 3-layer composite membranes suggests that conductivity comparison of these two membrane thicknesses is possible with thickness normalization. Consequently, physically assembling membranes with known ammonium ion compositions permit us to know the distribution of ammonium ions in a 3-layer composite membrane by measuring the content in each layer after conductivity measurement. In Fig. 4, the conductivities of Nafion membranes with a particular ammonium ion concentration ($y_{NH_4^+}$) were regressed with relative humidity using a power model and then the conductivities at specific humidities ranging from 30 to 100%RH were fitted by a 2nd order polynomial as follows:

$$\sigma_{RH, y_{NH_4^+}} = A_1(y_{NH_4^+})^2 + A_2(y_{NH_4^+}) + A_3 \qquad (3)$$

where $\sigma_{RH, y_{NH_4^+}}$ is the conductivity of a membrane having a composition of $y_{NH_4^+}$ at a given %RH. Parameters A_1–A_3 are given in Table 1 for anyone wishing to use these results in further modeling work. This functionality is not based on any theoretical implications.

3.2. Justification of the use of a 3-layer composite membrane to represent the non-homogeneity of ammonium ions in a membrane in a PEMFC

It is well known for PEMFC application that the membrane functions in the thickness direction and ammonia as an impurity in a H_2 stream is introduced at the anode. Therefore, the conductivity measurement configuration of an ammonium ion-poisoned membrane as shown in Fig. 5(a) would appear to be better for measuring practical conductivity under fuel cell conditions. However, due to the small thickness of the membrane, the sample arrangement in Fig. 5(a) unavoidably requires special sample preparation (i.e., hot-pressing [18]) and also lacks reproducibility and accuracy of the conductivity results [19]. In addition, since ammonium ion analysis (by ion-exchange techniques) of a membrane is, for all intents and purposes, limited to measuring only overall concentrations, the ammonium ion concentration profile in the thickness direction of a single membrane is essentially impossible to determine. Ammonium ion analysis by standard techniques such as Energy Dispersive X-ray Analysis (EDX) is also problematic. This is because ammonium ions adsorbed on $-SO_3^-$ sites can leave as ammonia when the membrane is heated in a vacuum chamber by the energy beam during measurement. Therefore, in this study, we used an equivalent conductivity measurement as illustrated in Fig. 5(b)–(d). The arrangement in Fig. 5(b) is an ideal equivalent of the set-up in Fig. 5(a). However, the ammonium ion analysis for the small portion (i.e., one-third portion) of a membrane may lack accuracy due to small amounts of sample. Also, conductivity measurements of the configuration as shown in Fig. 5(c), varying from low to high $y_{NH_4^+}$ in the thickness direction, do not yield precise results because the layer having less resistance (small $y_{NH_4^+}$) results in a short circuit. Therefore, the results obtained by this set-up may not represent the real conductivity of the whole composite membrane. The orientation in Fig. 5(d) where the Pt electrodes are in contact with layers of membrane having the same ammonium ion concentrations, therefore, was chosen as an equivalent circuit of that represented in Fig. 5(a), and it was used in this work to study the effect of ammonium ion distribution on Nafion conductivity. However, justification for this arrangement is still needed and is addressed next.

The plotted data in Fig. 6 show the overall conductivities under similar conditions of single membranes (with different ammonium ion concentrations at each end) and 3-layer composite membranes having similar average ammonium ion compositions ($y_{NH_4^+}$). The values of $y_{NH_4^+}$ presented in the figure were the ammonium ion
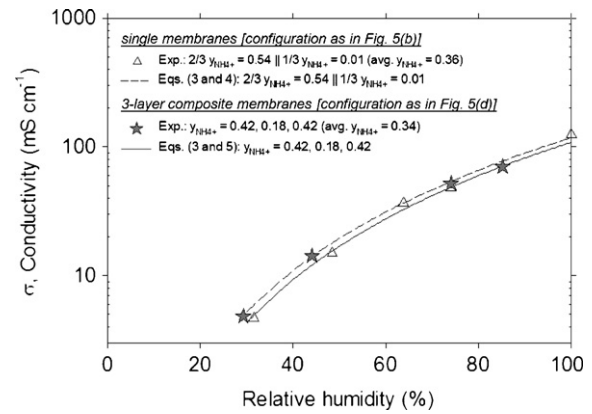

Fig. 6. Conductivities of single membranes having different ammonium ion concentrations ($y_{NH_4^+}$) at each end and of 3-layer composite membranes with similar average $y_{NH_4^+}$.

concentrations after conductivity measurements. It can be seen that the average values of $y_{NH_4^+}$ of these two membrane configurations were similar, but the ammonium ion concentration profiles were different. For the single membranes, $y_{NH_4^+}$ was initially 0 and 0.545 for one-third and two-thirds of the membrane, respectively. For the 3-layer composite membranes, on the other hand, $y_{NH_4^+}^T$, $y_{NH_4^+}^M$, and $y_{NH_4^+}^B$ were originally 0.51, 0, and 0.51, respectively. It is important to note that the migration of ammonium ions within the single membrane from high $y_{NH_4^+}$ region (two-thirds fraction) to low $y_{NH_4^+}$ region (one-third fraction) was much slower and less than the ammonium ion diffusion between the layers of a 3-layer composite membrane from high $y_{NH_4^+}$ layers (top and bottom) to low $y_{NH_4^+}$ layer (middle). This is due to the longer (longitudinal) transport pathway for ammonium ions in the single membrane, where ammonium ions were diffused in the in-plane direction and the length of the membrane was ca. 2.5 cm. For the multi-layer composite membrane, on the other hand, ammonium ions migrated in the thickness direction and the thickness of a composite membrane at these conditions (30–100%RH and 80 °C) was ca. 93 μm. Note that the thickness of the Nafion membranes in the dry state were 25 μm in general, but increased to 32–37 μm after being pretreated in 3% H_2O_2, 0.5 M H_2SO_4, and DI water for 1 h at 80–90 °C. The thicknesses of the 3-composite membranes after conductivity measurements in DI water at ambient temperature and in the gas phase at 80 °C were ca. 105–110 μm and 90–100 μm, respectively.

In Fig. 6, the unfilled triangles and filled stars represent the overall conductivities of the single membrane with non-homogeneous distribution of ammonium ions but having an average $y_{NH_4^+}$ equal to 0.36 and the composite 3-layer membrane with an average $y_{NH_4^+}$ equal to 0.34, respectively. The dashed and dotted lines represent the calculated conductivities obtained from Eqs. (3) and (4) and from Eqs. (3) and (5), respectively:

$$\sigma_{1\text{-layer}} = B_1\sigma_{RH, \ y_{NH_4^+}^1} + B_2\sigma_{RH, \ y_{NH_4^+}^2} \qquad (4)$$

$$\sigma_{3\text{-layer}} = \frac{1}{3}(\sigma_{RH, \ y_{NH_4^+}^T} + \sigma_{RH, \ y_{NH_4^+}^M} + \sigma_{RH, \ y_{NH_4^+}^B}) \qquad (5)$$

where $\sigma_{1\text{-layer}}$ and $\sigma_{3\text{-layer}}$ are the calculated overall conductivities of the single and 3-layer composite membranes at a particular humidity and 80 °C, respectively; $\sigma_{RH, \ y_{NH_4^+}^1}$ and $\sigma_{RH, \ y_{NH_4^+}^2}$ are the theoretical conductivities (based on the ammonium ion concentration measured for each fraction and based on measurements of uniformly ammonium ion-poisoned composite membranes; Eq. (3)) at a given %RH of each membrane region with $y_{NH_4^+} = y_{NH_4^+}^1$

Table 2
Ammonium ion composition of each layer in a 3-layer composite Nafion® membrane.

Initial $y_{NH_4^+}^{Ini}$ [a]			Final $y_{NH_4^+}^{F}$ [b]					
			He gas-phase			DI aqueous-phase		
Top	Middle	Bottom	Top	Middle	Bottom	Top	Middle	Bottom
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.51	0.00	0.51	0.42	0.18	0.42	0.35	0.34	0.33
0.69	0.00	0.69	0.56	0.27	0.56	0.47	0.43	0.48
1.00	0.00	1.00	0.80	0.37	0.83	0.66	0.66	0.68

[a] $y_{NH_4^+}^{Ini}$ is the average of initial ammonium ion composition in each membrane layer (before three membranes were physically stacked together) of a composite membrane.

[b] $y_{NH_4^+}^{F}$ is the average final ammonium ion content in each membrane layer of a composite membrane after conductivity measurements at a particular relative humidity. NH$_4^+$ ion analysis: error = ±7%.

and $y_{NH_4^+}^2$, respectively; parameters B_1 and B_2 are fractions of a membrane having $y_{NH_4^+} = y_{NH_4^+}^1$ and $y_{NH_4^+}^2$, respectively; and $\sigma_{RH, y_{NH_4^+}^T}$, $\sigma_{RH, y_{NH_4^+}^M}$, and $\sigma_{RH, y_{NH_4^+}^B}$ are the theoretical conductivities (based on the ammonium ion concentration measured for each layer of a 3-layer composite with $y_{NH_4^+} = y_{NH_4^+}^T$, $y_{NH_4^+}^M$, and $y_{NH_4^+}^B$ for the top, middle, and bottom layers, respectively and based on measurements of uniformly ammonium ion-poisoned composite membranes; Eq. (3)).

It can be seen in Fig. 6 that the experimental conductivities of single and layered membranes correspond very well with each other and with the predicted values obtained from Eqs. (3) and (5). This agreement indicates that the conductivity of an ammonium ion-poisoned membrane can be reasonably predicted by knowing both ammonium ion composition and concentration profile in the membrane. These observations justify that the configuration of conductivity measurement given in Fig. 5(d) produces equivalent results to that in Fig. 5(b), and by inference to that in Fig. 5(a). Consequently, this sample arrangement (Fig. 5(d)) was applied in this study because of its equivalent results to those in Fig. 5(a) and (b), simplicity of the membrane preparation, accuracy of an ammonia analysis, and reproducibility of the conductivity results.

3.3. Effect of ammonium ion distribution on gas-phase Nafion conductivity at 80 °C

Table 2 lists the average ammonium ion compositions of series of multi-layer composite membranes after conductivity measurements at different humidities. It shows that the ammonium ion distribution of non-uniformly poisoned membranes changed somewhat after the membranes were equilibrated at a particular humidity for 4 h before conductivity measurements. Since the time required for conductivity measurements was short (ca. 15 min), the change in ammonium ion distribution during measurement can be ignored.

Fig. 7 shows the conductivities of poisoned 3-layer composite membranes having similar overall ammonium ion compositions ($y_{NH_4^+}$), but different concentration profiles. The filled and unfilled symbols represent the conductivity of 3-layer composite membranes with non-uniform and uniform ammonium ion distributions, respectively. Solid lines represent a fit of data. It can be seen in Fig. 7 that, at low $y_{NH_4^+}$ ($y_{NH_4^+} \sim 0.34$), the effect of ammonium ion distribution of 3-layer composite membranes on the conductivity at relevant fuel cell conditions (30–100%RH and 80 °C) was minimal. However, as $y_{NH_4^+}$ increased, the conductivity difference between the non-uniformly and uniformly poisoned composite membranes with equivalent ammonium ion contents became more significant. In Fig. 7, the conductivities of non-homogeneous com-
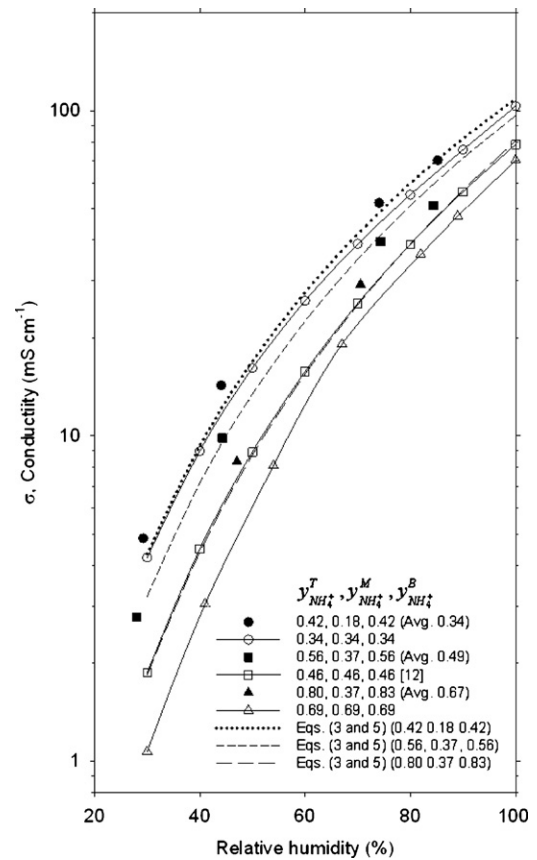
Fig. 7. Comparison of the conductivity at 80 °C of 3-layer composite membranes having homogeneously and non-homogeneously distributed ammonium ion concentrations.

posite membranes with average $y_{NH_4^+}$ of 0.34, 0.49, and 0.67, respectively, were ca. 7–23%, 34–86%, and 51–71% larger than those of homogeneously poisoned membranes with similar average $y_{NH_4^+}$ values of 0.34, 0.46 and 0.69, respectively. Thus, it can be seen that the conductivities under fuel cell operations of non-uniformly poisoned membranes were ca. 1.07–1.86 times larger than those of uniformly poisoned membranes depending on the relative humidity and ammonium ion distribution profile. The conductivity differences became smaller with an increase in humidity and ammonium ion distribution uniformity. Also, in Fig. 7, the dotted and dashed lines represent the predicted conductivities of non-uniformly contaminated membranes obtained from Eqs. (3) and (5) and based on the values of $y_{NH_4^+}$ given in the parentheses for each layer in the legend. It can be seen that these theoretical predictions correspond very well with the experimental results (filled symbols). This observation suggests that a conductivity model taking into account the non-homogeneity of ammonium ion concentration profile within a membrane or a catalyst layer would yield a more accurate prediction for a contaminated PEMFC performance. If the concentration profile is known, the overall conductivity ($\sigma_{overall}$) of a Nafion membrane [16] and that of a Nafion's catalyst layer [20] can be calculated as follows:

Nafion membrane:

$$\sigma_{overall, \; mem} = \int_{x_H}^{x_L} \sigma_{RH, \; y_{NH_4^+}} dx \qquad (6)$$

Nafion catalyst layer:

$$\sigma_{\text{overall, cat. layer}} = (1 - \varepsilon_{\text{cat}}) \left[1 + \frac{(\varepsilon_{\text{agg}} - 1)}{(1 + (\delta/r_{\text{agg}}))^3} \right] \int_{x_H}^{x_L} \sigma_{RH, \ y_{\text{NH}_4^+}} \, dx$$

where $x_H < x < x_L$ and $0 < y_{\text{NH}_4^+} < 1$ (7)

where $\sigma_{\text{overall, mem}}$ and $\sigma_{\text{overall, cat. layer}}$ are the estimated overall conductivities of a poisoned Nafion membrane (N-211) and a poisoned Nafion catalyst layer, respectively; $\sigma_{RH, \ y_{\text{NH}_4^+}}$ is the conductivity of an ammonium ion-contaminated Nafion polymer at a specific %RH with ammonium ion composition $y_{\text{NH}_4^+}$ and it was obtained from Eq. (3) and Table 1; ε_{cat} and ε_{agg} are the volume fractions of the pores and of the Nafion in the catalyst layer, respectively; δ is the thickness of the Nafion film coating the agglomerate (multiple particles of Nafion on Pt/C support surrounded by Nafion thin film); r_{agg} is the radius of the agglomerate; x is the normalized distance from the catalyst layer/membrane interface in the thickness direction, see Fig. 5(a); and x_L and x_H are the normalized distances from the interface of the contaminated area having the lowest and the highest $y_{\text{NH}_4^+}$, respectively (generally, $x_H = 0$).

3.4. Comparison of liquid-phase conductivities of composite membrane with those in the literature

The objective of this section is to compare the conductivity data of Nafion membranes in the present work with those available in the literature under the same conditions (in DI water at ambient temperature). It was found that under the same conditions and identical average of ammonium ion compositions, the conductivity of a uniform single membrane in this study was slightly higher (<7%) than those which have been reported by Halseid et al. [10] and Hongsirikarn et al. [12] due to the slight variation between each batch of the Nafion membrane. However, as expected, under the same batch of commercial Nafion® 211 membranes, the conductivities of composite membranes and of single membranes (data not shown) having identical ammonium ion concentrations and homogeneous ammonium ion distribution were similar.

3.5. Comparison for non-uniformly poisoned composite membranes of conductivities in DI water with those in the gas phase

Table 2 summarizes the ammonium ion contents in each layer of composite membranes initially and after conductivity measurements. It was found that the ammonium ion distribution of non-uniformly poisoned composite membranes rapidly changed to uniformly poisoned composite membranes within 15 min equilibration in DI water. While some ammonium ion diffusion took place between each layer of composite membranes in the gas phase at 30–100%RH and 80 °C, this was significantly slower than in DI water at room temperature. The experimental results indicate that the presence of large amounts of water in the Nafion facilitates the ammonium ions diffusion and ion-exchange process of ammonium ions with proton sites ($-SO_3^- - H^+$). In DI water, the transport pathway within layers of the composite membranes was very well-connected owing to high water sorption, open structure, and flexible hydrogen bond network throughout the Nafion ionic clusters, where equilibrium can exist between solution phase protons (H^+) and ammonium ions (NH_4^+) with protons and ammonium ions adsorbed on sulfonic sites ($-SO_3^- - H^+$, $-SO_3^- - NH_4^+$). On the other hand, in the gas phase at low to moderate humidity and high temperature (30–70%RH and 80 °C), the diffusion of ammonium ions is significantly inhibited. This is because strongly fixed anionic charges ($-SO_3^-$) at the pore walls of the hydrophilic clusters, high rigidity of hydrogen-bonded network, and contracted structure sta-
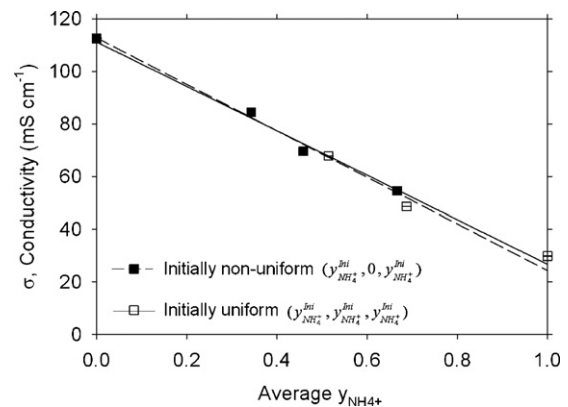

Fig. 8. Conductivity in DI water at room temperature for 3-layer composite membranes with initial uniform or non-uniform ammonium ion distributions.

bilize ammonium ions in their networks [11], leaving only small amounts of ammonium ions (NH_4^+) not attached to sites in a cluster.

Fig. 8 presents the conductivity of 3-layer composite membranes containing various ammonium ion compositions ($y_{\text{NH}_4^+}$). The average $y_{\text{NH}_4^+}$ in the x-axis is the average ammonium ion concentrations for each layer of a composite membrane. The filled squares in Fig. 8 give the conductivity data for 3-layer composite membranes with an initial non-homogeneous ammonium ion distribution of $y_{\text{NH}_4^+}^{\text{Ini}}$, 0, $y_{\text{NH}_4^+}^{\text{Ini}}$ which developed a uniform distribution having final composition of $(2/3)y_{\text{NH}_4^+}^{\text{Ini}}$, $(2/3)y_{\text{NH}_4^+}^{\text{Ini}}$, $(2/3)y_{\text{NH}_4^+}^{\text{Ini}}$ within 15 min equilibration in DI water. It can be seen that the liquid-phase conductivities of non-uniformly ammonium ion-poisoned membranes show the same variation with overall ammonium ion concentrations as uniform membranes, regardless of the initial ammonium ion distribution due to the high ammonium ion diffusivity at this condition.

The loss of ammonium ions from a composite membrane to liquid electrolyte (DI water) was also investigated. It was found that the conductivity of a 3-layer composite membrane with $y_{\text{NH}_4^+} = 0.67$, 0.67, 0.67 in DI water was more or less constant over 24 h (data not shown) and also the ammonium ion concentrations in DI water (250 mL) after the conductivity measurement were below detection limit (<1 ppm). This observation suggests that the loss of ammonium ion from a layered membrane was negligible.

4. Conclusions

In this study, the effect of ammonium ion distribution within composite Nafion membranes on the gas-phase and liquid-phase conductivities was quantitatively examined. Three membranes with known ammonium ion compositions were physically stacked together in order to ensure well-defined ammonium ion distribution within a 3-layer composite membrane.

Under conditions relevant to fuel cell operations (30–100%RH and 80 °C), it was found that the conductivities of non-homogeneously ammonium ion-poisoned composite membranes with $y_{\text{NH}_4^+}^T$, $y_{\text{NH}_4^+}^M$, $y_{\text{NH}_4^+}^B$ were ca. 1.07–1.86 times larger than those of homogeneously poisoned composite membranes having the equivalent ammonium ion content, depending on humidity, level of contamination, and ammonium ion concentration profile in the membranes. This finding indicates that the effect of ammonium ion distribution on Nafion conductivity at typical fuel cell conditions can be significant. Results from this study also suggest that concentration gradients for other poisoning cations in membrane electrode assemblies (MEAs) may also have an effect on fuel cell operations.

On the other hand, the influence of ammonium ion distribution on conductivity measured in DI water at ambient temperature (~25 °C) was small. Owing to fast diffusion of ammonium ions through the Nafion matrix, the ammonium ion distribution of non-homogeneously poisoned composite membranes was rapidly equilibrated to a homogeneous profile. It is clear that the quantitative study for the effect of cation distribution on conductivity at normal fuel cell operations cannot be investigated in a liquid electrolyte like DI water, even though measurement in such an electrolyte is easy, convenient, and fast compared to that in the gas phase.

Acknowledgments

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