



Influence of ammonia on the conductivity of Nafion membranes

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ABSTRACT

The effect of NH_3 and NH_4^+ poisoning on the conductivity of Nafion membranes was investigated via electrochemical impedance spectroscopy. The conductivities of membranes prepared with different NH_4^+ compositions were measured in deionized water at room temperature and compared to those at 80°C in a gas phase for various relative humidities. The liquid-phase conductivity decreased linearly with an increase in the NH_4^+ composition in the membrane ($y_{\text{NH}_4^+}$), with that of the NH_4^+ -form having a conductivity 25% that of the H^+ -form. The gas-phase conductivity of the NH_4^+ -form, on the other hand, declined by 66–98% relative to the H^+ -form depending on humidity. The conductivities of fresh membranes in the presence of gas-phase NH_3 at different humidities were also studied. The conductivity decreased with time-on-stream and reached the same conductivity at a given humidity regardless of the NH_3 concentration, but the time to reach steady-state varied with NH_3 concentration. The $y_{\text{NH}_4^+}$ at steady-state conductivity was equivalent for all the NH_3 concentrations studied. The kinetics of conductivity decrease was slower at higher humidities. The humidity and $y_{\text{NH}_4^+}$ appear to have a concerted effect on the conductivity. The quantitative conductivity data under practical fuel cell conditions should be useful for future fuel cell modeling.

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1. Introduction

Energy security, local pollution levels, and climate change are issues driving the development of alternative fuels for transportation applications. Hydrogen is a promising fuel for transportation that can be produced from a variety of sources. Fuel cells offer a highly efficient route to electrochemically produce energy from hydrogen in automotive applications [1]. Polymer electrolyte membrane fuel cells (PEMFCs) have high power density [2,3] and have been proposed for automotive, portable, and stationary applications [4,5]. However, high system costs and low stack durability have limited the adoption of PEMFC technologies [6]. The U.S. Department of Energy has targeted a 5000 h stack lifetime with less than 0.4 mg cm^{-2} of Pt per cell by 2010 to move toward automotive system requirements. Such stack durability should exist even when using commercial grade hydrogen that contains contaminants left over from the production process.

Currently, the majority of hydrogen used in industrial processes is generated by reforming methane or other hydrocarbons [7]. Three processes for hydrogen production are steam methane reforming (SMR), autothermal reforming (ATR), and partial oxidation (POX) [8,9]. These processes unavoidably generate small amounts

of contaminants such as CO , CO_2 , CH_4 , NH_3 , H_2S , and organic compounds [10]. Ammonia may be present in the hydrogen stream in the range of 30–150 ppm [8,11,12]. Contaminants in the reformed gas are typically converted using a catalytic reaction such as the water–gas shift for CO or separated using pressure swing adsorption (PSA). However, even the best contaminant removal processes leave trace levels of contaminants. These contaminants degrade the performance of PEMFC stacks and can irreversibly poison the membrane/electrode assemblies (MEAs) in the stack [10].

There are many kinetic steps that can determine the overall performance of a PEMFC. However, at intermediate current densities between 0.2 and 1.0 A cm^{-2} and in the absence of impurities, fuel cell performance is mainly limited by the proton conductivity of the membrane [13].

It has been found that ammonium ions reduce the proton conductivity of Nafion in the anode catalyst ionomer layer and membrane [8,12,14]. Researchers have shown, using current interrupt measurements, an increase in the membrane resistance with continuous poisoning. However, the amount of the voltage decrease during continuous poisoning experiments is not completely accounted for by the change in membrane resistance [8,11,14]. Therefore, ohmic losses in the membrane cannot completely explain ammonia poisoning.

Up to the present, most research groups have studied the effects of impurities on the overall fuel cell performance. However, very few have examined the effect on each component in

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the fuel cell. It has been suggested by different researchers that ammonium ions reduce the proton conductivity of Nafion in the anode catalyst ionomer layer and membrane [8,12,14]. However, few studies showing quantitative results have been published, especially for conductivity at similar conditions as fuel cell operation. Most of the conductivity experiments have been carried out in liquid electrolytes. This condition is very far from the real conditions in a fuel cell. Halseid et al. [12] measured the conductivity of N-117 in a liquid electrolyte by two-electrode AC impedance and observed that the conductivity of the membrane in the fully protonated form (97 mS cm^{-1}) was four times higher than that of the ammonium form (25 mS cm^{-1}). Uribe et al. [8] reported the conductivity of Nafion 105 in various cationic forms measured in deionized (DI) water at 25°C . The conductivities of the fully hydrated proton and ammonium forms were 133 and 32 mS cm^{-1} , respectively. Doyle et al. [15] examined the effects of cation type and “solvent” (the liquid electrolyte) on the ionic conductivity of N-117. They proposed that the cation radius and solvent significantly affect the conductivity. Generally, the conductivity decreased as the Pauling cation radius increased as the weight uptake of solvent increased. However, all the conductivity studies were performed in a liquid electrolyte at room and elevated temperatures.

The goal of the research reported here was to measure the conductivity of a Nafion membrane when it was exposed to ammonia in a controlled way, thereby permitting the ohmic losses in the membrane and potentially in the ionomer layer to be better understood. This could be especially useful for future modeling of impurity effects on fuel cell performance. The conductivity of Nafion membranes with various ammonium contents were measured both in DI water and a gas phase. This study also addressed the effect of humidity on ammonia poisoning of the Nafion membrane. The results reported herein comprise the most complete study to date on the effect of ammonia poisoning of a Nafion membrane at conditions typical of a fuel cell.

2. Experimental

2.1. Membrane preparation

The Nafion membranes with 1100 EW (DuPont Inc.), having nominal thicknesses of $183 \mu\text{m}$ (N-117, 360 g m^{-2}) and $25.4 \mu\text{m}$ (N-211, 50 g m^{-2}), were purchased from Ion Power, Inc. and pretreated to keep the membranes in a fully acidic form, free of contaminants. All membranes were heated separately at $80\text{--}90^\circ\text{C}$ for 1 h in 3 wt.% H_2O_2 (Fisher Scientific) in DI water to eliminate organic contaminants, for 1 h in 0.5 M H_2SO_4 (Acros Organics) to fully protonate the membrane, and for 1 h in DI water to remove the residual acid. Finally, all pretreated membranes were rinsed several times and stored in DI water in a dark environment at room temperature prior to experiment.

For certain studies, membranes with known concentrations of ammonium ions were prepared. The method for the equilibration of the membranes was the same as described in the literature [12]. Standard solutions with desired fractions of H^+ and NH_4^+ cations were prepared using HCl (Acros Organics), NH_4Cl (Ricca Chemical), and DI water. In these solutions, the chloride concentration was held constant at 0.1 M. Protonated membranes were ion-exchanged by immersing the membranes in a solution with a given concentration of NH_4^+ ions. The membrane was then allowed to equilibrate in the cation-chloride solution for 7 days at room temperature with constant shaking, and the exchange solutions were changed three times. After the exchange, the membranes were rinsed with DI water to remove excess solution and kept in DI water prior to the experiment. To ensure that no significant amounts of ammonium ions were released from the membrane during washing and stor-

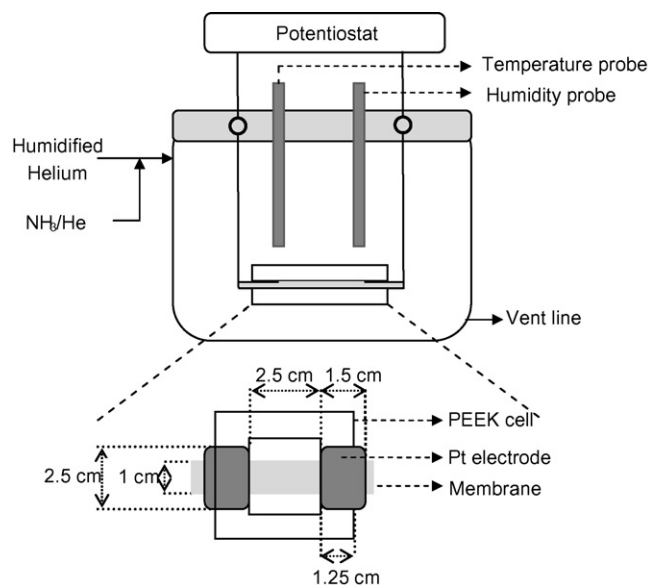


Fig. 1. Experimental set-up for measurement of gas-phase conductivity using impedance spectroscopy.

ing in DI water, the real time conductivity of the ammonium form of N-211 immersed in DI water at room temperature was monitored overnight. Neither a noticeable increase in conductivity nor ammonium ions in the DI water was detected.

2.2. Physical characterizations

2.2.1. Elemental analysis

In order to determine sulfur leaching, chlorine adsorption, and ammonium uptake in the Nafion membranes, elemental analyses of the membranes and the exchange solutions were carried out by Galbraith Laboratories in Knoxville, Tennessee.

2.2.2. Ion-exchange capacity (IEC)

The IECs of the membranes ($2.5 \text{ cm} \times 1 \text{ cm}$) were determined by ion-exchange with NaOH (Acros Organics). The N-117 and N-211 membranes were ion-exchanged with 0.05 and 0.005 M NaOH, respectively, for 2 days at room temperature in an Innova 4080 Incubator Shaker. Then, the membranes were taken out and the exchange solution was back-titrated with 0.05 and 0.005 M HCl (Acros Organics), respectively, using phenolphthalein as an indicator. The end point was determined at a pH of 7.

2.3. Conductivity measurements

The ionic conductivities in the lateral direction of the membranes were determined by a two-probe technique using a frequency response analyzer (Gamry Potentiostat Reference 600). A portion of membrane ($5.5 \text{ cm} \times 1 \text{ cm}$) was fixed in a custom-made polyetheretherketone (PEEK) sample holder that had a $2.5 \text{ cm} \times 2.5 \text{ cm}$ working window with 2 Pt foil electrodes (see Fig. 1).

2.3.1. Conductivity measurements of the pre-exchanged N-211 in liquid electrolyte (DI water)

The pretreated membranes were rinsed with DI water and then the thicknesses were measured by a micrometer at 5 different positions. A membrane was secured in the holder, and the cell was then filled with DI water. The conductivity measurements were carried out at room temperature, and a signal of 25 mV amplitude was applied in the 1 MHz to 100 Hz range to the custom-made cell.

The conductivity was calculated using the following equation in the frequency range of 1 MHz to 100 Hz by extrapolating the high frequency end of the Nyquist plot to the real axis using Zview® software:

$$\sigma = \frac{l}{R_{\text{mem}}A_{\text{mem}}} \quad (1)$$

where σ is the conductivity (S cm^{-1}); l is the distance between the electrodes (2.5 cm); R_{mem} is the resistance of the membrane (real component of the complex impedance, Ω); A_{mem} is the cross-sectional area of the membrane given by $1 \text{ cm} \times t \text{ cm}$; and t is the thickness of the membrane.

2.3.2. Conductivity measurements of the pre-exchanged N-211 in the gas phase as a function of humidity

Change in the length and width of a membrane fixed at both ends can cause strain in the membrane which affects the conductivity of the membrane by changing the orientation of the hydrophilic channel structure [16–21]. Therefore, after the conductivity measurement in DI water, each membrane was equilibrated overnight inside a specific temperature and humidity controlled chamber in order to prevent stretching or contracting of the membrane during conductivity measurements. Then, it was inserted into the PEEK sample holder and pretreated in a well-controlled temperature and humidity chamber (ID = 16 cm, H = 25 cm) under a flow of 130 sccm of He (UHP, National Specialty Gases) at 30%RH, and a particular temperature (60–90 °C, standard 80 °C) for 8 h until there was no change in conductivity. The humidity was then raised by 10%RH from 30%RH to 100%RH with the conductivity being measured after equilibration at each %RH.

The humidity was obtained using a syringe pump (Genie pump, Kent Scientific Corporation) to pump liquid water through a heated line into a heated chamber where it flash vaporized into a flow of He to give a homogeneous mixed gas stream. The humidified He was then flowed into the impedance measurement chamber and the real time relative humidity was monitored by a humidity and temperature transmitter (HMT 330, Vaisala).

The thickness of the membrane at the end of the experiment was obtained by averaging 5 measurements at different positions using a micrometer. After that, the membrane equilibrated at 100%RH was weighed immediately. Dry weight of the membrane was determined by drying the sample for 4 days in the chamber with flowing dry He at 110 °C. The membrane was then allowed to cool down and kept in a desiccator at 25%RH and room temperature. The water uptake was obtained as follows:

$$\lambda_{\text{H}_2\text{O}} = \frac{1100(W_{\text{eq}} - W_{\text{dry}})}{18W_{\text{dry}}} \quad (2)$$

where $\lambda_{\text{H}_2\text{O}}$ is the water uptake ($\text{mol H}_2\text{O}/\text{mol SO}_3^-$); W_{eq} are the weight of the membrane equilibrated at a given humidity and temperature (standard 80 °C); and W_{dry} is the dry weight of the membrane, respectively.

2.3.3. Conductivity measurements of fresh N-211 in the gas phase containing low concentrations of ammonia

A fresh membrane was equilibrated overnight at the specified humidity before it was mounted in the PEEK cell, placed inside the controlled chamber, and allowed to equilibrate in He atmosphere. A gas mixture of 500 ppm ammonia in He (National Specialty Gases) was diluted with humidified He downstream to obtain various ammonia ppm concentrations. Then, real time conductivity measurements were executed with time-on-stream as ammonia was introduced into the system under a total flow of 130 sccm at specific conditions. The thickness of the membrane was measured after reaching the final steady-state conductivity.

2.4. Measurement of ammonium ion concentration in a membrane

The ammonium ion content of N-211 ($y_{\text{NH}_4^+}$) was determined both for membranes prepared with a fixed ammonium concentration and after exposure of a membrane to the He gas phase containing ppm concentrations of ammonia. This was carried out using an aqueous solution with an excess of protons. The kinetics of proton replacement at room temperature occurred slowly and required a long time to complete the exchange. In this study, the membranes were allowed to back ion-exchange with 0.05 M HCl (Acros Organics) at room temperature in a shaker at 250 rpm. The ammonia uptake of the membranes was identical for either 7 or 10 days. Therefore, the exchange time used was set at 7 days for all of the measurements. The concentration of ammonium ions in the exchanged solution was analyzed by an ion selective electrode (ammonia electrode Thermo Scientific 9512 and Orion 4 Star pH benchtop meter).

3. Results and discussion

3.1. Equilibria relationship of ammonium uptake in Nafion membranes

Fig. 2 shows the equilibrium isotherm of ammonium content of N-211 equilibrated with different ammonium concentrations in solution at room temperature, where $x_{\text{NH}_4^+}$ is the fraction of ammonium ions in a 0.1 M Cl^- aqueous solution and $y_{\text{NH}_4^+}$ is the ammonium composition fraction neutralizing the sulfonic groups in the membrane. The results illustrate that ammonium ions have a slightly higher affinity for N-211 than protons. It was found by Leslie Jones et al. [22] that the anion concentration (Cl^-) in a N-117 membrane increases with an increase in Cl^- concentration in a solution. They suggested that the uptake of these anions by the hydrophobic polytetrafluoroethylene (PTFE) backbone of the Nafion could change some properties, for example, the amount of solvent uptake, swelling properties, and strength of the acidic sites. Consequently, for this study, the concentration of chloride in the prepared standard solutions was fixed at 0.1 M Cl^- .

As expected, the results here are in good agreement with those of Halseid et al. [12] who studied the equilibrium ammonium uptake of N-117. The ion-exchange and ammonia uptake capacities of Nafion membranes (N-211, N-117) are shown in Table 1. The IEC values of the hydrated membranes, determined by back-titration, were consistent with the results from the elemental analysis of sulfur in the membrane and the MSDS from DuPont. The differences

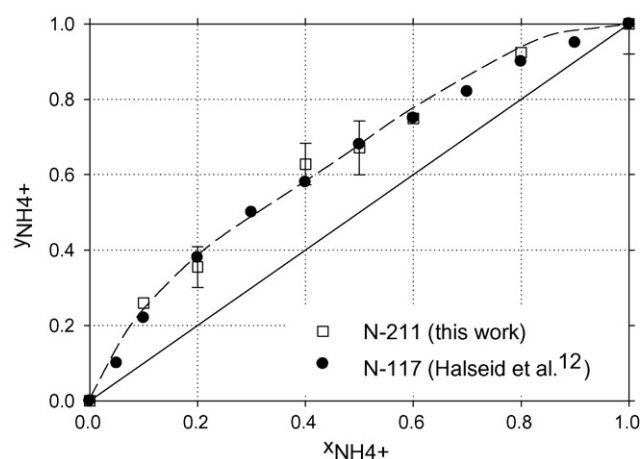


Fig. 2. Equilibrium of ammonium ions between an aqueous liquid phase and Nafion membranes at room temperature and 0.1 M Cl^- .

Table 1
IEC of Nafion membranes in fully protonated form.

Nafion membrane	Ion-exchange capacity (IEC, $\mu\text{mol g}^{-1}$)		NH ₃ uptake capacity ($\mu\text{mol g}^{-1}$)
	Titration ^a	Elemental analysis ^b	ISE ^c
N-211	920 ± 17	925	877 ± 38
N-117	902 ± 5	920	–

^a Membrane was ion-exchanged with 0.005 and 0.05 M NaOH at room temperature for N-211 and N-117, respectively; error = ±2%.

^b IEC was calculated by sulfur elemental analysis; error = ±5%.

^c NH₃ uptake was determined by an ion-selective electrode (ISE) of the ion-exchange liquid; error = ±5%.

between the acid ($920 \pm 17 \mu\text{mol H}^+ \text{g}^{-1}$) and maximum ammonium capacities ($877 \pm 38 \mu\text{mol NH}_4^+ \text{g}^{-1}$) of the membrane were not due to any significant loss of sulfur during exchange because sulfur leaching from the N-211 (originally $925 \mu\text{mol g}^{-1}$) determined by sulfur analysis of the exchanged solution was small (less than $32 \mu\text{mol g}^{-1}$), well within the margin of error of the measurements.

Previous studies have suggested that chloride adsorption of N-117 might explain this difference [12,22]. Elemental analysis in our study showed that the chlorine uptake (λ_{Cl^-}), expressed by the number of chloride ions per anion sulfonic site, from the 0.1 M Cl⁻ solution was $46 \pm 10 \mu\text{mol g}^{-1}$ ($\lambda_{\text{Cl}^-} = 0.04\text{--}0.06 \text{ mol Cl}^-/\text{mol SO}_3^-$), which was identical within experimental error for the different ammonium ion concentrations. The results correspond well with those of Leslie Jones et al. [22] and of Halseid et al. [12] who reported chloride contents of 46 and $37 \mu\text{mol g}^{-1}$, respectively, in membranes following ion-exchange.

3.2. Influence of ammonium ion concentration in Nafion on its aqueous phase behavior

3.2.1. Effect of ammonium composition in Nafion on conductivity in DI water

To ensure that no ammonium ion loss occurred during conductivity measurements, the conductivity of a membrane with a given ammonium concentration was first measured, and then the membrane was kept in DI water for 1 day. There was no increase in the conductivity, no ammonium ions were detectable in the DI water, and the ammonium concentration in the membrane remained constant.

The conductivities of Nafion membranes that had been ion-exchanged with specific fractions of ammonium ions and equilibrated in DI water at room temperature are presented in Fig. 3. The conductivities of both N-211 and N-117 decreased linearly with increasing ammonium concentration from 115 mS cm^{-1} with no ammonium ions to 24 mS cm^{-1} in the fully exchanged ammonium form. The 75% decrease in conductivity for the fully exchanged ammonium form compared to the protonated form agrees completely with literature data [8,11,12,15]. There are two possible explanations for this phenomenon which involves the size of the cations and the change in ion transport mechanism.

Doyle et al. [15] proposed that conductivity generally decreases with an increase in cation radius. The Pauling cation radius of NH₄⁺ ($\sim 1.52 \text{ \AA}$ [23]) is about four times bigger than that of H⁺ ($\sim 0.4 \text{ \AA}$ [24]). Also, Saito et al. [25] studied the effect of cations on the conductivity of N-117 in the temperature range 10–50 °C. They found that water diffusivities for cation forms of the Nafion membrane (H⁺, Na⁺, Li⁺) were almost identical. They proposed, thus, that protons may be transported by a hopping mechanism, whereas larger cations (Li⁺ and Na⁺) may migrate by the slower vehicle mechanism at these conditions, in agreement with the proposal of Thampan et al. [26] and of Paddison et al. [27].

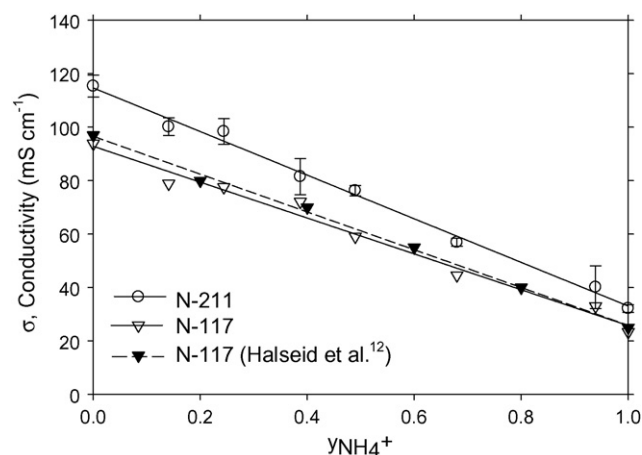


Fig. 3. Conductivity at room temperature in DI water for Nafion membrane (N-117 and N-211) containing various ammonium compositions ($Y_{\text{NH}_4^+} = 1$ for $877 \pm 7 \mu\text{mol NH}_4^+ \text{g}^{-1}$).

Fig. 3 also shows that the conductivity of N-211 was slightly higher than N-117 regardless of the ammonium content in the membrane. Although N-211 and N-117 have the same proton concentration, their conductivities are not comparable because of their differences. For example, it is known that preparation technique (N-211: dispersion-cast, N-117: extrusion-cast), thermal history, swelling ability, and operating conditions can have significant effects on the properties of a membrane [5,28–30].

3.2.2. Thickness of Nafion membranes as a function of NH₄⁺ concentration

In terms of dimensions, only the thickness changed with the fraction of ammonium ions in the membrane. There were no changes in the length and width of the membrane during the conductivity measurements because the membrane was pre-equilibrated in solution before it was placed into the cell assembly. The conductivities shown in Fig. 3 were corrected for the thickness change.

It was found that the thickness decreased (<10%) with an increase in ammonium composition (data not shown). This is probably due to the lone pair of electrons of nitrogen and of hydrogen in the N–H bond forming hydrogen bonds with adjacent water molecules (H–N···H–O–H, N–H···H–O–H) and causing the formation of a more compact structure.

3.3. Influence of ammonium ion concentration in Nafion on its gas phase behavior

3.3.1. Effect of ammonium composition in Nafion on conductivity in He (gas phase)

All the conductivities in the gas phase reported have been corrected for thickness change. Fig. 4(a and b) presents the ionic conductivities of N-211 with specific ammonium concentrations in contact with a He atmosphere with varying relative humidities at 80 °C. Fig. 4(a) shows the effect of ammonium ion concentration on the conductivity of N-211 at various humidities. It can be seen in Fig. 4(b) that in the fully NH₄⁺-form of Nafion, the ionic conductivity was reduced by 66% and 98% compared to the H⁺-form at 100%RH and 30%RH, respectively. This finding suggests that ammonia has a lesser effect on the conductivity at higher humidity. Therefore, operating a PEMFC at high humidity should help increase ammonia tolerance. In addition, it is clearly seen in Figs. 4(a and b) and 3 that ammonium ion content affects the conductivity of N-211 differently when it is measured in a gas phase at 80 °C vs. in an aqueous phase at room temperature. Ionic conductivity of N-211 decreased

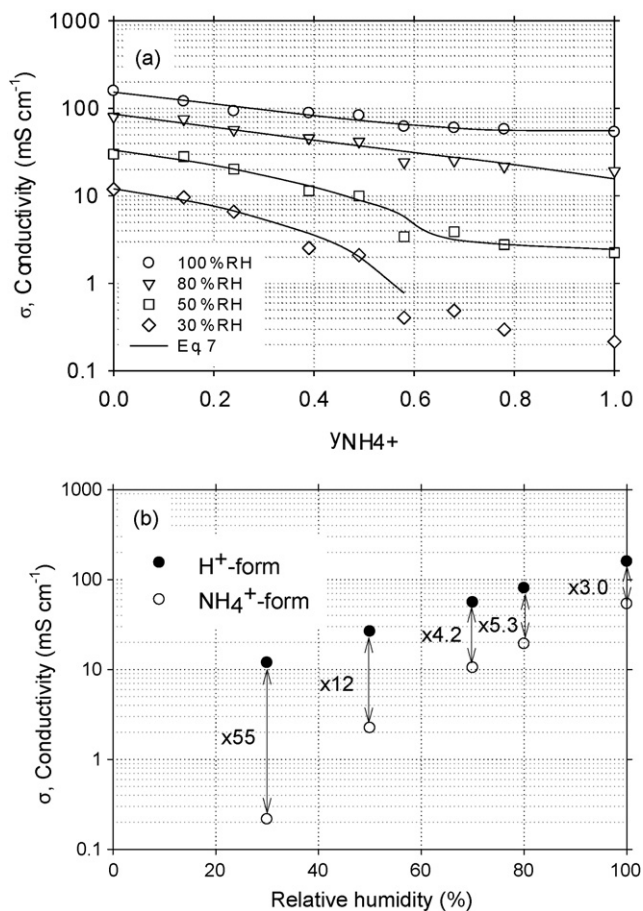


Fig. 4. Conductivity at 80 °C in a He gas phase for N-211 containing different ammonium ion fractions as a function of: (a) ammonium fraction; (b) conductivity of Nafion membranes in the H⁺-form and NH₄⁺-form (solid lines are based on the conductivity model of Pisani et al. [43,44]).

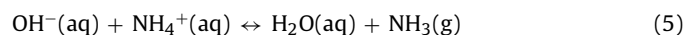
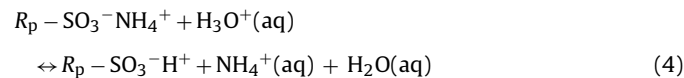
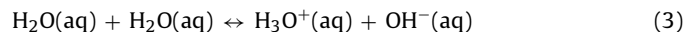
more dramatically with increasing ammonium content in the membrane when it was measured in the gas phase as opposed to in the aqueous phase. Thus, the simulation of fuel cell performance based on available conductivity results in liquid electrolytes would not provide as accurate a result as using gas-phase conductivity data.

The explanation for the difference in ammonium ion effect on the conductivity in gas vs. liquid phase is probably due to the lower water content and lack of complete swelling in the gas phase compared to in the aqueous solution. The water uptake of the membrane at a particular humidity and an elevated temperature (80 °C) was definitely less than that in DI water at room temperature because the condensation of water vapor on the hydrophobic fluorocarbon surface is less favorable than in an excess of liquid water [31–33]. It is well-known that the structure of water inside the ionic pore greatly impacts ionic conductivity, and the performance of a PEMFC is improved with an increase in the humidity [34–36]. Also, previous studies [13,37] have shown that proton tunneling between adjacent sulfonic groups plays a significant role in the conductivity in a high humidity environment. Zawodzinski et al. [38] and Hinatsu et al. [39] reported that the amounts of water uptake ($\lambda_{\text{H}_2\text{O}}$, defined as the number of water molecules per anion sulfonic site) of N-117 in DI water at 30 °C and in a gas phase with 100%RH at 80 °C were 21–22 and 9.5 mol H₂O/mol SO₃H, respectively. This lower water sorption in the gas phase in the pores and channels of the Nafion membrane causes shrinkage. Especially in a low humidity environment, where the water strongly binds with and solvates sulfonic sites, the average distance between adjacent sulfonic groups would decrease, resulting in a small increase in proton transport via the

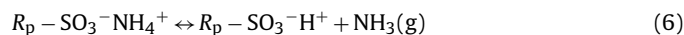
surface mechanism [33,40]. However, at this condition, each individual pore cluster would not be well-connected and the channels would be partially collapsed. At relative humidities less than 30%, Hashimoto et al. [36] observed only water bound to sulfonic groups. This contracted structure increased the strength of the hydrogen-bonded networks between ammonium ions and neighboring water molecules leading to a more rigid structure. Thus, this inflexible structure, non-continuous proton transport pathway, and lower water adsorption would be expected to dramatically lower proton migration. Previous studies have also found that the vehicle mechanism dominates proton conductance at high temperature (85 °C), while the Grotthuss mechanism governs at low to moderate temperature (25–55 °C) [41,42].

In the liquid electrolyte (DI water), where Nafion was in a fully swollen state, the distance between adjacent sulfonic groups on the wall of Nafion pores. On the other hand, in the presence of excess water, a continuous hydrophilic path for proton transport and a more liquid-filled structure were formed, where self-ionization of water and proton hopping via water networks can occur. The N-211 in the NH₄⁺-form of the membrane may ion-exchange with free protons in the inverted micelle and produce the H⁺-form and ammonium ions. However, given that the experimental results show that the ammonium ions confined in the ionic pore did not leach out of the membrane over 24 h in DI water at room temperature, this did not seem to occur to any significant extent. In the gas phase, where only small amounts of water vapor are present, the strong anion sulfonic sites stabilize the ammonium ion in the structure [11]. It appears that permanent ammonia poisoning occurs and the formation of the H⁺-form and free ammonia in the gas phase is very slow under normal fuel cell conditions in the absence of a current. Consequently, the effect of ammonia on conductivity is more severe in the gas phase than in an aqueous phase. The chemical reactions are as follows:

Aqueous phase



Vapor phase



where R_p is the polytetrafluoroethylene backbone of the Nafion polymer.

Fig. 4(a) shows the effect of ammonium ion concentration on the ionic conductivity at various humidities. The solid lines were obtained from the conductivity model proposed by Pisani et al. [43,44]. They found that the conductivity via the structure mechanism (Grotthuss mechanism, σ_s) for water sorption ($\lambda_{\text{H}_2\text{O}} < 9 \text{ mol H}_2\text{O/mol SO}_3^-$) was equal to zero. Their theoretical conductivity model (Eq. (7) [44]) involves the summation of three terms which are the conductances via the vehicular (σ_v), structure (σ_s), and drag (σ_{dra}) mechanisms: where, σ^{eff} is the effective conductivity which are the sum of conductivities from the three mechanisms (σ_v , σ_s , and σ_{dra}); K_v and K_s are the diffusion coefficients for the vehicular and structure mechanism; C_{H^+} and $C_{\text{H}_2\text{O}}$ are the proton and water concentrations, respectively; $\varepsilon_{\text{bulk}}$ is the fraction of bulk water; $\lambda_{\text{H}_2\text{O}}$ is the hydration level or the number of water molecules per sulfonic group; n_{sub} is the total number of water molecules in the Nafion pores less the number of bound water molecules per sulfonic group; $n_{\text{pol-}}$ and $n_{\text{pol+}}$ are the numbers of surface water molecules polarized by negative

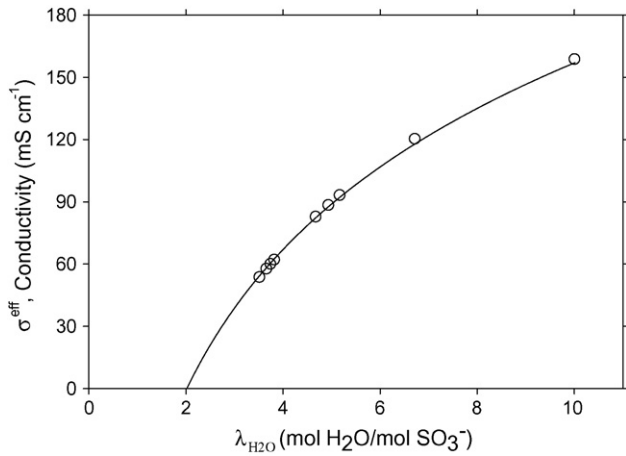


Fig. 5. Plot of effective conductivity at 80 °C (using Eq. (7)) with water sorption of N-211 containing various ammonium ion compositions.

charges and polarized water molecules by positive charges (H_3O^+) per sulfonate site, respectively; and ρ_{mem} is the density of the membrane; n_0^s is the maximum value of n_{pol^-} .

$$\begin{aligned} \sigma^{\text{eff}} = & \left(\frac{\lambda_{\text{H}_2\text{O}}}{(EW/\rho_{\text{mem}}) + \lambda_{\text{H}_2\text{O}}} - \varepsilon_0 \right)^t \\ & \times \left(\frac{K_V C_{\text{H}_2\text{O}}}{\lambda_{\text{H}_2\text{O}}} \left[1 - \frac{n_{\text{sub}}}{\lambda_{\text{H}_2\text{O}}} \right] + \frac{K_S C_{\text{H}_2\text{O}}}{\lambda_{\text{H}_2\text{O}}} e^{-[n_{\text{pol}^+}/(\lambda_{\text{H}_2\text{O}} - n_{\text{sub}})]} \right) \\ & \times \left[1 - \frac{n_{\text{sub}}}{\lambda_{\text{H}_2\text{O}}} - \left(\frac{\lambda_{\text{H}_2\text{O}}^4}{(n_0^s)^4} + 1 \right)^{-1/4} \right] \\ & + \frac{1}{32} C_{\text{H}_2\text{O}}^2 F^2 d_0^2 \sqrt{\frac{1}{(n_0^s)^4} + \frac{1}{(\pi \lambda_{\text{H}_2\text{O}})^4}} \end{aligned} \quad (7)$$

when $2 < \lambda_{\text{H}_2\text{O}} < 10$

The percolation threshold for the cluster-channel to form a continuous network is about 2 mol $\text{H}_2\text{O}/\text{mol SO}_3^-$ [45,46]. Below this value, the Nafion membrane performs like an insulator [43]. In this study, the range for predicted water sorption ($\lambda_{\text{H}_2\text{O}}$) obtained from Eq. (7) was between 2 and 10 mol $\text{H}_2\text{O}/\text{mol SO}_3^-$ under various humidities at 80 °C.

The experimental relationship between $\lambda_{\text{H}_2\text{O}}$ and σ^{eff} is presented in Fig. 5 along with a curve showing the fit of Eq. (7) to the data. The value of $\lambda_{\text{H}_2\text{O}}$ was calculated by fitting the param-

Table 2
Specific parameters for conductivity modeling.

Parameters	Value	Reference
K_V	0.040 S cm^{-1}	This work
K_V	0.251 S cm^{-1}	[43]
n_{sub}	2	[43,45,46]
n_{pot^+}	5	[43]
$C_{\text{H}_2\text{O}}$	$5.55 \times 10^4 \text{ mol m}^{-3}$	[43]
μ^a	$3.55 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}$	[38]
F	96,485 C mol^{-1}	Constant
d_0	$1.2 \times 10^{-9} \text{ m}$	[43]
t	1.75	[54,55]
EW	1100	Membrane
ρ_{mem}	2.05 g cm^{-3}	[56]
n_0^s	12	[43]
ε_0	0	[43]

^a Viscosity of water at 1 atm, 80 °C.

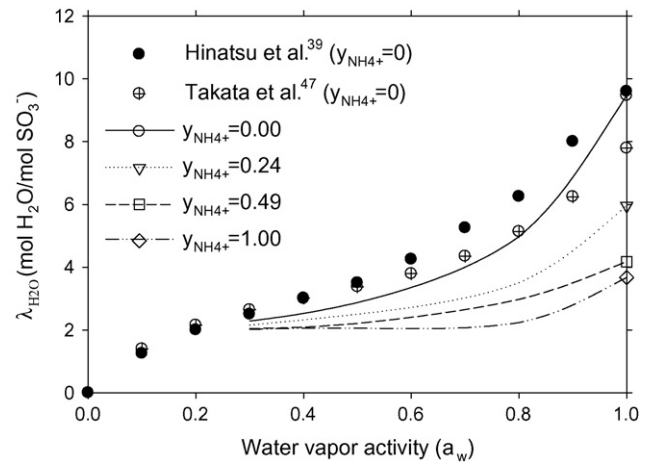


Fig. 6. Experimental and simulated and water sorption isotherms of N-211 with different ammonium ion concentrations at 80 °C (the hypothetical water uptake results were obtained from Pisani et al.'s model as shown in Eq. (7). Simulations are based on Eqs. (8)–(10)).

eters as indicated in Table 2 in Eq. (7). However, the value of K_V was adjusted to obtain the best fit with the experimental results and was calculated to be 0.043 S cm^{-1} , which is different from what has been reported by Pisani et al. [43] (0.081 S cm^{-1}). It is likely that the differences in pretreatment procedure, type of membrane, and measurement technique may slightly change the properties of the membrane. Moreover, the parameters used in Pisani et al.'s model were the values at 25 °C except for water viscosity (at 80 °C) and there was no parametric adjustment to account for the temperature difference.

Fig. 6 illustrates the plot of predicted water sorption ($\lambda_{\text{H}_2\text{O}}$) calculated from Eq. (7) against water vapor activity. Since the conductivity measurement of each pretreated membrane was performed at various humidities ranging from 30%RH to 100%RH, the wet weight of each membrane was determined at only 100%RH. Although the water sorption data of N-211 for various ammonium compositions at only 100%RH were used, the calculated water uptake results for humidities ranging from 30% to 100% for N-211 ($y_{\text{NH}_4^+} = 0$) obtained from Eq. (7) were similar to what has already been reported [39,47,48]. The water sorption ($\lambda_{\text{H}_2\text{O}}$) for different ammonium contents at various humidity ranges should be able to be reasonably predicted and it was determined using polynomials of water vapor activity (a_w) and ammonium fraction ($y_{\text{NH}_4^+}$) as also previously used in the literature [39,46]. The equations are shown as follows:

$$\begin{aligned} \lambda_{30-50\%RH} = & 1.405 + 2.933a_w + 1.202y_{\text{NH}_4^+} - 0.971y_{\text{NH}_4^+}^2 \\ & + 0.323y_{\text{NH}_4^+}^3 - 5.822a_w y_{\text{NH}_4^+} - 3.079a_w y_{\text{NH}_4^+}^2 \end{aligned} \quad (8)$$

$$\begin{aligned} \lambda_{80-100\%RH} = & -12.985 + 22.448a_w + 31.919y_{\text{NH}_4^+} - 15.155y_{\text{NH}_4^+}^2 \\ & - 7.288y_{\text{NH}_4^+}^3 - 51.081a_w y_{\text{NH}_4^+} + 35.812a_w y_{\text{NH}_4^+}^2 \end{aligned} \quad (9)$$

$$a_w = \frac{P_W}{P_W^S} = \frac{\%RH}{100} \quad (10)$$

where a_w is the water vapor activity; P_W and P_W^S are the water vapor pressure and saturated water vapor pressure at 80 °C; and $y_{\text{NH}_4^+}$ is the fraction of ammonium form in the Nafion membrane, respectively.

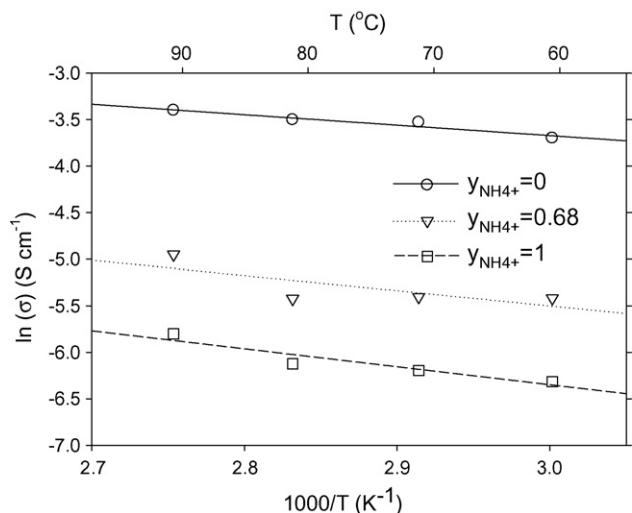


Fig. 7. Temperature dependence of conductivity of N-211 with different ammonium concentrations at 50%RH and 80 °C.

3.3.2. Thickness of Nafion membranes as a function of NH_4^+ concentration

It was found that the thickness change for membranes measured in a He gas phase (<5%) was smaller than that in the liquid electrolyte (<10%) (data not shown). This is because in the gas phase, the membrane was exposed to high temperature (80 °C) for a long period of time. Heat treatment may cause shrinkage of the inverted micelles and reorientation of the side chains in the Nafion membrane [31,39]. Conversely, the structure of the Nafion membrane equilibrated in liquid electrolyte is more free to expand and contract. This observation agrees well with Sone et al. [34] who studied the effect of thermal treatment at 80 and 105 °C on the proton conductivity of N-117. They reported that heat-treatments below the glass transition temperature caused the shrinkage of the membrane by connecting some of the micropores inside the Nafion membrane and closing others.

3.3.3. Effect of temperature on conductivity

Fig. 7 shows the temperature dependence of ionic conductivity of N-211 for different ammonium compositions in the range from 60 to 90 °C at 50%RH. The activation energy was calculated from the following Arrhenius relationship:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{RT}\right) \quad (11)$$

where E_a is the activation energy of ionic conductivity; σ_0 is the pre-exponential factor; R is the gas constant; T is the temperature (K), respectively.

As seen in Fig. 8, the activation energy for conductivity of the acid form of N-211 ($y_{\text{NH}_4^+} = 0$) decreases slightly with an increase in relative humidity from 9.8 kJ mol⁻¹ at 30%RH to 8.7 kJ mol⁻¹ at 100%RH. This experimental result is consistent with the activation energies for N-117, which has the same proton concentration but different thickness and casting technique than N-211, reported in the literature [1,25,26,46,49–53]. The activation energy of N-211 containing a known concentration of ammonium ions decreased to an even greater extent with an increase in relative humidity. In the presence of ammonium ions, particularly in a low humidity region, the energy barrier for ionic conductivity is high because the compact structure and strong hydrogen-bond network greatly decrease water mobility. As the concentration of water in the pores and channels increases, the individual ionic clusters are better able to connect to each other and form a continuous hydrated pathway [36,40]. Especially, at humidities more than 60%, Hashimoto

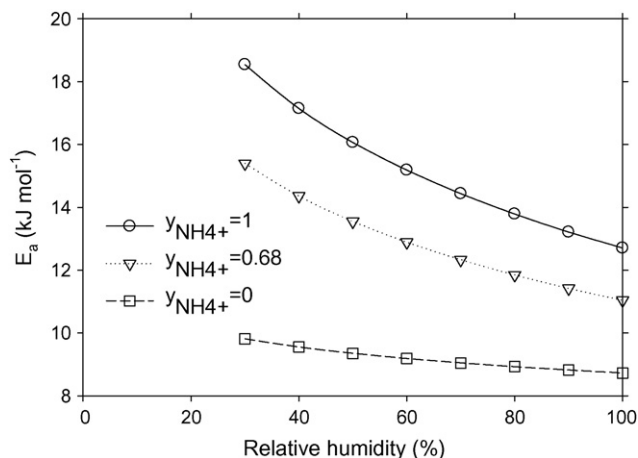


Fig. 8. The effect of %RH on the E_a for conductivity of N-211 at several NH_4^+ concentrations.

et al. [36] observed a large amount of free water which was essential for proton transport. This change in the state of water and the macroscopic structure of the membrane significantly favors bulk conductance, which results in a smaller activation energy.

Fig. 9 shows that the activation energy increased in a linear relationship with ammonium content in the membrane at a given humidity. This is possibly due to an increase in the amount of hydrogen bonds in the Nafion structure. Our findings are consistent with the available activation energy data for the effect of cations in the literature [12,25]. It is evident in Figs. 7–9 that the activation energy varies strongly with the humidity level and the amount of ammonium ion content in the membrane.

3.4. Influence of gas-phase ammonia impurity on the conductivity of a fresh Nafion membrane

3.4.1. Effect of ammonia concentration on the ionic conductivity

Fig. 10 shows the real time conductivity of N-211 at 50%RH and 80 °C in flowing He containing various ppm concentrations of ammonia with time-on-stream (TOS). The conductivity of N-211 decreased with TOS from 30 to 2.5 mS cm⁻¹ at steady-state, regardless of the partial pressure of ammonia. The ammonium compositions of the N-211 membranes at steady-state conductivity were also essentially identical ($895 \pm 26 \mu\text{mol g}^{-1}$) over the entire ammonia concentration range studied (5–30 ppm). After poisoning with ammonia, the flow of ammonia was stopped and only a flow

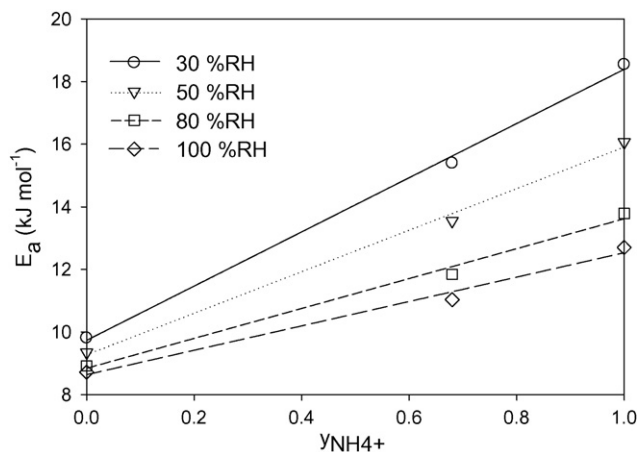


Fig. 9. The effect of ammonium ion composition on the E_a of conductivity of N-211 for different %RH.

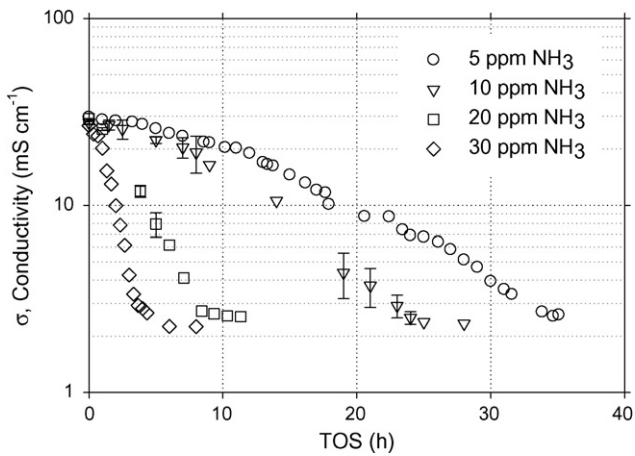


Fig. 10. Time-on-stream (TOS) ionic conductivity of N-211 at 50%RH and 80 °C in the presence of various NH_3 ppm concentrations.

of pure humidified He allowed for 1 day. The membrane conductivity did not recover during this time. This finding is in agreement with literature reports [8,11]. The kinetics of ammonia adsorption in this study, however, was a function of ammonia partial pressure, flow pattern in the chamber, and experimental configuration. The decrease in conductivity vs. TOS in other particular systems may be different from this result. However, the steady-state results should be identical.

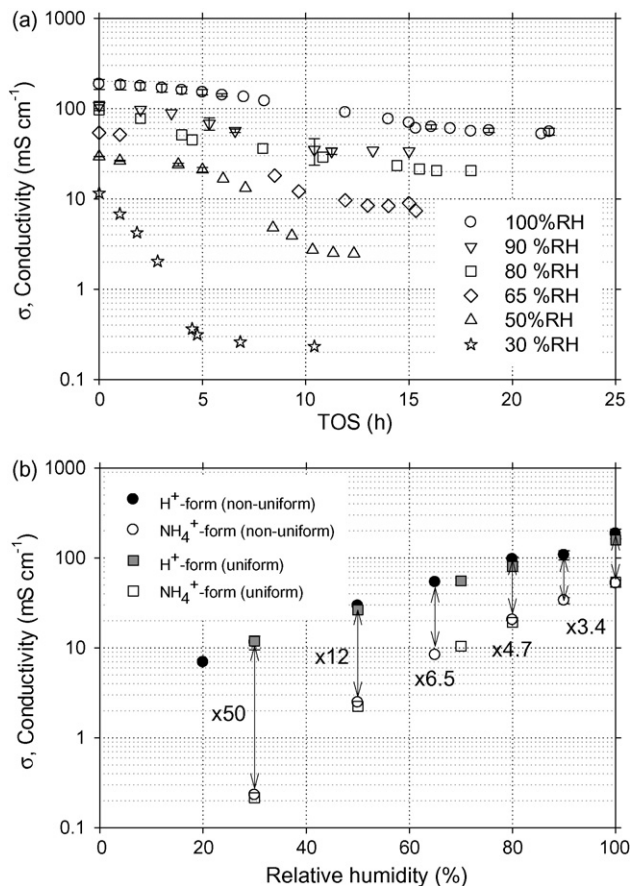


Fig. 11. Ionic conductivity of N-211 at different humidities and 80 °C in the presence of 20 ppm NH_3 as a function of: (a) time-on-stream (TOS); (b) relative humidity. Symbols: (○, ●) represents for the conductivities of non-uniform ammonia poisoned membranes; (□, ■) represents for the conductivities of pre-ammonium poisoned or uniform ammonium poisoned membranes.

3.4.2. Effect of humidity on the conductivity

Fig. 11(a and b) shows the impact of gas-phase ammonia on the real time conductivity at various humidities and 80 °C. The ammonia adsorption at high humidity was much slower than at low humidity and the steady-state conductivity was much greater, although the uptake of ammonia at final conductivity was still about the same (ca. $877 \pm 23 \mu\text{mol g}^{-1}$).

The circle symbols in Fig. 11(b) illustrate the conductivities of non-uniform ammonia poisoned membranes, where gas-phase ammonia was first adsorbed in the outer layer of a membrane before penetrating further. It can be seen that the conductivities of N-211 in the H^+ -form (at time equal 0) were higher than those in the NH_4^+ -form (at steady-state) by a factor of 50 and 3.4 at 30%RH and 100%RH, respectively. The results were similar to the results given by the rectangular symbols in Fig. 11(b) for uniform pre-poisoned membranes prepared with given ammonium concentrations, but the initial and steady-state conductivities were slightly higher than the conductivity values for $y_{\text{NH}_4^+} = 0$ and 1 as shown in Fig. 4(a) at every humidity level, respectively. The small differences could be due to the uptake of chloride into the membrane. Pisani et al. [43] found that the anions appeared to form bonds and polarize water molecules surrounding them. For example, chloride lowers the mobility in the membrane by forming hydrogen bonds with four water molecules causing a more rigid structure than pure bulk water. It is conclusive that the ionic conductivity of N-211 is strongly affected by the level of humidity and the ammonium content in the Nafion membrane, and an increase in the PEMFC's performance and impurity tolerance would be expected at high humidity, which is consistent with our other results.

4. Conclusions

Conductivity measurements of N-211 membranes exchanged with ammonium ions were performed both in an aqueous solution and in gas phase. In the liquid phase, the conductivity in DI water at room temperature in the NH_4^+ -form decreased linearly by a factor of 4 compared to that in the H^+ -form. In the gas phase, the conductivity also decreased with increasing ammonium content in the membrane and with decreasing relative humidity. However, the impact of relative humidity on the ionic conductivity of N-211 with a particular ammonium content was significant. The conductivity of N-211 in the NH_4^+ -form at 80 °C decreased by a factor of 55 or 3 compared to that in the H^+ -form at 30%RH or 100%RH, respectively. In addition, the presence of ammonium ions in the N-211 caused a significant increase in the activation energy of ionic conductivity. It was found that the activation energy increases linearly as the ammonium content increased at particular humidities and decreases as the relative humidity increases.

The conductivity of a fresh membrane exposed to gas-phase ammonia was also studied under conditions similar to that of operating fuel cells. The conductivity of N-211 declined with TOS and reached the same steady-state conductivity over the entire ammonia partial pressure range investigated (5–30 ppm NH_3) at the same relative humidity and temperature. The kinetics of ammonia adsorption onto the sulfonic groups at low humidity was much faster than at high humidity and the final steady-state conductivities of N-211 in the NH_4^+ -form were significantly increased with an increase in humidity. The experimental results suggest that operating PEMFCs at high relative humidity enhances their ammonia tolerance. The initial and final steady-state conductivities of a fresh N-211 were in good agreement with the study where the pre-exchanged N-211 with $y_{\text{NH}_4^+} = 0$ and 1 was used to measure the conductivity isotherm of pretreated N-211 with $y_{\text{NH}_4^+} = 0$ and 1 can be reasonably applied to predict the conductivity of N-211 in the H^+ -form and NH_4^+ -form under various conditions.

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Appendix A.

For the convenience to apply these experimental results in simulation work, we report here some equations which represent the data. There is no theoretical or physical interpretation implied by these equations.

- Thickness correction for the conductivity measurement in:

DI water at room temperature :

$$t_{DI} = -2.24y_{NH_4^+} + 35.31$$

He gas phase at 60–90 °C :

$$t_{He} = -2.37y_{NH_4^+} + 4.10a_W - 0.0947T + 35.80$$

- From Figs. 7–9, activation energy as a function of $y_{NH_4^+}$ and a_W :

$$E_a = 12.46 + 5.87y_{NH_4^+} - 5.20a_W$$

where t is the thickness of the Nafion membrane (μm); $y_{NH_4^+}$ is the ammonium composition in a Nafion membrane, a_W is the water activity; T is the operating temperature ($^{\circ}\text{C}$, $60 < T < 90$); and E_a is the activation of ionic conductivity (kJ mol^{-1}); respectively.

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