Effect of cations (Na$^+$, Ca^{2+}, Fe^{3+}) on the conductivity of a Nafion membrane

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ABSTRACT

It is known that trace amounts of cations have a detrimental effect on the liquid-phase conductivity of perfluorosulfonated membranes at room temperature. However, the conditions used were very different from typical fuel cell conditions. Recent research has shown the impact of conductivity measurement conditions on NH$_4^+$ contaminated membranes. In this study, the impact of nonproton-containing cations (M^{n+} = Na$^+$, Ca^{2+}, and Fe^{3+}) on Nafion membrane (N-211) conductivity was investigated both in deionized (DI) water at room temperature ($\sim$25 °C) and in the gas phase at 80 °C under conditions similar to in a PEMFC. These conductivities were compared with those of Nafion membranes contaminated with NH$_4^+$ ions. Under the same conditions, the conductivity of a metal cationic-contaminated membrane having the same proton composition (y_{H^+m}) was similar, but slightly lower than that of an NH$_4^+$-contaminated membrane. The conductivity in the purely H$^+$-form of N-211 was more than 12 times greater than the M^{n+}-form form at 25 °C in DI water. At 80 °C, the gas-phase conductivity was 6 times and 125 times greater at 100%RH and 30%RH, respectively. The quantitative results for conductivity and activation energy of contaminated membranes under typical fuel cell conditions are reported here for the first time.

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1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are promising candidates to replace engines in many 5–200 kW power generation applications. PEMFCs provide many advantages over internal combustion engines including high energy efficiency, quiet operation, and quick start up with zero emissions [1,2]. Poly(perfluorosulfonic acid) membranes, especially Nafion®, are attractive for the use in PEMFCs because of their high proton conductivity, high water uptake, and chemical, mechanical, and thermal stabilities [3]. However, during MEA preparation and/or fuel cell operation, the membrane can be contaminated by foreign cationic ions such as Na$^+$, Ca^{2+}, Fe^{3+} originating from the gas supply or coolant reagent, fabrication of the fuel cell, corrosion of materials, and other sources [4–6]. These metal cations are even worse than some impurities containing protons (e.g., ammonia) because they are not proton carriers and are harder to remove [7]. To date, information about the effect of these cations on membrane conductivity under typical fuel cell conditions has been very limited.

Previous studies have shown that even trace amounts of cations (i.e., Na$^+$, Li$^+$, Ca^{2+}, Cu^{2+}, Ni^{2+}, Fe^{3+}, etc.) significantly decrease the liquid-phase conductivity of membranes at room temperature [4–6,8–11]. Okada and co-workers investigated the kinetics, thermodynamics, and transport properties of alkali and transition metal cations. It was found that the replacement of protons by these foreign cations, except Cu^{2+}, considerably decreases conductivity in deionized (DI) water [4,5,8,10,12–15]. This is because these cationic ions have a higher affinity than protons for the sulfonic acid groups (–SO$_3^-$) in Nafion. Multivalent cations (divalent and trivalent cations) have been shown to more preferably exchange with the polymer network than monovalent cations [4,8,10]. The ionic mobilities of these cations (mono-, bi-, and trivalent cations) in a Nafion membrane are fairly low compared to the mobility of protons [6]. In addition, the presence of cationic impurities in the Nafion significantly impacts water movement and the state of water inside the hydrophilic region [9]. However, all of these above studies were carried out in a liquid electrolyte (i.e., DI water, organic solvents, etc.) at low to moderate temperature (25–60 °C). More recently, however, some experiments have been performed at conditions similar to normal fuel cell operations. It was found that water management and transport in a contaminated PEMFC are drastically affected, particularly at the cathode where the accumulation of contamination cations occurs over time [7,16]. This is because of the mass transfer (diffusion of protons and foreign cations) due to water formation at the cathode and the slow removal rate of these cations comparing to the rate of uptake [7,17]. This finding suggests that PEMFC performance is very vulnerable to cationic contamination [7]. Recently, results of a performance test

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of a NaCl-contaminated PEMFC by Mikkola et al. [1] suggested that performance degradation is primarily caused by ohmic losses (conductivity losses in the membrane). This conclusion is in agreement with Greszler et al. [17] who studied Li-contaminated membrane electrode assemblies (MEAs). They found that, at 100%RH, the loss of performance of an MEA with proton composition (y_{H^+m}) below 0.31 is attributable to proton starvation (depletion) at the cathode, where y_{H^+m} is the fraction of protons neutralizing anionic charges in the MEA. It is without doubt that the performance of a PEMFC is severely affected by proton displacement by these foreign cations. Accordingly, a quantitative study of the effect of cationic ions on membrane conductivity is highly important to better understand the impact of impurities in fuel cells.

To date, most conductivity studies on nonproton cationic impurities (i.e., ionic metal cations) and proton cations (i.e., NH_4^+) have been conducted in liquid electrolytes at low to moderate temperature (room temperature $-60\,^\circ$C). It is possible that these cationic contaminants affect liquid-phase conductivity differently from gas-phase conductivity at various humidities. These ionic cations may influence proton migration via different mechanisms than proton-containing cations like NH_4^+. This is because proton conductivity in the membrane involves the transport of the proton (H^+) itself and any proton carrier compounds (i.e., OH^-, H_2O, H_3O^+, NH_4^+, etc.) via the Grotthuss and vehicle mechanisms, respectively [18]. Nonproton-containing contaminants should have a more drastic effect on the conductivity than proton-containing impurities.

In this study, conductivity measurements of Nafion membranes in the binary-cationic form (H^+/M^{n+} form, $M^{n+} = Na^+$, Ca^{2+}, and Fe^{3+}) were performed both in the liquid phase and in the gas phase at typical fuel cell conditions (30–100%RH and $80\,^\circ$C). The ionic conductivities of N-211 containing these nonproton cations were compared to the conductivities of N-211 with proton-containing cations (e.g., NH_4^+). In addition, the activation energy for the ionic conductivity of cationic-contaminated membranes was investigated.

2. Experimental

2.1. Material and membrane preparation

Nafion® 211 membranes (DuPont Inc.) which are 25 μm thick and have an equivalent weight (EW) of 1100 [g (mol $-SO_3^-$)$^{-1}$] were cut into 5.5 cm × 1 cm rectangles and sequentially pretreated for 1 h at $90\,^\circ$C in solutions of: 3% H_2O_2 (Fisher Scientific), 0.5 M H_2SO_4 (Acros Organics), and then DI water. Afterwards, the membranes were rinsed several times with DI water to remove all the residual acid and kept in the dark in DI water at room temperature prior to use.

Reagent-grade 1.0 M HCl (Fisher Scientific), 99.99 wt.% NaCl (Fisher Scientific), 96 wt.% $CaCl_2$ (Acros Organics), and 98 wt.% $FeCl_3$ (Acros Organics) were used to prepare various cationic compositions of N-211s in the H^+/M^{n+}-form ($M^{n+} = Na^+$, Ca^{2+}, and Fe^{3+}). The H^+-form of N-211 was allowed to ion-exchange in aqueous solutions containing various metal cation compositions with a total concentration of Cl^- ions of 0.1 M for at least 10 days at room temperature under continuous shaking. The contaminant-containing solutions were changed periodically during exchange equilibration.

2.2. Membrane cationic content

The ionic contents of the H^+/M^{n+}-form ($M^{n+} = Na^+$, Ca^{2+}, and Fe^{3+}) of the exchange solution and of N-211 are defined as follows:

$$x_{H^+} = \frac{C_{H^+}}{C_{Cl^-}} \tag{1}$$

$$x_{M^{n+}} = \frac{nC_{M^{n+}}}{C_{Cl^-}} \tag{2}$$

$$y_{H^+m} = \frac{C_{H^+-SO_3^-}}{[C_{H^+SO_3^-}]_0} \tag{3}$$

$$y_{M^{n+}m} = \frac{nC_{M^{n+}-SO_3^-}}{[C_{H^+SO_3^-}]_0} \tag{4}$$

$$x_{H^+} + x_{M^{n+}} = 1 \tag{5}$$

$$y_{H^+m} + y_{M^{n+}m} = 1 \tag{6}$$

where C_{H^+}, $C_{M^{n+}}$, and C_{Cl^-} are the concentrations of H^+, metal cations M^{n+}, and anion Cl^- in the exchange solution (mol L^{-1}), respectively; x_{H^+} and $x_{M^{n+}}$ are the fractions of Cl^{-1} ions neutralized by protons and metal cations, respectively, in the exchange solution; $C_{H^+-SO_3^-}$ and $C_{M^{n+}-SO_3^-}$ are the concentrations of H^+ and metal cation M^{n+} adsorbed on sulfonic sites ($-SO_3^-$) in the Nafion membrane [mol (mol $-SO_3^-$)$^{-1}$], respectively; $[C_{H^+SO_3^-}]_0$ is the ion-exchange capacity of the fully protonated form of a Nafion membrane (N-211) [mol H^+ (mol $-SO_3^-$)$^{-1}$]; and y_{H^+m} and $y_{M^{n+}m}$ are the fractions of sulfonic sites replaced by protons and metal cations, respectively, in the membrane.

Following membrane preparation in solutions and conductivity measurement in DI water and a He atmosphere, the ionic composition for Na and Ca ions in the membranes was determined using standard analytical chemistry methods. First, ion-exchange was performed by immersing a membrane sample in 0.005 M NaOH aqueous solutions at room temperature under constant shaking for 2 days, allowing Na^+ to neutralize the remaining acid sites. The membrane was then removed and the excess NaOH solution was back-titrated with 0.005 M HCl using phenolphthalein indicator. The end point was determined at pH 7.

The compositional analysis of the Fe^{3+}-contaminated membrane in the dry state was determined by energy dispersive X-ray (EDX, SEM-Hitachi S-3400N) as used by Kelly et al. [6]. Although EDX is a surface technique, the elemental analysis of the bulk membrane in the H^+/Fe^{3+} form could be obtained assuming the composition of the bulk membrane was the same as that at the surface. This assumption should be valid because, in this study, the contaminated membranes were prepared by ion-exchange in aqueous solutions over a long period of time (at least 10 days). Thus, the distribution of Fe^{3+} in the membrane should be homogeneous. The cationic site fractions in the membrane were obtained from the atomic ratio as follows:

$$y_{Fe^{3+}m} = \frac{([Fe]/[F])y_{Fe^{3+}m}}{([Fe]/[F])y_{Fe^{3+}m} = 1} \tag{7}$$

where $y_{Fe^{3+}m}$ is Fe composition in the membrane; $([Fe]/[F])y_{Fe^{3+}m}$ is the signal intensity of the elements Fe and F in the dry Nafion membrane containing Fe^{3+} cations; and $([Fe]/[F])y_{Fe^{3+}m}$ is the intensity ratio of the membrane in the fully Fe^{3+}-form which was used as the reference. F, a major element in a Nafion membrane, was used as the internal standard instead of S (sulfur) because the S signal was too small and noisy.

Inductively coupled plasma mass spectrometry (ICP-MS) elemental analyses (Na, Ca, and Fe), carried out by Galbraith Laboratories in Knoxville, TN, were used to confirm the cationic composition of the membrane.

The Fe composition was calculated by Eq. (7) using the intensity ratio of the membrane in the fully Fe^{3+}-form ($x_{H^+} = 0.39$) as the reference because elemental analysis showed that the Fe exchange capacity of the Nafion membrane (N-211) exchanged in a standard solution with $x_{H^+} = 0.39$ was equivalent to the maximum proton exchange capacity [(896 μmol H^+) g^{-1}] of the membrane.

2.3. Conductivity

2.3.1. Conductivity measurement in DI water at room temperature ($\sim 25\,^{\circ}C$)

The ion-exchanged membrane was taken from the cation-chloride solution and rinsed several times with DI water before it was sandwiched between two pieces of Pt foil and two blocks of polyetheretherketone (PEEK). After that, the conductivity cell was filled with DI water and conductivity in the liquid phase at room temperature ($\sim 25\,^{\circ}C$) was measured. The impedance of N-211 in the lateral direction was determined in a two-probe cell using an impedance analyzer (Gamry Potentiostat Reference 600) with 25 mV ac amplitude in a frequency range of 10^6 to 100 Hz. The membrane thickness was measured by a micrometer immediately after the conductivity measurement and an average of the thickness at five different positions determined. The conductivity was calculated from the following expression:

$$\sigma = \frac{l}{RA} \qquad (8)$$

where σ is the conductivity (in S (Siemens) cm^{-1}); l is the distance between two Pt electrodes (cm); R is the membrane resistance (Ω); A is the cross-sectional area of the membrane (cm^2) given by t cm $\times$ w cm; and t and w are the average thickness and average width of the membrane, respectively.

2.3.2. Conductivity measurement in the gas phase at $80\,^{\circ}C$

Details about the experimental procedure have been described elsewhere [19] but are briefly described here. The membrane sample was equilibrated in ca. 30% relative humidity (RH) at 80 °C in a He atmosphere for 8 h. The membrane was then put in a custom-made cell, placed in the gas phase chamber and allowed to equilibrate. The humidity was ramped from 30%RH to 100%RH to measure conductivity at various %RH with constant conductivity for 1 h being maintained before the %RH was changed. The procedure was the same as that in the previous section except a 50 mV ac modulation was applied instead of 25 mV because of high membrane resistance at low humidity conditions and low proton composition (y_{H^+m}).

3. Results and discussion

3.1. Membrane ionic composition at equilibrium

To ensure that the membranes reached equilibrium, the cation exchange was performed over at least a 10-day period. Equilibrium was assumed when there was no conductivity difference in DI water for the membrane over a 2-day interval of exchange. Fig. 1(a) presents the relationship of membrane composition, expressed as a fraction of sulfonic sites occupied by protons (y_{H^+m}), and the composition of protons in the aqueous solution (containing 0.1 M Cl$^-$) after exchange (x_{H^+}). Fig. 1(b) shows the equilibrium of protons and nonproton cations in solution with a Nafion membrane. The ionic compositions (Na$^+$, Ca^{2+}, and Fe^{3+}) of exchanged membranes determined by titration and EDX are in good agreement with elemental analysis. It can be seen that the neutralizing protons in a Nafion membrane are significantly displaced by these cations, especially for the multivalent cations, at even low concentrations in the liquid phase (x_{H^+} high). For example, in Fig. 1(b), the Na$^+$ concentrations in exchange solutions of 2–23 ppm (mass basis) ($x_{H^+} = 0.999 - 0.9999$) neutralize ca. 0.6–2.1% of sulfonic sites, respectively. Similarly, the cationic concentrations in solutions of 4–20 ppm Ca^{2+} ($x_{H^+} = 0.999 - 0.9998$) and 1.4–5.6 ppm Fe^{3+} ($x_{H^+} = 0.9997 - 0.9999$) (mass basis) result in an exchange with ca. 4.2–16.2% and 5.2–16.6% of sulfonic sites, respectively.
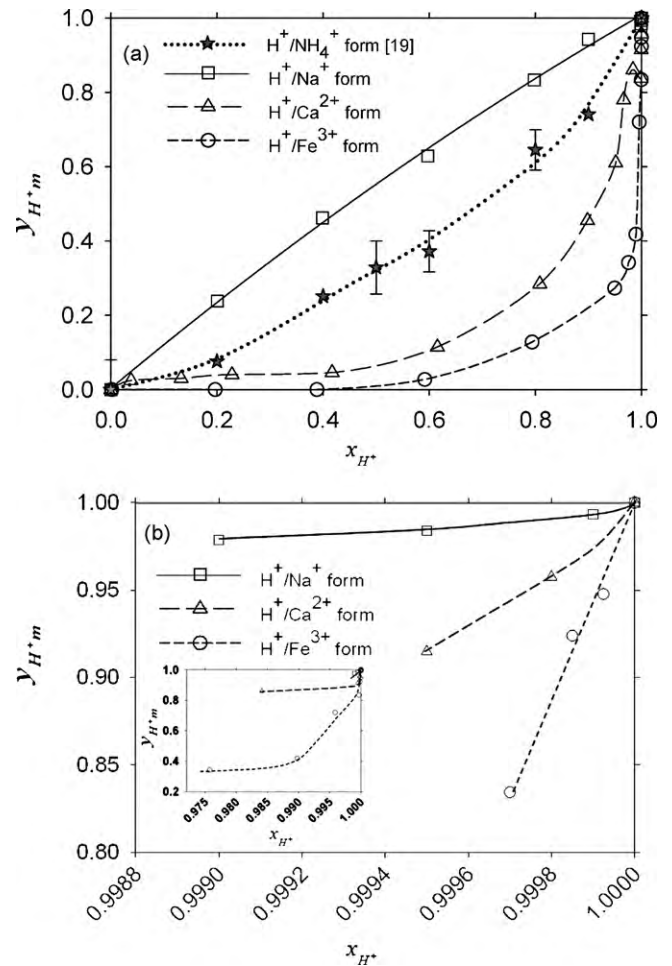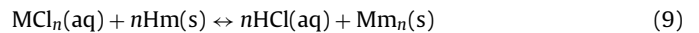

Fig. 1. Equilibrium of protons between an aqueous phase (x_{H^+}) at constant Cl$^-$ content in solution (0.1 M), and a N-211 membrane (y_{H^+m}) at room temperature: (a) for $0 \le y_{H^+m} \le 1$ and (b) for high y_{H^+m} region (very low cationic compositions).

Table 1 lists the equilibrium constants for the exchange reaction of these ionic cations (M^{n+} = Na$^+$, Ca^{2+}, and Fe^{3+}) and NH$_4^+$ ions with proton sites in a N-211 membrane. The equilibrium exchange constant, K_{eq}, for binary cation membranes is as follows:

$$MCl_n(aq) + nHm(s) \leftrightarrow nHCl(aq) + Mm_n(s) \qquad (9)$$

$$K_{eq} = \frac{(a_{H^+,\ aq})^n (a_{M^{n+}m})}{(a_{M^{n+},\ aq})(a_{H^+m})^n} = \frac{(\gamma_{H^+,\ aq} x_{H^+})^n (\gamma_{M^{n+}m} y_{M^{n+}m})}{(\gamma_{M^{n+},\ aq} x_{M^{n+}})(\gamma_{H^+m} y_{H^+m})^n}$$

$$= \frac{(\gamma_{H^+,\ aq} x_{H^+})^n (y_{M^{n+}m})}{(\gamma_{M^{n+},\ aq} x_{M^{n+}})(y_{H^+m})^n} \qquad (10)$$

where $a_{M^{n+},\ aq}$ and $a_{H^+,\ aq}$ are the activities in the liquid phase of the cations M^{n+} and H$^+$, respectively; $a_{M^{n+}m}$ and a_{H^+m} are the activities in the membrane phase of the cations M^{n+} and H$^+$, respec-

Table 1
The equilibrium constant for the binary-cationic form of a Nafion membrane in a liquid solution at room temperature ($\sim 25\,^{\circ}C$).

N-211	K_{eq}[a]	Reference
H$^+$/NH$_4^+$	2.55 ± 0.56	[19]
H$^+$/Na$^+$	0.84 ± 0.08	This work
H$^+$/Ca^{2+}	90.6 ± 38.6	This work
H$^+$/Fe^{3+}	4848 ± 1190	This work

[a] K_{eq} is the average value obtained from Eq. (10) using all the data in Fig. 1 for a given cation except that for the two extreme concentrations ($y_{H^+m} \approx 0$ and 1).

tively; $\gamma_{M^{n+}, \, aq}$ and $\gamma_{H^+, \, aq}$ are the activity coefficients in the liquid phase of the cations M^{n+} and H^+ obtained from previous studies [20–24], respectively; $\gamma_{M^{n+}m}$ and γ_{H^+m} are the activity coefficients in the membrane phase of the cations M^{n+} and H^+ assumed to be 1, respectively, since in the solid phase; $x_{M^{n+}}$ and x_{H^+} are the fractions of the Cl^- anions neutralized by the cations M^{n+} and H^+ in liquid exchange solutions, respectively; and y_{H^+m} and $y_{M^{n+}m}$ are the fractions of $-SO_3^-$ sites neutralized by protons and metal cations in the contaminated membranes, respectively.

It can be seen in Table 1 that K_{eq} for N-211 with bi- and trivalent cations (H^+/Ca^{2+} and H^+/Fe^{3+}) is much larger than those for N-211 with monovalent cations (H^+/Na^+- and H^+/NH_4^+-forms). Previously, Okada and co-workers [4,5,8] studied equilibrium and transport properties (i.e., water transference coefficient, water content, equilibrium constant, etc.) of various cation-exchanged Nafion membranes (N-117). In their study, the exchange reaction between cationic ions in the solution and membrane was expressed in the reverse reaction of Eq. (9). Therefore, the reciprocal of K_{eq} constants in that study was used to compare with the values of K_{eq} in this study and found to correspond well (on the same order of magnitude). The results indicate that the higher order valence cations interact with the polymer network more strongly and preferably exchange with the sulfonic sites than the lower valence cations. These interactions could affect the ion–water interaction, water transport, and eventually the ionic conductivity of the contaminated membrane.

3.2. Effect of cations on the conductivity of N-211 in DI water at room temperature (25 °C)

Although the objective of this work was to study the effect of cations on Nafion conductivity at practical fuel cell operations, we report the equilibrium between protons in solutions (x_{H^+}) and membranes (y_{H^+m}) and the conductivity in DI water. These conditions are very far removed from normal fuel cell operations. However, these measurements were done to justify the experimental set-up in this study by comparing our results with those available in the literature and to validate the conductivity results at other conditions.

In Fig. 2(a) and (b), the conductivities in DI water at room temperature of N-211 in the H^+/M^{n+} form ($M^{n+} = Na^+, Ca^{2+}$, and Fe^{3+}) and H^+/NH_4^+ form are shown. It was found that at very low cation compositions in the membrane ($y_{H^+m} > 0.95$), the effect of cations on the liquid-phase conductivity is minimal and is proportional to y_{H^+m}. The conductivities decreased in a similar linear fashion with the fraction of sites occupied by protons (y_{H^+m}) and were essentially identical regardless of the nature of the second metal cation with H^+ in the membrane. Only NH_4^+/H^+ had a much higher conductivity for the same value of y_{H^+m}. However, its decrease in conductivity with decreasing y_{H^+m} was parallel to that for the metal cations. It is known that ionic conductivity depends strongly on the state of water and cation–water interactions inside the Nafion polymer [9]. Therefore, the explanation for the similarity in conductivity of the metal cation-contaminated membranes could be due to the similarity in cation properties (see Table 2) resulting in a similarity
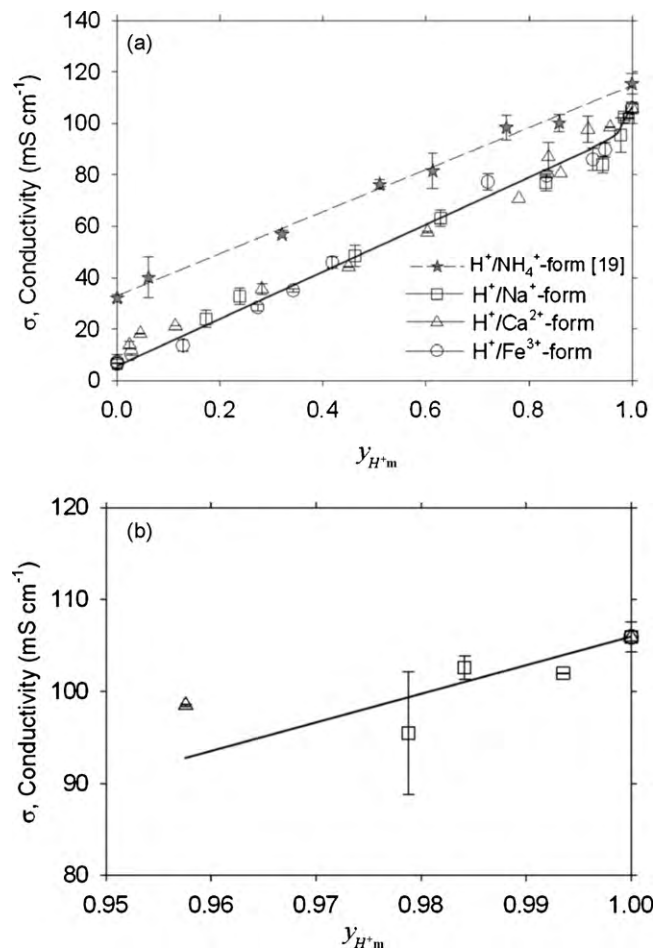

Fig. 2. Conductivity in DI at room temperature for N-211 membranes containing various cation compositions: (a) for $0 \leq y_{H^+m} \leq 1$ and (b) for high y_{H^+m} region (very low cationic compositions).

in orientations of water molecules in the vicinity of the cations and in the metal cation–water interactions, which is in agreement with the results from previous studies [25–29]. It has been found that the cation–water clusters, $[M-(H_2O)_m]^{n+}$, of these metal cations are similar $\{Na^+(H_2O)_6, Ca^{2+}(H_2O)_6$, and $Fe^{2+}(H_2O)_8\}$ [25–29]. On the other hand, as mentioned above, the conductivity of the NH_4^+-poisoned membrane was significantly higher than that of the metal cation-contaminated membranes having the same proton composition (y_{H^+m}). The experimental results indicate that NH_4^+m is more conductive than $M^{n+}m$. The difference in the intermolecular force between water molecules and the cations in the Nafion structure can explain this behavior. The hydrogen-bond network between water molecules and NH_4^+ ions is not the same as the dipole–dipole force between water molecules and metal cations.

Table 3 summarizes the conductivities in DI water at room temperature for the fully cationic exchanged Nafion membranes

Table 2
Literature values of the physical properties of mono- and multivalent cations.

Cation	Average ion-water distances (Å) [53]	Ionic radii in aqueous solutions (Å)	$t_{H_2O}^a$	$\lambda_{H_2O}^b$ [54]
H^+	–	0.40 [55]	2.6 [54,56,57]	20.1
NH_4^+	–	1.52 [58]	7.0 [54]	14.0
Na^+	2.39	1.74 [53]	9.6 [54]	16.5
Ca^{2+}	2.41	1.62 [53]	12.1 [54]	17.2
Fe^{3+}	2.03	0.98 [53]	–	–

[a] t_{H_2O} is the water transference coefficient. It expresses the number of water molecules transported per Faraday through the polymer.
[b] λ_{H_2O} is the water content of a Nafion membrane (N-117) in the fully hydrated state [mol H_2O (mol $-SO_3^-$)$^{-1}$].

Table 3
Conductivities measured in DI water at room temperature of various (fully) cationic forms of the N-211 Nafion membrane.

N-211	Conductivity (mS cm^{-1})	Reference
H$^+$-form	105.9 ± 1.7	This work
NH$_4^+$-form	32.1 ± 1.5	[19]
Na$^+$-form	26.5 ± 1.5	This work
Ca^{2+}-form	14.0 ± 1.4	This work
Fe^{3+}-form	5.8 ± 0.2	This work

(N-211, 25 μm). Our experimental conductivities agree well with those of Nafion 117 (N-117, 183 μm) reported by Doyle et al. [11] (Na$^+$, Ca^{2+}, and Fe^{3+}) and Halseid et al. [30] (NH$_4^+$). However, our results were only partially consistent with those reported by Okada and co-workers (Na$^+$, Ca^{2+}, and Fe^{3+}) who studied the conductivity of cationic-contaminated Nafion 117 (N-117, 185 μm) [4,5,8,10]. In this study, the conductivities as a function of y_{H^+m} had the same trend with those reported by Okada and co-workers, but the absolute values were lower. Nevertheless, the conductivity of the H$^+$-form of Nafion 117 measured by Okada et al. [5,10] (150–200 mS cm^{-1}) was much higher than our experimental conductivity and that reported by almost every other study (90–100 mS cm^{-1}) [11,19,30–37].

3.3. Effect of cations on the conductivity of N-211 in the gas phase at 80 °C

In Fig. 3(a)–(c), the gas-phase conductivities of contaminated N-211 membranes are plotted against the membrane proton composition (y_{H^+m}). Eqs. (11) and (12) are empirical equations that best fit the experimental results and have no physical or theoretical interpretation. As expected, the effect of cations on the gas-phase conductivity of a membrane with trace amounts of cations ($y_{H^+m} > 0.98$) is fairly minimal, which corresponds very well with the conductivity results in DI water. The conductivity, however, decreases exponentially with y_{H^+m}. Under the same conditions and y_{H^+m}, the conductivities of N-211 membranes contaminated with monovalent cations (i.e., Na$^+$, NH$_4^+$) were similar, but were just slightly higher than those with higher valent cations (i.e., Ca^{2+}, Fe^{3+}). Thus, not including the NH$_4^+$ membrane, the conductivities of the H$^+$/M^{n+}-forms (M^{n+} = Na$^+$, Ca^{2+}, and Fe^{3+}) of the membrane at 80 °C having the same y_{H^+m} were practically identical, in good agreement (all nearly identical, not in terms of absolute conductivities) with what was found in DI water as shown in Fig. 2(a) and (b) for these contaminated membranes. In practical fuel cell operations, the effect of ammonium ions on PEMFC performance should be less than that of ionic metal cations because of the ability of ammonium ions to act as a proton carrier and the possibility of ammonia removal at the cathode. Ammonium ions can transport protons by the vehicle process [18] and can be slowly oxidized and leave the cathode as N$_2$ and H$_2$O. It was reported that the performance of an ammonia-poisoned PEMFC could be partially recovered by operating in neat H$_2$ for some period of times (16 h - 3 days) [38–40]. Conversely, the metal cations cannot carry protons. It can be partially removed by stopping fuel cell operation and flooding the cell for a certain period of time [41]. It was found that the release rate of these nonproton cations from contaminated membranes was relatively slow over the order of days to weeks [7,16] and the performance of a partial Na-contaminated fuel cell could not be recovered even when the contaminated feed was stopped and replaced with a clean stream for several days [1].

Also, it can be seen in Fig. 3(a)–(c) that the gas-phase conductivity is vulnerable to cationic contamination because the proton transport by the Grotthuss and vehicle processes could be significantly affected by these cationic species (NH$_4^+$, Na$^+$, Ca^{2+}, and Fe^{3+}). It is well-known that the Grotthuss mechanism requires protons
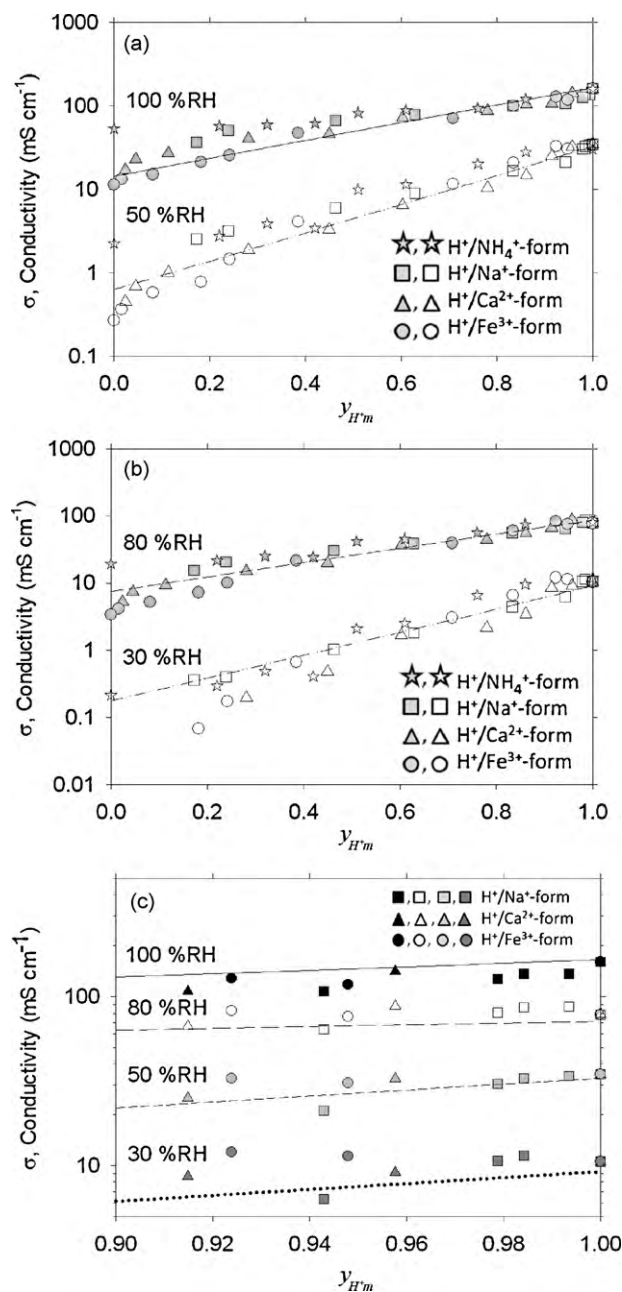

Fig. 3. Conductivity of cationic-contaminated N-211 membranes at 80 °C in the gas phase: (a) for 30 and 80%RH, (b) for 50 and 100%RH, and (c) at very low cationic compositions. Lines represent average conductivities of the metal cationic (Na$^+$, Ca^{2+}, and Fe^{3+}) contaminated membranes and were obtained using the empirical Eqs. (11) and (12).

$$\sigma_{y_{H^+m}} = e^{(0.106y_{H^+m}^2 + 3.846y_{H^+m} - 2.650)}[84.53a_W^2 - 35.457a_W + 5.532]$$
$$\text{where } 0.3 < a_W < 0.5 \tag{11}$$

$$\sigma_{y_{H^+m}} = e^{(-0.058y_{H^+m}^2 + 2.506y_{H^+m} - 1.528)}[145.255a_W^2 - 105.652a_W + 26.270]$$
$$\text{where } 0.5 < a_W < 1.0 \tag{12}$$

where $\sigma_{y_{H^+m}}$ is the conductivity of the cationic-poisoned Nafion membrane (N-211) having proton composition y_{H^+m}; and a_W is the water activity (%RH/100).

in the vicinity of water molecules because this process involves the hopping of protons from water molecules to the surrounding water molecules and the rotation of water molecules [42]. On the other hand, the vehicle mechanism relates to the diffusion of H$_3$O$^+$ throughout the Nafion structure [9]. The presence of these foreign ionic cations in the polymer network essentially impacts the Grot-

thuss transport by decreasing the connectivity of water network and also affects the vehicle mechanism by hindering the ionic diffusion in the hydrophilic region. The diffusion of H_3O^+ is much faster than that of the complex cation–water clusters $[M-(H_2O)_m]^{n+}$ [9].

It has been recently reported that the performance of a cationic-contaminated fuel cell (Li and Co) having low y_{H^+m} (high cationic content) was severely affected by proton depletion at low humidity and by the combination of slow rate of the oxygen reduction reaction and proton transport at humidities more than 75%RH [17]. The percentage loss of performance for a Li-contaminated fuel cell with $y_{H^+m} = 0.31$ operating at 50%RH and 90 °C was ca. 29.4% and 81.9% at current densities of 0.2 and 0.3 A cm^{-2}, respectively. In this study, the decrease in conductivity at 50%RH and 80 °C of a membrane contaminated with a monovalent cation (Na$^+$, $y_{H^+m} = 0.31$), having similar properties to Li$^+$, was 81.5%, which corresponds well with the results of Greszler et al. [17]. This observation indicates that at this condition, the overall performance of a cation-contaminated PEMFC is primarily governed by the rate of proton transport.

3.4. Comparison of aqueous-phase and gas-phase ionic conductivities

As shown in Figs. 2(a), (b) and 4, foreign impurities have more a detrimental effect on gas-phase conductivities at 80 °C than on liquid-phase conductivities at room temperature. The conductivity of the membrane in an aqueous electrolyte (Fig. 2(a) and (b)) increased almost linearly with an increase in proton composition, while that in a gas phase (Fig. 3(a) and (b)) increased exponentially. In the fully metal cationic state, the liquid-phase conductivity of the N-211 in the H$^+$/M^{n+}-form (M^{n+} = Na$^+$, Ca^{2+}, and Fe^{3+}) was ca. 13 times less than that in the H$^+$-form (see Fig. 2(a) and (b)), whereas the gas-phase conductivity was a factor of 6–125, less depending on humidity (see Fig. 4). The effect of the cationic ions on conductivity decreased as humidity increased. The explanation for the different effect on conductivity in the liquid- and gas-phases is probably due to the dissimilarities of proton transport via the Grotthuss and vehicle mechanisms in these two phases. The conductivity of the membrane in the H$^+$-form in DI water at room temperature is mainly dominated by the Grotthuss mechanism, whereas, that measured at 80 °C in the gas phase is probably primarily governed by vehicle transport [43,44]. The results imply that the presence of the counter metal cationic ions in the Nafion structure significantly affected proton transport by reducing the connectivity of the water network in the ionic cluster, particularly in a membrane containing low water content (at 80 °C) that caused
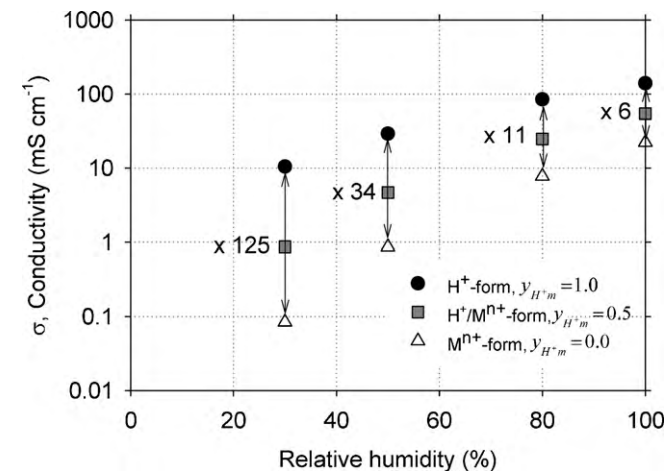
Fig. 4. Gas-phase conductivity at various humidities and 80 °C for N-211 membranes having different cationic fractions.
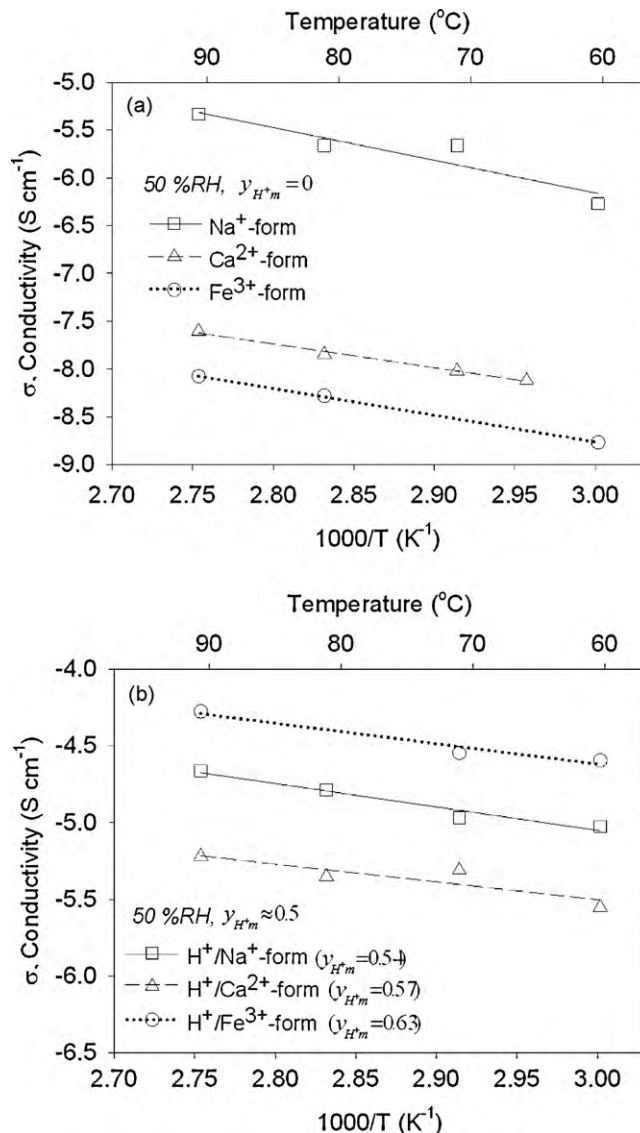
Fig. 5. Temperature dependence at 50%RH, and 80 °C of the conductivity of N-211 in the H$^+$/M^{n+}-form having: (a) $y_{H^+m} = 0$ and (b) $y_{H^+m} \approx 0.5$[M^{n+} = Na$^+$, Ca^{2+}, and Fe^{3+}].

a more rigid structure. Since the metal cation–water clusters were transported by the vehicle mechanism [9], the experimental data suggest that the cation–water interactions at 80 °C and 30–100%RH (Fig. 3(a)–(c)) severely influenced the diffusion of the cation–water clusters more than the hopping of protons at room temperature in DI water through the cation–water network (Fig. 2(a) and (b)).

3.5. Effect of cations on the activation energy for ionic conductivity

Fig. 5(a) and (b) presents the temperature dependence of ionic conductivity of N-211 for several cationic forms ($y_{H^+m} = 0$ and ~0.5) in the range 60–90 °C and at 50%RH. The activation energies were obtained from the Arrhenius relationship as follows:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{RT}\right) \tag{13}$$

where E_a is the activation energy of conductivity; σ_0 is the pre-exponential factor; R is the gas constant; and T is the temperature (K).
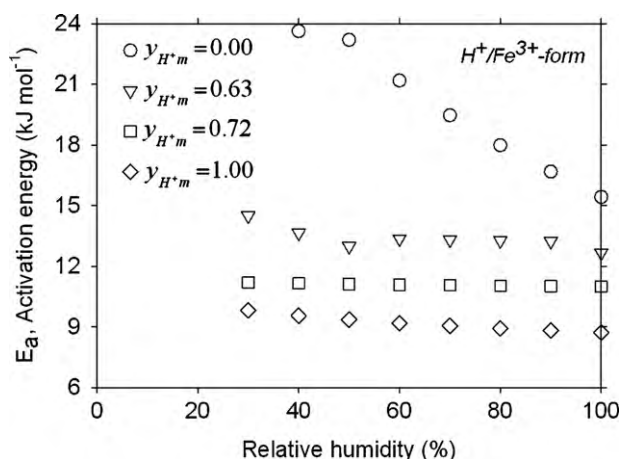
Fig. 6. The effect of humidity and proton composition on E_a for conductivity of N-211 in the H^+/Fe^{3+}-form.

As can be seen in Fig. 1, the trivalent cation (Fe^{3+}) is more preferentially exchanged with sulfonic sites in Nafion than protons. Even trace amounts of Fe^{3+} ions in solution ($x_{H^+} = 0.99$) displace protons significantly ($y_{H^+m} = 0.42$). Thus, the preparation of a Fe^{3+}-contaminated membrane having a proton composition $1 > y_{H^+m} > 0.42$ is difficult. In this section, y_{H^+m} of the Fe^{3+}-contaminated membrane was 0.63, which was much more than in the Na^+- and Ca^{2+}-contaminated membranes. Consequently, the conductivity plot of the H^+/Fe^{3+}-form in Fig. 5(b) appears to be higher than those of the H^+/Na^+- and H^+/Ca^{2+}-forms.

In Fig. 6, the activation energy as a function of humidity for the H^+/Fe^{3+}-form of N-211 is shown. The activation energy plots of other binary-cationic forms (H^+/Na^+ and H^+/Ca^{2+}) having the same proton compositions (y_{H^+m}) are similar to those for the H^+/Fe^{3+}-form (data not shown). The activation energy results for the fully protonated state ($y_{H^+m} = 1$) of the N-211 Nafion membrane at different humidities are in reasonable agreement with literature values for the same type of membrane but with a different thickness (N-117, 178 μm, and EW = 1100 g $(mol SO_3{}^-)^{-1}$) [9,45–52]. It can be seen in Fig. 6 that the activation energy increases as the proton composition decreases at any particular humidity ranging from 30 to 100%RH. Since protons mainly migrate by the vehicular mechanism at this temperature [43,44], the experimental data suggest that the movement of protons by the diffusion process is significantly affected by the presence of the metal cations in N-211. Also, in Fig. 6, the activation energy of the membrane with the same $y_{H^+m}(0.63 \leq y_{H^+m} \leq 1)$ is only slightly influenced by humidity. Zawodzinski et al. [37] found that the ratio of proton transport by the Grotthuss mechanism to the vehicular mechanism increases with an increase in water content for the H^+-form of N-117. One would expect lower activation energies at higher humidities. The results imply that at high y_{H^+m} (low cationic content), the presence of the metal cation only slightly affects the water uptake of Nafion membranes.

Fig. 7(a) and (b) presents the activation energy for conductivity of N-211 membranes poisoned with metal cations (Na^+, Ca^{2+}, and Fe^{3+}) and a proton-containing cation ($NH_4{}^+$) as a function of proton composition (y_{H^+m}) at 50 and 100%RH, respectively. The dotted lines for the E_a of the metal ionic cations contaminated membranes with $0 \leq y_{H^+m} \leq 0.5$ were based on a 2nd polynomial fit of the experimental data. The prediction in this range is only a rough estimation. It can be seen that the energy barriers for metal cations are higher than those for $NH_4{}^+$ ions, particularly at low $y_{H^+m}(y_{H^+m} < 4$, high cationic content). This is probably due to the difference in intermolecular forces within cation–water clusters and the dissimilarity of the hydrogen bond among water molecules in the
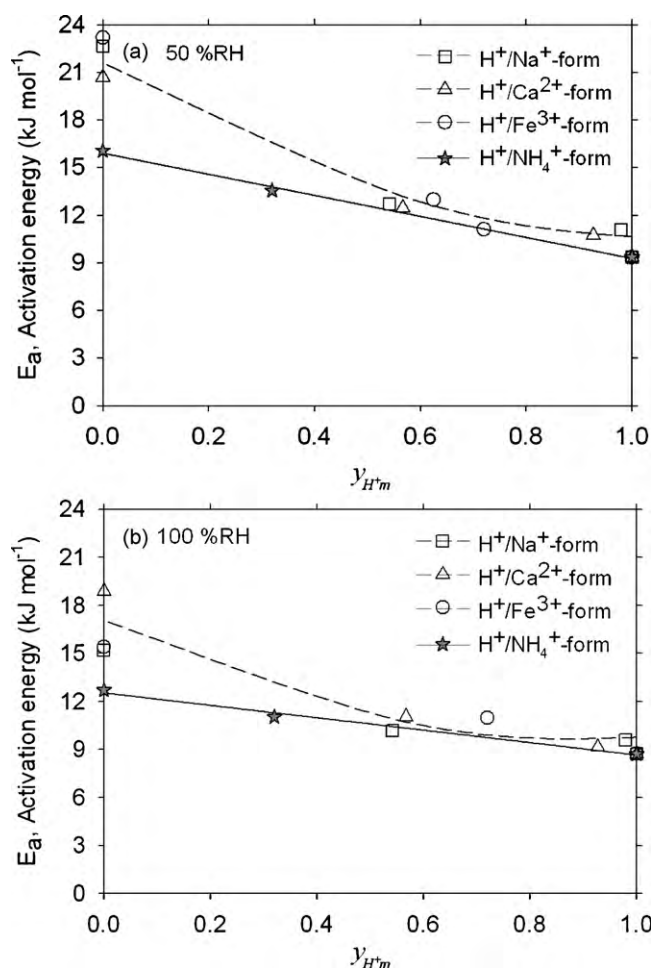

Fig. 7. The effect of proton fraction on the E_a for conductivity of N-211 in the various cationic forms at: (a) 50%RH and (b) 100%RH. Solid lines represent an empirical polynomial fit of the E_a in the H^+/M^{n+}-form ($M^{n+} = Na^+$, Ca^{2+}, and Fe^{3+}) as follows:

$$E_a = -23.58y_{H^+m} + 9.00y_{H^+m}^2 - 9.04a_W + 7.25y_{H^+m}a_W + 26.13 \qquad (14)$$

vicinity of these cations. Unlike $NH_4{}^+$ ions, metal cation ions cannot form a H-bond with neighboring water molecules, but exhibit a dipole–dipole interaction with surrounding water molecules. Additionally, the strength of the H-bond between water molecules in the cation–water clusters may be differently influenced by the different cations because the cationic properties (charge, polarizability, size, shape, etc.) of the $NH_4{}^+$ and metal ions are not alike. Also, it can be seen in Fig. 7(a) and (b) that the activation energies decrease with y_{H^+m} at all humidities (the data for humidities other than 100 and 50%RH are not shown here). It is apparent that the concentration of protons in a Nafion membrane and the humidity considerably influence the activation energy for ionic conductivity in a poisoned membrane.

4. Conclusions

The effect of monovalent and multivalent cation types on the conductivity of a Nafion membrane (N-211) under various conditions was studied. It was found that higher valence cations exhibit strong interaction with and have a stronger preference for the sulfonic sites than lower valence cations. The ionic conductivities in DI water at room temperature ($\sim$25 °C) of three different H^+/M^{n+}-forms ($M^{n+} = Na^+$, Ca^{2+}, and Fe^{3+}) of N-211 were found to be similar, but lower than those in the $H^+/NH_4{}^+$-form of N-211 having the same proton composition (y_{H^+m}). The aqueous-phase conductivities of all

cationic-poisoned membranes decreased in a similar linear fashion with the y_{H^+m}.

As expected, the gas-phase conductivities at 80 °C of N-211 in various binary-metal cationic forms with identical y_{H^+m} were similar, but slightly lower than that in the NH_4^+-form, which was consistent with the results in DI water. It is clear that the influence of measurement conditions (temperature and humidity) and the proton content in the membrane on the gas-phase conductivity are significant. Conductivity in the gas phase declined more dramatically with y_{H^+m} than that in an aqueous phase. The conductivity decreased exponentially with y_{H^+m} at a particular humidity and increased with the humidity. In liquid electrolyte (DI water) at room temperature, the conductivities of N-211 in the fully H^+-form were ca. 12 times higher than those in the fully metal cationic forms. In humidified gas at 80 °C, on the other hand, those in the fully metal cationic forms were lower by a factor of approximately 125 or 6 compared to those in the protonic form at 30 and 100%RH, respectively.

The activation energy (E_a) for ionic conductivity through the pre-contaminated membrane in the temperature range 60–90 °C and 30–100%RH was also studied. It was found that the E_a for the conductivity of a cationic-contaminated membrane increased as y_{H^+m} decreased. This could be because the presence of these foreign cations in a Nafion structure causes the discontinuity of the proton transport pathway through the water network and the movement of cationic water clusters is lower than H_3O^+ clusters, which ultimately affects the ionic movement by the Grotthuss and vehicular mechanisms. The energy barriers for the binary-cationic forms of N-211 (H^+/M^{n+}-forms, $M^{n+} = Na^+$, Ca^{2+}, and Fe^{3+}) having the same y_{H^+m} were similar, but slightly more than that for the NH_4^+-form at the same conditions. It is clear that the presence of cationic species in the hydrophilic region of a Nafion membrane affects the physical properties of the membrane, for example, ion transport, water uptake, interaction between cations and water, swelling property, etc. Accordingly, the experimental results suggest that the complex cation–water clusters of the Nafion membranes contaminated with nonproton cations (i.e., Na^+, Ca^{2+}, and Fe^{3+}) were not the same at these conditions as those in the membrane contaminated with a proton-containing cation (i.e., NH_4^+). The quantitative conductivities and the activation energies of various cationic contaminations at conditions similar to normal fuel cell operation are reported for the first time in this study and should be beneficial for PEMFC simulation work.

Acknowledgements

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