



An experimental approach to investigate the transport of ammonia as a fuel contaminant in proton exchange membrane fuel cells



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HIGHLIGHTS

- The data support a diffusion-solubility mechanism in a N_2/N_2 system at OCV.
- Ammonia did not move across the membrane when the feed to both electrodes was dry.
- With humidified feeds, the ammonia was transported from the anode to the cathode.
- Diffusion coefficients of NH_3 at 80 °C are obtained as $\sim 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at RH = 50 and 80%.

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ABSTRACT

Data are presented for the transport of NH_3 from the anode to the cathode for various inlet conditions in a N_2/N_2 laboratory-scale fuel cell at open circuit voltage (OCV). The data were obtained with a material balance technique, which uses an ion selective electrode (ISE) to determine the concentration of ammonium ions. The results show that ammonia did not move across the membrane when the feed to both electrodes was dry. However, with humidified feeds on either side, the ammonia was transported from the anode to the cathode. The data include changes in the relative humidity of the anode inlet and the flowrate on the cathode. The data support a diffusion-solubility mechanism in a N_2/N_2 system at OCV.

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1. Introduction

The quality of H_2 and the presence of contaminants like CO, NH_3 , H_2S is a major concern for international standards for proton exchange membrane fuel cells (PEMFCs) used for transportation [1]. Several research groups have published papers showing the effects of NH_3 on the performance of PEMFCs [2–10]. Uribe et al. [2], Soto et al. [3], and Halseid et al. [4] concluded that performance degradation resulted from the loss of conductivity in the anode catalyst layer and the membrane in which ammonium ions displaced proton sites. They also observed that NH_3 was not electrochemically active on the surface of a Pt catalyst by using cyclic voltammetry (CV) scans on both electrodes. They focused on the anode side because ammonia is a fuel contaminant. However,

Halseid et al. [4–7] postulated that ammonia could transfer to the cathode side and influence the oxygen reduction reaction (ORR) by oxidizing ammonia at higher potentials than 0.7 V. They postulated that the main reason for performance degradation in the fuel cell was likely due to the cathode, not the anode. Furthermore, they showed that N_2 and NO could be generated through an NH_3 oxidation reaction by using differential electrochemical mass spectrometry [7]. Hongsirikarn et al. [9,10] investigated the effect of NH_3 and NH_4^+ in the aqueous and vapor phases on the conductivity of a Nafion[®] membrane, and concluded that the operation of PEMFCs at relatively high humidity improves the ammonia tolerance. Zhang et al. [11] proposed NH_3 or NH_4^+ could reduce the active area of the catalyst by adsorbing onto Pt surface in contrast to the evidence in Refs. [2] and [3].

Prior to these PEMFC studies, Cussler and co-workers [12–14] suggested three possible mechanisms for NH_3 transport in Nafion[®]: diffusion-solubility, diffusion-reaction, and mobile carrier facilitation. In the diffusion-solubility mechanism, the ammonia

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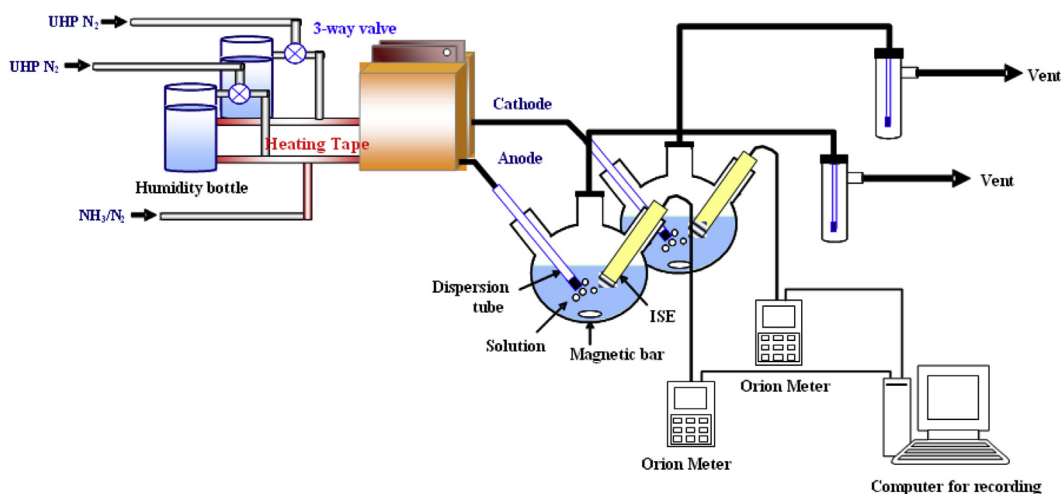


Fig. 1. Schematic of the material balance experimental apparatus.

flux varies linearly with the ammonia partial pressure difference. With the diffusion-reaction mechanism, ammonia reacts with the membrane to produce regions of high salt concentration that later dissolve preferentially so that the ammonia flux depends on the first power of ammonia partial pressure at high pressures and the square of this pressure at low pressures. In the mobile carrier mechanism, the membrane reacts selectively with the solute to form a complex, which diffuses across the membrane and releases the ammonia on the permeate side. Upon release, the complex-free carrier diffuses back to the high partial pressure side of the membrane so that a plot of ammonia flux against ammonia pressure shows a concave or downward curvature. In an attempt to provide a basis for understanding the ways in which ammonia affects the performance of the fuel cell, we present here experiments to understand the transport of ammonia in PEMFCs.

2. Experimental

2.1. In-situ single cell for NH_3 transport through MEA

The MEA used in this study was the GORE™ PRIMEA® Series 5621 and 5710. To reduce the experimental error for mass balance experiments, we chose the higher capacity PRIMEA® 5621 (≈ 2 times acid capacity), and the thinner (less acid capacity) PRIMEA® 5710 to minimize the time to reach equilibrium for the diffusion experiments. The MEA had a nominal thickness of 35 μm and a catalyst loading of 0.45 mg cm^{-2} Pt–Ru alloy catalyst on the anode and 0.6 mg cm^{-2} Pt/C on the cathode for the GORE™ PRIMEA® Series 5621, and a catalyst loading of 0.1 mg cm^{-2} Pt/C on the anode and 0.4 mg cm^{-2} Pt/C on the cathode for the GORE™ PRIMEA® Series 5710 (25 μm). The gas diffusion layer (CARBEL™ CL) and silicon coated glass fiber gaskets were used on the anode and cathode sides. Eight lubricated bolts were threaded into tapped holes on one of the end plates, and the cell was compressed with a torque of 50 in lbf/bolt. The experiments were performed using a model 890CL load made by Scribner Associates, Inc. Mass flow controllers (MKS Instruments) were calibrated for gas flow with a bubble flow meter at room temperature. The feed gas to the anode was humidified by using bottles supplied by Fuel Cell Technologies, Inc. These humidity bottles were calibrated with a VAISALA dew point meter to establish the set-point temperature for RH = 50%, 80% and 100% at a given flowrate. The tubing between the humidity bottles and the fuel cell was heated 10 °C higher than that of the humidity bottle to prevent water vapor condensation. A graphite

triple-path serpentine flow field was used on each side of the MEA. The temperature of the cell was fixed at 70 °C for the GORE™ PRIMEA® Series 5621, and at 80 °C for the GORE™ PRIMEA® Series 5710 experiment. The back pressures were held at 101 kPa on both sides.

An Ion Selective Electrode (ISE, Cole–Parmer® Combination Ion-Selective Electrodes, EW-27502-03) was employed for the transient monitoring of NH_4^+ concentrations. The concentration of NH_4^+ was converted from the potential measured by an Orion 4-stars meter (Thermo scientific Orion 4-star Plus pH/ISE meter, #1215000) with a 0.1 mV resolution. The electrode slope for conversion from potential to concentration was calibrated with 1, 10, and 100 ppm standard solutions (from Hach) before each experiment. The buffer solution for the Ionic Strength Adjustment (ISA) was prepared by mixing 0.25 M magnesium acetate and 0.5 M acetic acid. The ISA maintained the pH of solution at approximately 4.7 during the experiments so that all of the NH_3 was converted to NH_4^+ for detection with the ammonium ISE. Initially, 100 mL of 1 ppm NH_4Cl and 20 mL ISA were added to the flask and used for capturing NH_3 and NH_4^+ in the exit streams from the anode and cathode.

All experiments were performed at open circuit conditions (OCV); thus, our designation of anode and cathode refers to the sides of the MEA and the cell where the NH_3 entered (anode) and the NH_3 was transported (cathode). The MEA was exposed to 100 ppm NH_3 in UHP N_2 by dry injection on the anode with neat UHP N_2 on the cathode. The flowrate was 150 sccm^1 for both the anode and cathode sides. At the start of some experiments and after assembling the MEA in the cell, the cell was purged with heated N_2 for 20 h to dry the cell and MEA.

The material balance apparatus is illustrated in Fig. 1. The gases were bubbled into the flasks containing the ISA, and NH_3 was collected from each side of the cell during the experiment. Each flask had three necks which contained the dispersion tube from the outlet of the fuel cell, the ISE, and a connection to a knock-out for collecting water condensation from the flask and subsequent venting. A magnetic stir bar was used in the flask and a fan beside the flask was used to prevent an increase of solution temperature from the PEMFC gases. All experiments were carried out with a N_2/N_2 UHP system feed.

The experiments to study the transport of NH_3 were composed of four steps:

¹ sccm = standard $\text{cm}^3 \text{min}^{-1}$.

- 1) Neat, heated N_2 flowed to both electrodes for 20 min to confirm no potential changes of the ISE without NH_3 .
- 2) 100 ppm dry NH_3/N_2 was injected to the anode with dry N_2 being fed to the cathode until steady state was reached.
- 3) The anode gas was changed to a humid condition while keeping a dry cathode gas feed until steady state was attained. The humid condition on the anode was obtained by mixing humid N_2 gas with a dry NH_3/N_2 mixture gas.
- 4) When the amount of NH_3 exiting from both electrodes reached steady state in #3, humidified gas was fed to the cathode.

The solution in flasks was changed and the ISE was calibrated between each step. Experiments were performed at two levels of Relative Humidity (RH = 50% and 80%) and three concentrations of NH_3 in the N_2 (100, 200 and 300 ppm). The flux of NH_3 to the cathode was calculated from the moles of ammonia collected using a value of 23 cm^2 of active MEA area.

2.2. Ex-situ diffusivity measured by NH_3 mass uptake

Membrane strips ($9 \text{ cm} \times 4 \text{ cm}$ of N117 for each sample) were partially (only 2.5 cm length) soaked in 500 mL solutions of mixed ratios of 1 M ammonium chloride (NH_4Cl) and 1 M hydrochloric acid (HCL), and stored at different temperatures (i.e., 23 and 70°C). After being allowed to reach equilibrium between membrane strips and solutions, the membrane strip was cut into 9 pieces 1 cm in length, and the amount of ammonium ions in each membrane was measured by titration method. More details of the mass uptake methods for self-diffusivity are introduced in Ref. [15]. The diffusivity was then obtained by fitting the experimental curve (x-axis, distance of membrane and y-axis, normalized available capacity) using the least square method. To describe the diffusion of NH_4^+ in N117, the diffusion equation was solved using Fick's law, and the solution was used to fit the experimental curve below.

$$\frac{\partial C_{NH_3(m)}}{\partial t} = D \frac{\partial^2 C_{NH_3(m)}}{\partial z^2} \quad (1)$$

where, C = the equivalent ionic fraction of ammonium in the membrane (unity represents full saturation of membrane), t = time, z = length in the vertical direction, D = diffusion coefficient of $NH_3(m)$ in N117.

To solve this partial differential equation, one initial and two boundary conditions are required. These could be written:

$$C_{NH_3}|_{t=0} = 0 \quad (2)$$

$$C_{NH_3}|_{z=0} = 1, \quad C_{NH_3}|_{z=\infty} = 0 \quad (3)$$

These could also be written by defining a transformation variable $\eta = z/\sqrt{4Dt}$:

$$C_{NH_3}|_{\eta=0} = 1, \quad C_{NH_3}|_{\eta=\infty} = 0 \quad (4)$$

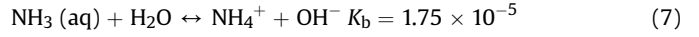
The boundary conditions are full exchange ($C_{NH_3}|_{z=0} = 1$) at the membrane–liquid interface and no exchange ($C_{NH_3}|_{z=\infty} = 0$) infinitely far from the interface. The solution to this diffusion equation is:

$$C_{NH_3} = 1 - \text{erf}(\eta) \quad (5)$$

3. Results and discussion

3.1. The detection of NH_3

Ammonia gas is extremely soluble in water, where it exists in equilibrium as a molecular form (NH_3) associated with water and the ionized form (NH_4^+) as shown in reaction (6) and (7).



Total ammonia can be obtained from the sum of ammonia (NH_3) and ammonium (NH_4^+) concentrations and the ratio of NH_3 and NH_4^+ in the solution strongly depends on the pH of solution. From reaction (7), a low pH causes NH_4^+ to dominate in the solution and hence to detect all NH_3 by the ammonium ISE, the buffer solution is required to keep the solution acidic. To test the capacity of buffer solution, 997 ppm NH_3 in N_2 was injected into the solution and the change of pH in the buffer solution was measured. The pH remained constant at 4.7 for a total injection of 2500 μmol NH_3 . The buffer solution was replaced in these experiments prior to obtaining this total molar dosage of NH_3 .

To check the collection efficiency a second collection flask was inserted prior to the knock-out so that the NH_3 – N_2 introduced to the first flask passed to the second flask. The amount of NH_4^+ was determined by the ISE continuously and the detection results are presented in Fig. 2 for an experiment where 100 ppm of NH_3 was introduced for 140 min without the fuel cell. A material balance for NH_3 gave agreement to within the accuracy of the ISE between the inlet and the outlet, and Fig. 2 shows that the NH_4^+ concentration in the first flask increased, while the concentration in the second flask did not change. Upon stopping the NH_3 injection, the concentration of solution was still increasing for 3 min while the residual NH_3 in the solution reacted. The accuracy of measurement was $\pm 2\%$ which is consistent with the accuracy suggested from an ISE manufacturer. Since no NH_3 was detected in the second flask for these initial experiments, the second flask was removed in subsequent experiments and those material balances agree to the same $\pm 2\%$ or less.

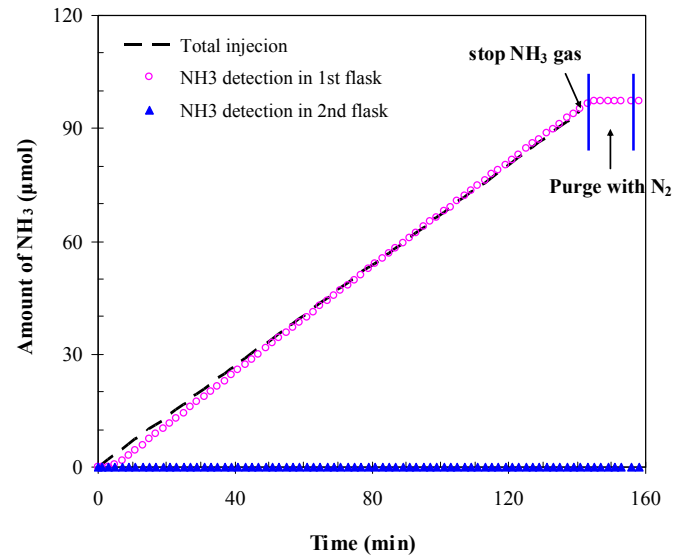


Fig. 2. Comparison of injection and collection of NH_3 with 100 ppm NH_3 in N_2 ; Flowrate = 150 sccm of mixture NH_3/N_2 tank and the UHP N_2 tank (Dry injection, Pre-heated to 90°C).

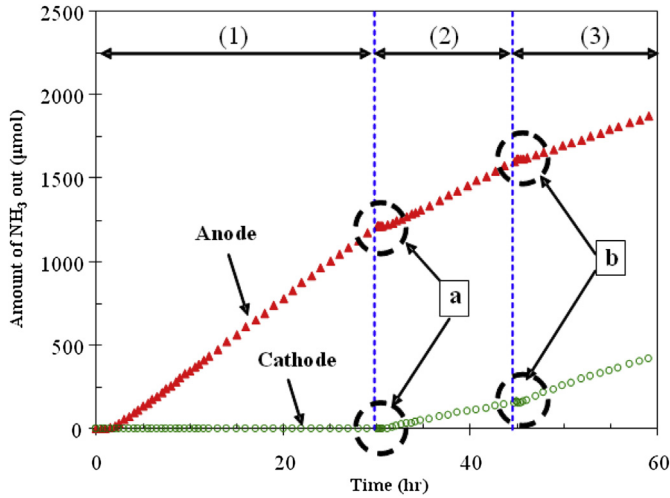


Fig. 3. Amount of NH_3 detected from both sides of the PEMFC at OCV showing the effect of anode humidity with 100 ppm NH_3/N_2 . A/C = Anode/Cathode. Regions: (1) A/C = dry/dry (2) A/C = humid/dry (3) A/C = humid/humid (Flowrate A/C = 150 sccm, $T_{\text{cell}} = 70^\circ\text{C}$, RH = 100%).

3.2. Factors affecting the transport of ammonia

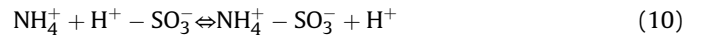
3.2.1. The effect of moisture

Since the performance of fuel cells depend on the humidity [16], experiments were performed to determine how the moisture affects the transport of ammonia. First, the cell and ISA solutions were allowed to stabilize with neat N_2 for 20 min before 100 ppm NH_3 was fed to the fuel cell. Fig. 3 shows the amount of ammonia exiting from both sides as the gas streams to the cell changed from dry conditions to humid conditions. Here, 100% RH corresponds to our humid condition. As shown in Fig. 3, when both electrodes were dry (region 1), all of the ammonia injected exited from the anode, indicating no measurable transfer to the cathode. A dead time about 2 hr (0–2 hr) was observed and this dead time could indicate accumulation of the NH_3 (~80 μmol) in the MEA by interacting with available acid sites of the PFSA membrane. This initial dead time changed on different RHs. Note that the available acid sites depend on water contents with water vapor activities in the PFSA membrane.

When the anode gas stream was humidified and the cathode feed remained dry (region 2), ammonia was detected exiting from the cathode after the other certain “dead time” shown by the circles labeled (a) in Fig. 3. The amount of NH_3 exiting at the anode decreased, and the difference in amount of NH_3 was found captured

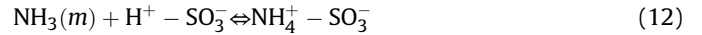
at the cathode side. The “dead time” (recall shown by the circles labeled (a) in Fig. 3) corresponds to approximately 1 hr, and during this time a significant amount of NH_3 (~40 μmol) as discussed below with Table 1 was retained in the cell with little exiting from either side. After retaining a measurable amount of NH_3 for about 1 hr, NH_3 exited simultaneously from both electrodes. When both streams were changed to a humidified condition (region 3), some additional NH_3 was retained (~40 μmol) again as indicated by the circles labeled (b).

These results can be explained by the presence of water in membrane enhancing the hydrophilic regions around the ionic clusters of sulfonic side chains in the PFSA membrane. These regions absorb relatively large amounts of water; thus, NH_3 in the gas phase could be dissolved in these regions. The equilibrium process governing NH_3 solubility in MEA can be described by the next reactions:



where the notation (m) indicates a form in the membrane without distinguishing the specific species and the $\text{H}^+ - \text{SO}_3^-$ indicates the proton form of the membrane.

It can be assumed that the reactions in the MEA are fast so that the net reaction is.



The reaction in equation (12) has the following equilibrium constant, K.

$$K = \frac{C_{\text{NH}_4^+}}{C_{\text{NH}_3(\text{m})} C_{\text{H}^+}} \quad (13)$$

The sites of H^+ binding with sulfonic groups in the ionomer of the electrode and membrane are converted to NH_4^+ form. Here $C_{\text{NH}_4^+}$, $C_{\text{NH}_3(\text{m})}$ and C_{H^+} are the concentrations of $\text{NH}_4^+ - \text{SO}_3^-$, $\text{NH}_3(\text{m})$, and $\text{H}^+ - \text{SO}_3^-$ respectively. The concentration of dissolved NH_3 in MEA is obtained by the following equation.

$$C_{\text{NH}_3(\text{m})} = H^* P_{\text{NH}_3} \quad (14)$$

where P_{NH_3} is partial pressure of ammonia gas in the flow channel; H^* is a partition coefficient between the adjacent gas and the membrane. Note that each concentration is within the MEA and total amount of sulfonic acid groups (C_t) are fixed by the original ion exchange capacity (IEC) of the membrane or MEA. Also note, however, that the fraction of exchangeable sites may depend on the degree of hydration of the MEA. Assuming a completely hydrated system, the total ammonia absorbed in the membrane is obtained by the sum of physically dissolved $\text{NH}_3(\text{m})$ and the exchanged $\text{NH}_4^+ - \text{SO}_3^-$.

$$C_t = C_{\text{H}^+} + C_{\text{NH}_4^+} \quad (15)$$

$$\begin{aligned} C_{\text{NH}_3(\text{t})} &= C_{\text{NH}_3(\text{m})} + C_{\text{NH}_4^+} = C_{\text{NH}_3(\text{m})} + K C_{\text{NH}_3(\text{m})} C_{\text{H}^+} \\ &= C_{\text{NH}_3(\text{m})} (1 + K C_{\text{H}^+}) \end{aligned} \quad (16)$$

In the perfluorosulfonic acid (PFSA) membrane the initial H^+

Table 1

Total injection and detection from both electrodes for different anode and cathode humidity with 100 ppm NH_3/N_2 (Flowrate A/C = 150 sccm, $T_{\text{cell}} = 70^\circ\text{C}$, RH = 100%). The loss column for the dry/dry case can be used to estimate the accuracy of the material balance detection technique as 0.4%. The loss columns for the Humid/Dry and Humid/Humid conditions indicate the amount of NH_3 accumulated in the MEA.

Condition			Time [h]	NH ₃ (μmol)			Loss
		In		Out			
Anode	Cathode	Anode		Anode	Cathode		
A	Dry	Dry	30	1204.5	1210.1	0.0	−5.6
	Humid	Dry	15	602.3	402.2	157	43.06
	Humid	Humid	14	565.5	264.2	260.2	41.1
B	Dry	Dry	30	1204.5	1204.1	0.0	0.4
	Humid	Dry	15	602.3	369.0	198.2	35.1
	Humid	Humid	14	565.5	263.0	252	50.5

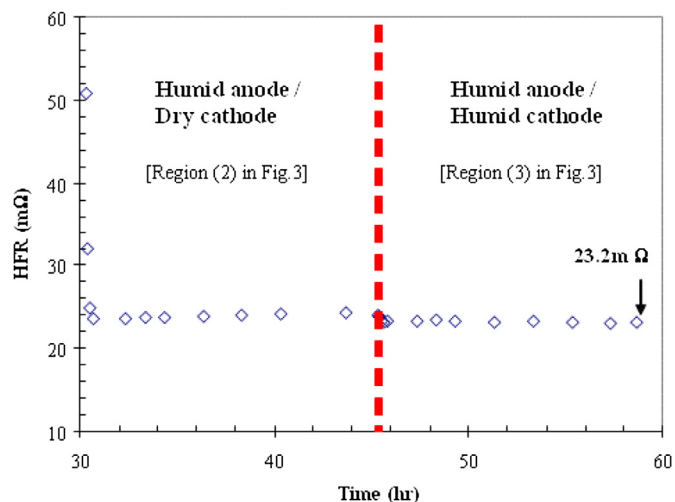


Fig. 4. Change of HFR with humidity changes to both electrodes: flowrate A/C = 150 sccm, $T_{\text{cell}} = 70^\circ\text{C}$, RH = 100%. The HFR was $0.096\ \Omega\ \text{cm}^2$ after conditioning.

concentration is large so the ion-exchange process in reaction (12) is shifted far towards the $\text{NH}_4^+ - \text{SO}_3^-$. Under the initial highly acidic conditions in the membrane, the ion exchange process appears irreversible and the amount of ammonium species in the MEA depends on the IEC and the cumulative dosage of NH_3 . Further, steady state for the injection/transport process is not attained until the IEC is filled by NH_4^+ . Thus, the decrease of C_{H^+} (or increase of $C_{\text{NH}_4^+}$) is time dependent and this is consistent with Hanson et al. [17] who showed that the mass accommodation coefficient of NH_3 was essentially unity over the wide range concentration of sulfuric acid.

The apparent loss of vapor phase NH_3 , shown by the initial dead-time, circles (a) and (b) in Fig. 3, corresponds to approximately $160\ \mu\text{mol}$ and is probably a result of absorption by formation of some NH_4^+ with the sulfonic groups in the MEA. Although the amount accumulated was significantly less than the measured $210\ \mu\text{mol}$ IEC of the $23\ \text{cm}^2$ GORE™ PRIMEA® 5621 in the liquid phase [18], we believe the difference results from an incomplete or partial hydration (sometimes known as a conditioning process) for the MEA.² This degree of hydration correlates with the high frequency resistance (HFR) of the MEA as shown in Fig. 4 where the membrane HFR is shown to change significantly as the stream was humidified from a dry condition [16]. The interaction with water was so fast [19], that the resistance dropped suddenly and reached a steady state value of about $0.60\ \Omega\ \text{cm}^2$ within 10 min for region 2 and $0.58\ \Omega\ \text{cm}^2$ for region 3. Note that HFR of 0.23, 0.13, and $0.096\ \Omega\ \text{cm}^2$ are obtained without contamination at RH = 20, 50, and 80% respectively, while HFR of 5.27, 1.12, and $0.61\ \Omega\ \text{cm}^2$ are obtained with NH_3 contamination at RH = 20, 50, and 80% respectively. The fast exchange process of ammonium ion with the membrane and aqueous phase has been verified by Halseid et al. [4]. Thus, the loss of NH_3 during the dead times of (a) and (b) should be attributed to the amount retained by ion exchange in the membrane and in the ionomer of both electrodes. Alternatively, some NH_3 may be retained somewhere in the flow channel of the graphite plate or the GDL, but this should be negligible due to the

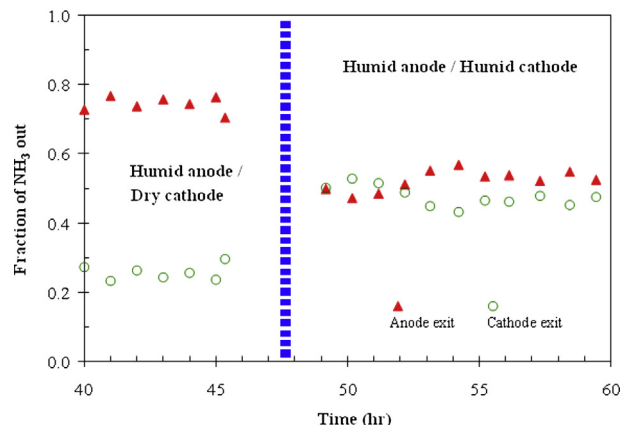


Fig. 5. The fraction of NH_3 exiting each electrode during conditions of Region (2) and Region (3) in Fig. 3.

very small amount of water in those locations compared to the potential accumulation in the MEA by ion-exchange.

Fig. 5 shows the fraction of NH_3 exiting the anode and the cathode with the same flowrate (150 sccm) on both sides. With a humid anode and a dry cathode, approximately 75% of the injected NH_3 left the anode and the remaining 25% exited the cathode. In the case of humidified feed streams (RH = 100% to both electrodes),

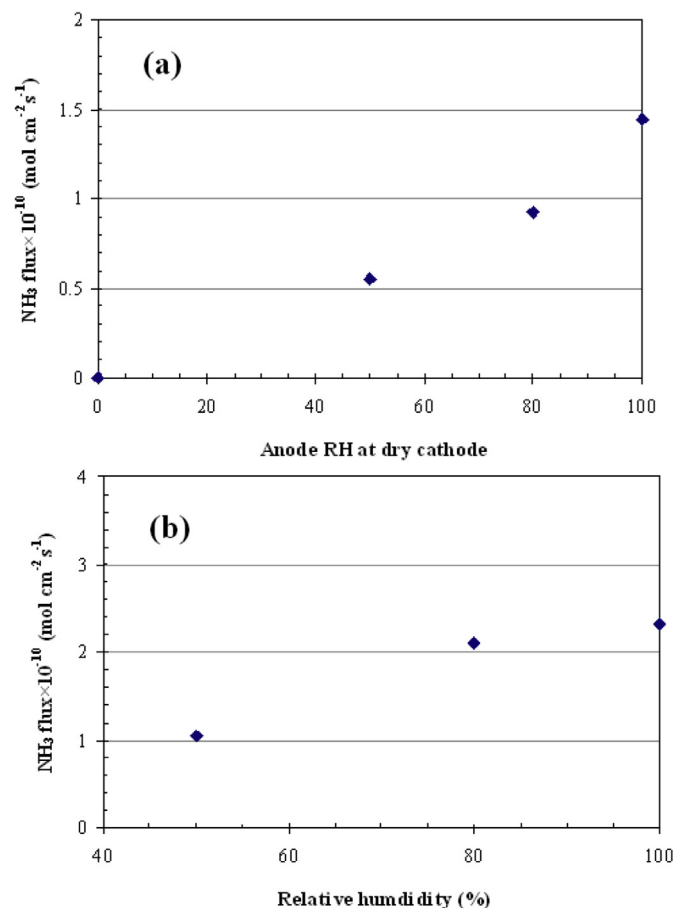


Fig. 6. Effect of relative humidity (RH) on the NH_3 flux across the MEA; (a) The effect of anode RH with a dry cathode; (b) The effect of RH on both electrodes; 100 ppm NH_3 , flowrate A/C = 150 sccm, $T_{\text{cell}} = 70^\circ\text{C}$.

² In subsequent material balance followed by ion-exchange experiments with only the membrane of this MEA we confirmed, for the dry/dry case, that ion-exchange accounts for the loss or accumulation of NH_3 to within the accuracy of the detection device and the material balance measurements.

approximately 50% of NH_3 exited from each electrode, indicating that more humidification resulted in more crossover of ammonia.

To check that the results in Figs. 3 and 5 were independent of the humidification side, a different set of experiments was performed. In these experiments, the humidification started from the cathode rather than the anode. In other words, we continued to feed the NH_3 on the anode side but after the dry/dry condition, the cathode feed stream was humidified, and then after the same duration of time as in region 2 of Fig. 3, both feed streams were changed to the humidified condition. Again, the NH_3 was transported to the cathode side only in existence of some humidity as shown by the material balance data in Table 1.

In Table 1, the amount lost was approximately the same (i.e., 43.1 μmol for case A and 35.1 μmol for case B) for the change from dry/dry to humid/dry or dry/humid. Also, note that the total loss of NH_3 from the dry/dry condition was equal for the two cases. The loss column for the dry/dry case can be used to estimate the accuracy of the material balance detection technique as 0.4%. The loss columns for the humid/dry and humid/humid conditions indicate the amount of NH_3 accumulated in the MEA during each process.

3.2.2. The effect of relative humidity

The RH of the anode stream was changed to 0, 50, 80 and 100% with a dry cathode. As found in previous experiments, all the feed NH_3 stayed on the anode and was collected in the anode flask when both electrodes were dry. As the RH of anode increased with a dry cathode feed, more NH_3 was transported to the cathode with a maximum flux of $1.48 \times 10^{-10} [\text{mol cm}^{-2} \text{s}^{-1}]$ as indicated in Fig. 6(a). The change of RH for both streams also led to the increase of NH_3 transport (Fig. 6(b)) with a maximum of $2.3 \times 10^{-10} [\text{mol cm}^{-2} \text{s}^{-1}]$ at 100% RH. The trends seen in Fig. 6 are consistent with the well known significant increase of water content with increasing water vapor activity [20]. Thus, even though the NH_3 gas in the N_2 with RH 50% is in the vapor phase, the transport of NH_3 through the MEA increases because of the increase of available acid sites due to water absorption in the MEA. If the ammonia (hydrophilic) diffuses mainly through the hydrophilic domains with SO_3^- group and not the hydrophobic domains with Teflon backbone, adding more moisture increases the swelling of hydrophilic domain and the solubility of ammonia in that domain. Water molecules in the interfacial regions produce the hydrated shell and branched network from ion-dipole interaction and lead to the easier transport of NH_3 [13,14,21].

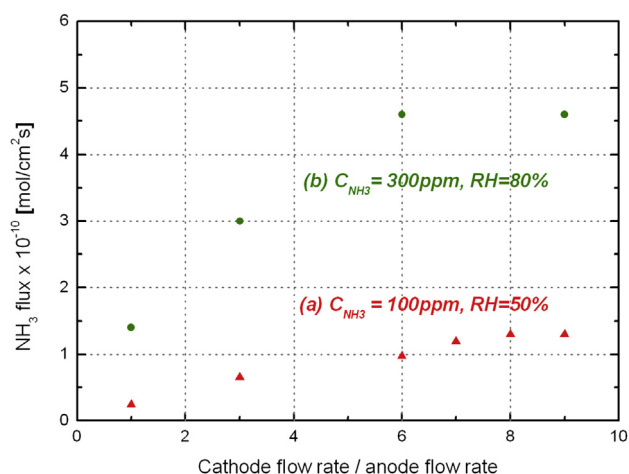


Fig. 7. The dependence of the NH_3 flux across the MEA on changes in the cathode flowrate at constant anode feed; 100 and 300 ppm NH_3 in N_2 , Anode flowrate = 150 sccm, Gore™ PRIMEA® 5710 at $T_{\text{cell}} = 80^\circ\text{C}$, RH = 50 and 80%.

3.2.3. The effect of cathode flowrate

Fig. 7 shows the effect of changing the cathode flowrate on the transport of NH_3 . Here, the anode flowrate was constant at 150 sccm and the cathode flowrate was increased to 1, 3, 6, 8, and 9 times greater than that of the anode flowrate. The high flowrate of the cathode resulted in an increased NH_3 mole flux to the cathode, probably due to a decrease in the partial pressure of NH_3 in the cathode, which increased the concentration gradient across the MEA. To calculate the diffusion coefficient of ammonia through MEA in the following section, we chose the ratio of cathode/anode flowrate as 8 (i.e., anode/cathode flowrate = 150/1200 sccm) so that we could assume the partial pressure of ammonia in the cathode to be zero. In other words, ammonia transport at OCV condition depends on the concentration gradient between anode and cathode.

3.3. Transport mechanism of ammonia in membrane

We believe the evidence above indicates that at OCV, when ammonia gas is introduced to the MEA, ammonia is dissolved in the MEA according to a partition coefficient, which is dependent on the RH. The dissolved NH_3 reacts with H^+ quickly, leading to the formation of NH_4^+ as the protonated species in the ionomer. This reaction proceeds until all of the available proton sites at the particular RH are fully exchanged with NH_3 . Then, the dissolved NH_3 crosses over to the other side through hydrophilic domains. At the boundary of the membrane and gas phase on the cathode, the transported NH_3 (m) converts again to NH_3 (g) according to the value of the partition coefficient and then comes out of the cell in the gas phase. Thus, NH_3 (g), NH_3 (m), and the NH_4^+ form are equilibrated throughout the MEA but a steady state is obtained which involves the diffusion of NH_3 through the MEA from the anode to the cathode, after all of the available proton sites have exchanged. The self diffusion of NH_4^+ ions can also be suggested, but the diffusion of molecules through the membrane after exchange is the limiting factor of NH_3 transport rather than NH_4^+ [22].

To describe these phenomena simply, we begin with a 1-D time dependent material balance which includes reaction of the NH_3 with the acid sites in the ionomer of the MEA (equation (12)) and disregards any gradients in the axial direction (i.e., down the channel length).³ Our description above indicates that there are two distinct sets of governing equations separated by the extent of ion-exchange. For the first set which occurs prior to complete ion-exchange, the time dependent accumulation of NH_3 in the MEA is governed by the very fast reaction rate (reaction 18). For the second set, all of the available H^+ sites have reacted and a steady state occurs so that the flux of NH_3 is constant and dependent on the concentration gradient in the gas streams (i.e. reaction 19).

$$\frac{dC_{\text{NH}_3(m)}}{dt} = -\frac{dN_{\text{NH}_3(m)}}{dz} + R \quad (17)$$

$$\frac{dC_{\text{H}^+}}{dt} = R \quad (18)$$

$$0 = \frac{dN_{\text{NH}_4^+}}{dz} \quad (19)$$

For the later set of equations, the flux of dissolved ammonia is obtained by integrating equation (19) with a constant diffusion

³ This approximation will be analyzed in subsequent publications and it should be recognized that it ignores the variation or the crossover flux due to accumulation of partial pressure of NH_3 in the cathode stream and it lumps the electrode layers with the membrane for the thickness calculations.

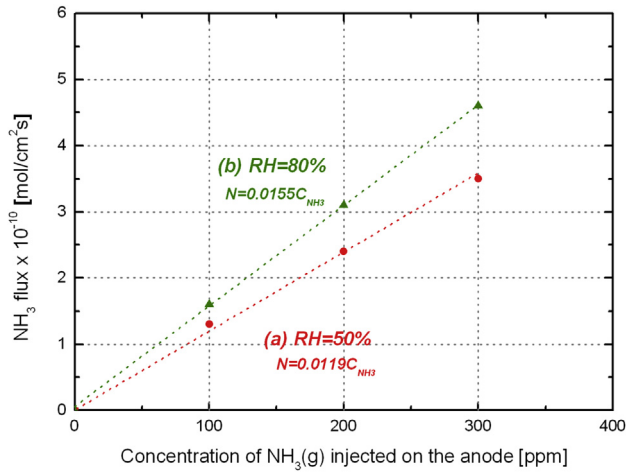


Fig. 8. Verification of diffusion-solubility mechanism at OCV; 100 and 300 ppm NH_3 in N_2 . Flowrate A/C = 150/1200 sccm, Gore™ PRIMEA® 5710 at $T_{\text{cell}} = 80^\circ\text{C}$; (a) RH = 50% (b) RH = 80%.

coefficient and a zero cathode concentration. Recall that the ammonia mole flux from anode to cathode reached steady state at the ratio of flowrate A/C = 1/8 as shown in Fig. 7.

$$N_{\text{NH}_3(m)} = D_{\text{NH}_3} \frac{C_{\text{NH}_3(m)} - 0}{l} = D_{\text{NH}_3} \frac{H^* P_{\text{NH}_3}}{l} \quad (20)$$

where $N_{\text{NH}_3(m)}$ is the flux of ammonia from the anode to the cathode; and l is total distance for ammonia diffusion which includes, for this simple approximation, the thickness of the catalyst layers and the membrane. In other words, NH_3 transport behaves like the diffusion-solubility mechanism and the data collected here as shown in Fig. 8, indicate that the flux had a linear relation with the ammonia concentration depending on the RH. Thus, the diffusion coefficient of ammonia through the MEA can be calculated as:

$$D_{\text{NH}_3} = \frac{N_{\text{NH}_3(m)} H^*}{P_{\text{NH}_3} l} \quad (21)$$

Note that a partition coefficient of ammonia in the MEA is similar to Henry's law constant ($\text{mol cm}^{-3} \text{atm}^{-1}$) in water, which for ammonia depends on temperature and is expressed by Ref. [23]:

$$H^* = 10^{-3} \exp\left(-7.44 + \frac{3214.4}{T}\right) \quad (22)$$

Thickness of MEA for Gore™ PRIMEA® Series 5710 was measured as 25 μm . For these assumptions, the diffusion coefficients of ammonia at the different RHs (i.e., RH = 50 and 80%) are listed in Table 2. Timashev et al. [22] reported the D_{NH_3} (i.e., $3.5 \times 10^{-7} \text{cm}^2 \text{s}^{-1}$) obtained in PFSA polymer hollow-fibers at 23°C (not report humidity). The reported diffusion coefficient is 1-order

Table 2
Diffusion coefficients of ammonia in PRIMEA® 5710 at $T_{\text{cell}} = 80^\circ\text{C}$ (obtained in Fig. 8).

RH [%]	C [ppm]	P_{NH_3} [atm]	$N_{\text{NH}_3} \times 10^{-10}$ [mol $\text{cm}^{-2} \text{s}^{-1}$]	D [$\text{cm}^2 \text{s}^{-1}$]
50	100	8.50E-05	1.3	$2.4 (\pm 0.15) \times 10^{-6}$
	200	1.70E-04	2.4	
	300	2.50E-04	3.5	
80	100	7.60E-05	1.6	$3.4 (\pm 0.10) \times 10^{-6}$
	200	1.50E-04	3.1	
	300	2.30E-04	4.6	

Table 3

Comparison of literature value with diffusion coefficients of ammonia through Gore™ PRIMEA® 5710 at $T_{\text{cell}} = 80^\circ\text{C}$ and in plane of N117 for different temperatures.

Methods	RH	D_{NH_3} [$\text{cm}^2 \text{s}^{-1}$]	
		23 $^\circ\text{C}$	80 $^\circ\text{C}$
In-situ single cell mass balance technique	50%	4.1×10^{-7}	2.4×10^{-6}
	80%	1.0×10^{-6}	3.4×10^{-6}
Ex-situ mass-uptake method in N117	100%	$2.6 \pm 0.3 \times 10^{-6}$	$1.1 \pm 0.2 \times 10^{-5}$
		$D_{\text{Na}^+} = 5.0 \pm 0.4 \times 10^{-6}$	$D_{\text{Na}^+} = 1.5 \pm 0.2 \times 10^{-5}$
Gas permeability measurement	N/A	3.5×10^{-7} [22]	
Pulsed-field gradient nuclear magnetic resonance spectroscopy	100%	$D_{\text{Na}^+} = 1.03 \times 10^{-6}$ [24]	
Nonstationary radiotracer diffusion method	100%	$D_{\text{Li}^+} = 1.4 \times 10^{-6}$ [25]	
Radiotracer permeation	100%	$D_{\text{Na}^+} = 1.7 \times 10^{-6}$ [26,27]	

lower than ours (i.e., $2.4 \times 10^{-6} \text{cm}^2 \text{s}^{-1}$ at RH = 50% and $3.4 \times 10^{-6} \text{cm}^2 \text{s}^{-1}$ at RH = 80%) and obtained at higher temperature (i.e., $T = 80^\circ\text{C}$). Also, D_{NH_3} measured by ex-situ mass-uptake method obtained in Nafion® membranes (N117) were $2.6 \times 10^{-6} \text{cm}^2 \text{s}^{-1}$ and $1.1 \times 10^{-5} \text{cm}^2 \text{s}^{-1}$ at 23°C and 70°C respectively (shown in Table 3), which are reasonable when compared with reported values of diffusivities for other cations in N117 (e.g., $1.03 \times 10^{-6} \text{cm}^2 \text{s}^{-1}$ for Na^+ , $1.4 \times 10^{-6} \text{cm}^2 \text{s}^{-1}$ for Li^+ at 23°C) [24,25]. These ex-situ values represent 100% of RH condition because they are obtained in liquid phase and not in gas phase, thereby, we can conclude that the diffusion of NH_3 in MEA or membrane from anode to cathode logarithmically increased as RHs increased. Also, the higher temperature (80°C) leads to 1-order faster diffusion of NH_3 than the diffusion at room temperature. These results also support the diffusion-solubility mechanism. That is, the important role of water for the diffusion of NH_3 through MEA or membrane can be considered as we described above. Note that the fuel cell electrode has an ionomer with Pt/C catalyst and the ionomer has a larger surface area, which may increase the dissolution of NH_3 , even if the ionomer has the same chemical structure as the PFSA membrane. However, both ex-situ and in-situ measurements are still comparable because the ionomer in the electrode has typically 1 order less (1/10) acid capacity than the membrane capacity.

4. Conclusions

The transport of NH_3 was studied at OCV in a N_2/N_2 system. NH_3 , added as the anode contaminant, was transported to the cathode stream, but only in existence of moisture in the MEA, which is independent of the feed from either the anode or the cathode. NH_3 appears to dissolve in the water in the MEA, exchange with the acid sites, and generate the NH_4^+ form of the ionomer while it moves through the membrane to the cathode. Ion exchange occurred prior to the observation of NH_3 transport and all available proton sites appear to be exchanged by NH_4^+ before the transport. NH_3 transport was observed at RHs less than 100%. The mole flux of NH_3 through MEA at steady state increased more at higher RH conditions. Also, the increase of cathode flowrate at the fixed anode flowrate induced an increase in the mole flux of ammonia through MEA or membrane to the cathode and reached steady state, which allowed us to obtain the diffusivity of NH_3 through MEA or membrane.

Finally, the results showed that the transport of ammonia is governed by the combined mechanisms of diffusion-solubility and diffusion-reaction in the N_2/N_2 system for RHs greater than 50%. Diffusion coefficients of NH_3 at $T_{cell} = 80^\circ C$ were also calculated at different values of RH ($2.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at RH = 50% and $3.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at RH = 80%). Also, diffusion coefficients obtained by *ex-situ* mass uptake in N117 reported to compare.

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