

# The Effect of Impurity Cations on the Transport Characteristics of Perfluorosulfonated Ionomer Membranes

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Ion and water transport characteristics of perfluorosulfonated ionomer membranes are investigated in the mixed cation form of H/Fe, H/Ni, and H/Cu systems. Nafion membranes, which were equilibrated with HCl/FeCl<sub>3</sub>, HCl/NiCl<sub>2</sub>, or HCl/CuCl<sub>2</sub> mixed aqueous solutions of various mixing ratios, were prepared as test samples, and equilibrium and transport properties were measured systematically. Membrane cationic composition showed that trivalent cations had more affinity than divalent cations. Also larger valence cations caused less water content in the membrane. The membrane ionic conductivity was markedly influenced by counterions, and H<sup>+</sup> mobility  $u_{\text{H}^+}$  was altered according to the nature of coexisting cations. In the presence of Cu<sup>2+</sup>,  $u_{\text{H}^+}$  increased from its inherent value, while in the presence of Fe<sup>3+</sup>,  $u_{\text{H}^+}$  decreased to a large extent, Ni<sup>2+</sup> bringing about nearly no change in  $u_{\text{H}^+}$ . The ionic transference number of H<sup>+</sup> was also influenced by coexisting cations in several ways. Despite the unique influence of impurity cations on the mobility of H<sup>+</sup>, the mobility of impurity cations was not affected by the presence of H<sup>+</sup>. The interaction between adjacent cationic species in the membrane ion exchange sites, although plausible in general for multivalence cations, appeared to be not specific due probably to the shielding of the cationic charge by water molecules or by sulfonic acid groups. The water transference coefficient  $t_{\text{H}_2\text{O}}$  as measured by streaming potential measurements showed unique changes with membrane ionic composition, and  $t_{\text{H}_2\text{O}}$  increased from 2.5 to over 13 by the presence of impurity ions. These impurity ions were found to result in more water molecules dragged than in the case of individual ions, when coexisting with the H<sup>+</sup> ion. Overall, it was noted that the water molecules within the influence of impurity cations appeared to play a large role in the H<sup>+</sup> movement in the membrane.

## 1. Introduction

Perfluorosulfonic acid polymer electrolyte membranes are of current interest in applications such as polymer electrolyte fuel cells, water electrolysis, chlor-alkali electrolysis, and so on.<sup>1–3</sup> In relation to technological aspects, the performance evaluations have so far been concentrated on the membranes in a single cation system, especially on H-form membranes.<sup>1,4–9</sup> However, it was pointed out that the membrane characteristics with binary cation systems are also of major importance, particularly in relevance to the problems of selective membrane operation in mixed ion systems, or in the case of membrane contamination by foreign impurities.<sup>10–12</sup> For example, H/Na and H/Ca systems were investigated on the basis of the newly developed methods for membrane transport measurements.<sup>13,14</sup> Those systems involved mainly alkali and alkaline earth metal cations as the second cations (impurities) into H-form membranes. It was predicted that the presence of those cations into the membrane would result in deterioration of performances such as electric conductivity, water content, and water transport in relation to water management in, e.g., fuel cells.<sup>13,14</sup>

From the point of view of membrane contamination by foreign cations in a fuel cell, some ions of the transitional metal group should also be examined as possible contaminants, because these ions will easily enter into the fuel cell system by way of the reactant gas, the air stream at the cathode side, corrosion of piping materials, and other sources. Also for the mechanism elucidation of transport of ions and water molecules in the membrane, mixed cation systems are of research interest because these systems would give much information about the ion–ion, ion–water, ion–polymer and water–polymer interactions, and in this context, transitional metal systems are a new and challenging field.

In this study it is intended to clarify the transport and equilibrium properties of perfluorosulfonic acid polymer membranes of H/Fe, H/Ni, and Fe/Cu counterion systems, with a methodology established in previous works.<sup>13,14</sup> Cations Fe<sup>3+</sup>, Ni<sup>2+</sup>, and Cu<sup>2+</sup> were selected as second counterions to the membrane ion exchange site, because these cations are not only of practical importance as probable contaminants but also of fundamental interest being categorized as incomplete d-orbital transitional metal ions with oriented aquo ligands, which is of different nature from that of alkali and alkaline earth metal cations.

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## 2. Experimental Section

**2.1. Materials and Membrane Preparation.** As membrane materials, Nafion 115 and 117 of DuPont (Polymer Products Department, Wilmington, DE) were used. The thickness of Nafion 115 and Nafion 117 membranes in H-form were 125 and 175  $\mu\text{m}$  in the dry state, and 160 and 220  $\mu\text{m}$  in the wet state, respectively. The nominal equivalent weight value was  $\text{EW} = 1100 \text{ g equiv}^{-1}$ . Membranes were cut into  $25 \times 25 \text{ mm}$  pieces, pretreated first in  $80^\circ\text{C}$  water with 2%  $\text{H}_2\text{O}_2$  for 2 h, immersed in  $0.1 \text{ mol dm}^{-3}$  HCl for 24 h, and finally rinsed with pure water.

$\text{FeCl}_3$ ,  $\text{NiCl}_2$ , and  $\text{CuCl}_2$  were reagent grade powders from Wako Pure Chemical Industries Ltd., Osaka, Japan, and used without further purification. HCl was from Merck Titrisol ampulae  $1.000 \text{ mol dm}^{-3}$  (Merck, Darmstadt, Germany). Mixtures of solutions were prepared from  $0.03 \text{ mol dm}^{-3}$  HCl and  $0.06/(n+1) \text{ mol dm}^{-3}$   $\text{ACl}_n$ , where  $\text{A}^{n+} = \text{Fe}^{3+}$ ,  $\text{Ni}^{2+}$ , or  $\text{Cu}^{2+}$ , using deionized water. The equivalent fraction of HCl in the solution,  $x_{\text{HCl}}$ , defined as  $x_{\text{HCl}} \equiv c_{\text{HCl}}/(c_{\text{HCl}} + nc_{\text{ACl}_n})$  using the molar concentration of HCl and  $\text{ACl}_n$ ,  $c_{\text{HCl}}$ , and  $c_{\text{ACl}_n}$ , respectively, were  $x_{\text{HCl}} = 0.000, 0.158, 0.333, 0.529, 0.750, 0.871, 0.934, 0.967, 0.985, 0.990$ , and  $1.000$ .

Membranes were equilibrated in  $\text{HCl/ACl}_n$  ( $\text{A}^{n+} = \text{Fe}^{3+}$ ,  $\text{Ni}^{2+}$ , or  $\text{Cu}^{2+}$ ) solutions of various compositions at  $25^\circ\text{C}$  for at least 1 month prior to the measurements. Former measurements have shown that for thick membranes more than 2 weeks are needed, for the attainment of true equilibrium between solution and membrane phases. During equilibration, solutions were replaced at least four times.

**2.2. Membrane Ionic Composition, Density, and Water Content.** Ionic composition in the membrane was determined by X-ray fluorescence spectroscopy in the dry state.<sup>14</sup> The equivalent fraction of a cation  $\text{A}^{n+}$  in the membrane,  $x_{\text{AM}}$ , is defined as follows, using concentration of cations  $\text{H}^+$  and  $\text{A}^{n+}$ ,  $c_{\text{H}^+}$ , and  $c_{\text{A}^{n+}}$ , respectively, in the membrane:

$$x_{\text{AM}} = \frac{nc_{\text{A}^{n+}}}{c_{\text{H}^+} + nc_{\text{A}^{n+}}} \quad (1)$$

A Seiko Electric Co. model SEA2010 X-ray fluorescence spectroscopic analyzer was used for component analysis, and elements A ( $\text{A} = \text{Fe}, \text{Ni}, \text{Cu}$ ), S, and Cl were picked from the spectra. Element Cl was only within the error amount and was not further analyzed. Note also in EPMA measurement in the system H/Na and in the streaming potential measurement for H-form Nafion, no detectable  $\text{Cl}^-$  was found in the membrane phase contacting solutions of salt concentrations at the  $0.03 \text{ mol dm}^{-3}$  level.<sup>13,15</sup> The cationic site fraction of  $\text{H}^+$  in the membrane,  $x_{\text{HM}}$ , was calculated from the atomic ratio  $[\text{A}]/[\text{S}]$  in the spectra.

$$x_{\text{HM}} = 1 - \frac{[\text{A}]/[\text{S}]}{([\text{A}]/[\text{S}])_{x_{\text{HCl}}=0}} \quad (2)$$

where  $[\text{A}]$  and  $[\text{S}]$  are intensities of the elements A and S in the spectra, and the value in the denominator means the ratio  $[\text{A}]/[\text{S}]$  at  $x_{\text{HCl}} = 0$ . The analysis was further verified by inductively coupled plasma emission spectrography (ICP), after the ion was extracted into the liquid solution by soaking the membrane in  $0.1 \text{ mol dm}^{-3}$  HCl.

The water content in the membrane was determined by the gravimetric method. A membrane sample was taken from the equilibrating solution, blotted lightly with tissue paper, and weighed immediately ( $W_{\text{wet}}$ ). The sample was first dried in a vacuum at room temperature for 24 h and then in a vacuum at

$110^\circ\text{C}$  for 12 h. After the sample was cooled in a deccicator, it was weighed ( $W_{\text{dry}}$ ), and from the weight difference the water content was calculated as the number of water molecules per cationic site  $\lambda \equiv n_{\text{H}_2\text{O}}/n_{\text{SO}_3^-}$ :

$$\lambda = \frac{(W_{\text{wet}} - W_{\text{dry}})\text{EW}}{18W_{\text{dry}}} \quad (3)$$

The density of the membrane in the wet state,  $d_{\text{wet}}$  ( $\text{g cm}^{-3}$ ) was also calculated by a gravimetric method in two ways. In the first method the weight of the wet membrane,  $W_{\text{wet}}$ , was divided by the volume in wet state,  $V_{\text{wet}}$ , that was measured by a micrometer:

$$d_{\text{wet}} = W_{\text{wet}}/V_{\text{wet}} \quad (4)$$

In the second method the membrane weight was measured in water, i.e.,  $W_{\text{water}}$ , and

$$d_{\text{wet}} = \frac{W_{\text{wet}} \rho_{\text{water}}}{W_{\text{wet}} - W_{\text{water}}} \quad (5)$$

where  $\rho_{\text{water}}$  ( $\text{g cm}^{-3}$ ) is the density of water.

**2.3. Membrane Conductivity Measurements.** A Solartron S-1260 frequency response analyzer (Solartron Instruments) was used for measuring the impedance of the membrane together with a Teflon cell, as described elsewhere.<sup>16</sup> The impedance of the Nafion 117 membrane was measured in the lateral direction with 20 mV ac modulation over a frequency range from  $10^7$  to  $10^3 \text{ Hz}$  at the open-circuit potential at  $25^\circ\text{C}$ . The electrode was black-platinized Pt foil contacting the membrane on each of two sides. During the measurement, the membrane was in contact with the equilibrating solution by way of a  $10 \times 5 \text{ mm}$  window on each side. The specific conductivity of the membrane  $\kappa$  ( $\text{S cm}^{-1}$ ) was obtained from the real part of the impedance  $R(\text{O})$  of the membrane:

$$\kappa = \frac{0.5}{Rl} \quad (6)$$

$l$  is the thickness (cm) of the membrane, which was measured for each sample.

**2.4. Ionic Transference Number Measurements.** The membrane-contact emf (electromotive force) method was used where a pair of Nafion 117 membranes, each equilibrated with a solution of fixed ionic composition, were overlapped at one end, and the other ends were contacting the equilibrating solution with Ag/AgCl electrodes.<sup>13</sup> One of the membranes was a reference membrane contacting the solution of  $x_{\text{HCl}} = 0.529$ , and the other was a test membrane contacting solutions of various kinds of  $x_{\text{HCl}}$  levels. Under the present experimental setup, emf  $E$  that arises as a result of the difference in chemical potentials of existing species across the membrane is expressed as follows:<sup>17</sup>

$$E = -\frac{1}{F} \sum_i \frac{t_i}{z_i} \Delta \mu_i \\ = -\frac{1}{F} (t_{\text{H}^+} \Delta \mu_{\text{H}^+} + \frac{1}{n} t_{\text{A}^{n+}} \Delta \mu_{\text{A}^{n+}}) \quad (7)$$

where  $t_{\text{H}^+}$  and  $t_{\text{A}^{n+}}$  are transference numbers of  $\text{H}^+$  and  $\text{A}^{n+}$  in the membrane, respectively, and are assumed constant throughout the membrane. At equilibrium between membrane and solution phases, the chemical potentials of membrane counterions  $i = \text{H}^+$  and  $\text{A}^{n+}$  are equated with those of  $\text{H}^+$  and  $\text{A}^{n+}$  in

the contacting solution at each side.<sup>26</sup> By adding the chemical potential of  $\text{Cl}^-$  with an equal amount, those are converted to chemical potentials of  $\text{HCl}$  and  $\text{ACl}_n$  in the solution at each side, e.g., as  $\mu_{\text{HCl}} = \mu_{\text{H}^+} + \mu_{\text{Cl}^-}$ . Using the Gibbs–Duhem equation at isothermal and isopiestic conditions, and disregarding the chemical potential difference of  $\text{H}_2\text{O}$  at each side of the membrane for the present experimental setup, eq 7 is rewritten as

$$E = -\frac{1}{F} \left( t_{\text{H}^+} \Delta \mu_{\text{HCl}} + \frac{1}{n} t_{\text{A}^{n+}} \Delta \mu_{\text{ACl}_n} \right) \\ = -\frac{1}{F} \left\{ t_{\text{H}^+} \Delta \mu_{\text{HCl}} + \frac{1}{n} t_{\text{A}^{n+}} \left( -\frac{n x_{\text{HCl}}}{x_{\text{ACl}_n}} \Delta \mu_{\text{HCl}} \right) \right\} \quad (8)$$

The ionic transference number of  $\text{H}^+$  in the membrane gives  $t_{\text{H}^+} + t_{\text{A}^{n+}} = 1$  and the solution composition  $x_{\text{HCl}} + x_{\text{ACl}_n} = 1$ ; then the following formula results in

$$t_{\text{H}^+} = x_{\text{HCl}} - (1 - x_{\text{HCl}}) \frac{d\Delta\phi}{d\Delta\mu_{\text{HCl}}} \quad (9)$$

where  $\Delta\phi = EF$  ( $\text{J mol}^{-1}$ ),  $E$  is the membrane-contact emf (V),  $F$  is the Faraday, and  $\Delta\mu_{\text{HCl}}$  ( $\text{J mol}^{-1}$ ) is the difference in the chemical potentials of  $\text{HCl}$  in two solutions contacting the membranes. All measurements were performed using a Teflon cell at 25 °C, as described before.<sup>13</sup>

The mobility of ions in the membrane  $u_i$  ( $\text{m}^2 \text{V}^{-1} \text{s}^{-1}$ ) was calculated from the following equation:<sup>14</sup>

$$u_{\text{H}^+} = \frac{t_{\text{H}^+} \kappa}{F c_{\text{SO}_3^-} x_{\text{HM}}} \quad (10)$$

$$u_{\text{A}^{n+}} = \frac{(1 - t_{\text{H}^+}) \kappa}{F c_{\text{SO}_3^-} (1 - x_{\text{HM}})} \quad (11)$$

The charge number of the metal ion does not appear in this equation, because  $x_{\text{AM}}$  is expressed by site occupation in the membrane cation exchange sites (see eq 1), and when it is written in terms of concentration ( $\text{mol dm}^{-3}$ ), it cancels with the charge of the ion.

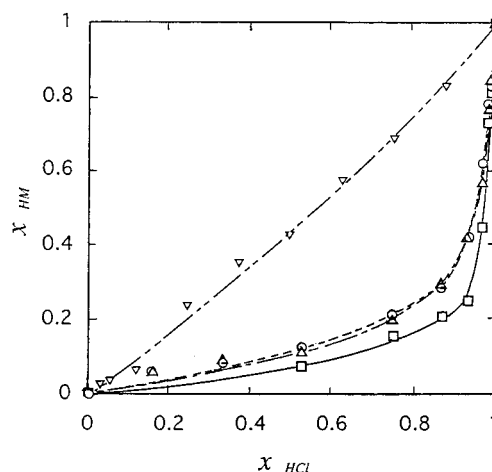
**2.5. Streaming Potential Measurements.** Potential difference (emf) that arises for applied pressure difference  $\Delta p$  across the membrane was measured as a function of time, and emf was plotted against the square root of time.<sup>18</sup> Thereby the membrane was contacting identical solutions on both its sides, and emf was measured by a pair of  $\text{Ag}/\text{AgCl}$  electrodes immersed in the same solutions. From this curve, two kinds of parameters, water transference coefficient  $t_{\text{H}_2\text{O}}$  and water permeability  $L_p$  ( $\text{m}^4 \text{J}^{-1} \text{s}^{-1}$ ), were obtained in a single measurement.<sup>13,14,18</sup>  $t_{\text{H}_2\text{O}}$  arises due to the water movement associated with the charge transport, and  $L_p$  arises due to the pressure-driven flow of water in the membrane.<sup>18</sup> The emf is expressed by

$$EF = a - b\sqrt{t} \quad (12)$$

where the intercept and the slope of this line are given as follows:

$$a = - \left( t_{\text{H}^+} V_{\text{HCl}} + \frac{1}{n} t_{\text{A}^{n+}} V_{\text{ACl}_n} + t_{\text{H}_2\text{O}} V_{\text{H}_2\text{O}} + \Delta V_{\text{el}} \right) \Delta p \quad (13)$$

$$b = - \frac{f L_p \Delta p}{F} \quad (14)$$



**Figure 1.** Membrane ionic fraction  $x_{\text{HM}}$  at equilibrium state vs solution composition  $x_{\text{HCl}}$  for Nafion 117 at 25 °C: (□) H/Fe system; (Δ) H/Ni system; (○) H/Cu system; (▽) H/Na system.<sup>13</sup>

here  $V_i$  ( $\text{cm}^3 \text{mol}^{-1}$ ) is the molar volume of species  $i$  and  $\Delta V_{\text{el}} = V_{\text{Ag}} - V_{\text{AgCl}}$ . The amount of dissolved gas in the membrane is very small compared with other species and is neglected here. The following values were used for calculation:  $V_{\text{HCl}} = 18.2$ ,  $V_{\text{NiCl}_2} = 13.1$ ,  $V_{\text{CuCl}_2} = 9.39$ ,  $V_{\text{H}_2\text{O}} = 18.0$ , and  $\Delta V_{\text{el}} = -15.5$ .  $f$  is given by

$$f \equiv 4RT\pi^{-1/2} \left\{ [t_{\text{H}^+} - t_{\text{H}^+(l)}] \left( D_{\text{HCl}}^{-1/2} - \frac{1}{n} D_{\text{ACl}_n}^{-1/2} \right) + \right. \\ \left. t_{\text{Cl}^-(l)} \left[ \frac{1}{n} D_{\text{ACl}_n}^{-1/2} + \frac{c_{\text{HCl}}^0 D_{\text{HCl}}^{-1/2} + n c_{\text{ACl}_n}^0 D_{\text{ACl}_n}^{-1/2}}{c_{\text{HCl}}^0 + n c_{\text{ACl}_n}^0} \right] \right\} \quad (15)$$

for  $x_{\text{HM}} \neq 0$  and  $x_{\text{HM}} \neq 1$ , and

$$f \equiv 4RT \frac{n+1}{n} t_{\text{Cl}^-(l)} (\pi D_{\text{ACl}_n})^{-1/2} \quad \text{for } x_{\text{HM}} = 0 \quad (16)$$

$$f \equiv 8RT t_{\text{Cl}^-(l)} (\pi D_{\text{HCl}})^{-1/2} \quad \text{for } x_{\text{HM}} = 1 \quad (17)$$

here  $t_i(l)$  is the transference number of ion  $i$  in the solution, and  $c_i^0$  and  $D_i$  are concentration and diffusion coefficients of species  $i$  in the solution, respectively.<sup>18</sup> Note that all the parameters except  $t_{\text{H}^+}$  in eqs 15–17 are those in aqueous solutions and can be obtained from the literature.<sup>19</sup>  $t_{\text{H}^+}$  is obtained by the measurements described in section 2.4.

The experiments were performed for Nafion 115 in deaerated solutions using a computer-aided homemade apparatus at 25 °C.<sup>15</sup> Pressure was applied by  $\text{N}_2$  gas with pressure control model 250C-1-D of MKS Instruments, Inc.

### 3. Results and Discussion

**3.1. Membrane Composition.** The calculated membrane composition  $x_{\text{HM}}$  using eq 2 is shown in Figure 1 as a function of the solution composition  $x_{\text{HCl}}$ , for membranes exchanged with three kinds of cation systems, H/Fe, H/Ni, and H/Cu, together with the previous data for H/Na.<sup>13</sup> The membrane composition values measured by X-ray fluorescence spectroscopy were consistent with those measured by ICP analysis. The equilibrium constant  $K_{\text{ex}}$  of the exchange reaction between the solution phase and the membrane phase,  $n\text{HCl}(\text{aq}) + \text{AM}_n = \text{ACl}_n(\text{aq}) + n\text{HM}$  ( $\text{A} = \text{Fe}, \text{Ni}, \text{Cu}$ ), is defined as follows:

$$K_{\text{ex}} = \frac{x_{\text{ACl}_n} x_{\text{HM}}^n}{x_{\text{HCl}}^n x_{\text{AM}_n}} \quad (18)$$

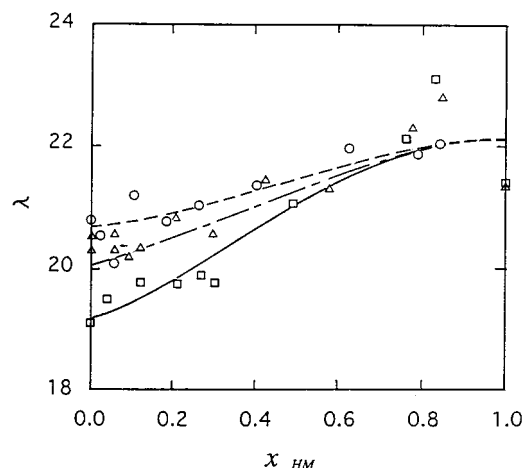
$K_{\text{ex}}$  is calculated to be  $0.003 \pm 0.002$  for H/Fe,  $0.025 \pm 0.006$  for H/Ni, and  $0.029 \pm 0.010$  for H/Cu systems, respectively.

In Figure 1, there can be seen two kinds of trends. First, higher order valence cations have stronger affinity to the membrane than lower valence ones, and the  $\text{Fe}^{3+}$  ion was exchanged into the membrane more preferably than the  $\text{Ni}^{2+}$  or  $\text{Cu}^{2+}$  ions. Second, cations with smaller absolute values of hydration enthalpy have larger affinity to the membrane than ones of larger absolute value of hydration enthalpy, meaning less hydrated cations have larger affinities to the membrane. It is interesting to note that for membranes exchanged with cations of larger affinity, the ionic conductivity becomes smaller (see discussions below). In comparison with  $\text{Ni}^{2+}$  or  $\text{Cu}^{2+}$  ions, the  $\text{Ca}^{2+}$  ion was almost to the same extent exchanged with the membrane ( $K_{\text{ex}}$  of the H/Ca system was  $0.021 \pm 0.007$ , while  $K_{\text{ex}}$  of the H/Na system was  $0.72 \pm 0.15$ ).<sup>13,14</sup> It can be conceivable that having the same valence and the extent of hydration as compared with these cations,  $\text{Ca}^{2+}$  was able to sit in the cation exchange site of the membrane in the similar affinity. However, as will be shown in the following discussion, the mobility of  $\text{H}^+$  in the membrane is differently influenced by different divalent cations (see the ionic conductivity section). In any case,  $\text{H}^+$  in a Nafion membrane was easily exchanged with any kind of foreign cations tested.

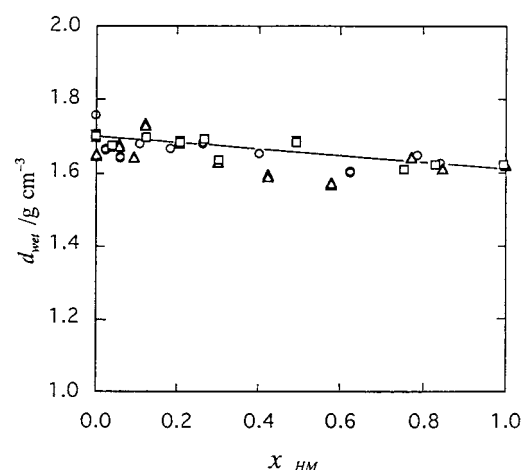
The water content in the membrane  $\lambda$  is shown in Figure 2 as a function of membrane ionic composition  $x_{\text{HM}}$  for three kinds of systems. If  $\lambda$  is plotted against the solution composition with which the membrane is equilibrated,  $\lambda$  falls more sharply than the curves shown in Figure 2.  $\lambda$  did not differ much among different cation form membranes for high  $\text{H}^+$  content, but for low  $\text{H}^+$  content  $\lambda$  decreased in the following order of exchanged cations:  $\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Fe}^{3+}$ . This trend was consistent with the trend as observed in membrane cationic compositions; i.e., membranes exchanged with cations of higher affinity show lower water content.

The density in the wet state of the membrane is shown in Figure 3 as a function of membrane composition  $x_{\text{HM}}$ . Different methods of measuring density gave the same results within experimental errors. In all cases, the density increased almost linearly with the composition of foreign cations, when the membranes were exchanged with these cations. This is in contrast to the case of water content, where the amount of water decreased with increasing foreign cations in the membrane. Note that cations tested are all less hydrophilic compared with  $\text{H}^+$ , and these cations bring about fewer water molecules inside the membrane. Moreover, since these cations are multivalent, they can bind more strongly to sulfonic acid sites and might form ion pairs between cations and sulfonic acid sites, or cross-linking among polymer networks by way of multivalent counterions as linking knots. This would in turn bring about the smaller volume of hydrophilic domains inside the membrane, and accordingly, higher density of the membrane by shrinkage of the overall volume. The same trend was observed in the H/Ca system.<sup>14</sup>

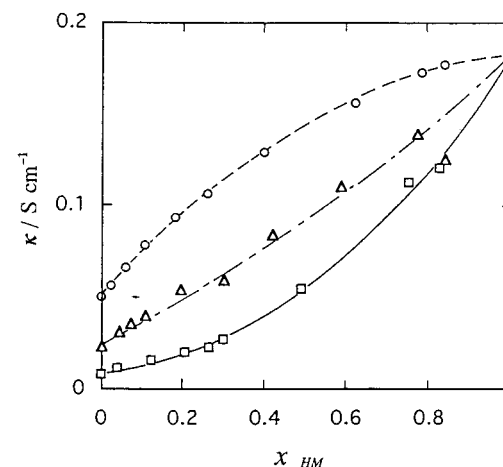
**3.2. Membrane Ionic Conductivity.** In Figure 4 the membrane specific conductivity  $\kappa$  is plotted against the membrane composition  $x_{\text{HM}}$ . Three modes of curves are seen between  $\kappa$  and  $x_{\text{HM}}$  for different kinds of exchanged cations. For membranes exchanged with  $\text{Fe}^{3+}$ ,  $\kappa$  changed in a concave fashion with membrane ionic composition, showing that a small amount



**Figure 2.** Membrane water content  $\lambda \equiv n_{\text{H}_2\text{O}}/n_{\text{SO}_3^-}$  plotted against membrane ionic fraction  $x_{\text{HM}}$  for Nafion 117: (□) H/Fe system; (Δ) H/Ni system; (○) H/Cu system.



**Figure 3.** Density of the Nafion 117 membrane in the wet state plotted against membrane ionic fraction  $x_{\text{HM}}$ : (□) H/Fe system; (Δ) H/Ni system; (○) H/Cu system.



**Figure 4.** Membrane ionic conductivity  $\kappa$  in the fully hydrated state plotted against membrane ionic fraction  $x_{\text{HM}}$  for Nafion 115: (□) H/Fe system; (Δ) H/Ni system; (○) H/Cu system.

of  $\text{Fe}^{3+}$  in the equilibrating solution results in a large decrease in  $\kappa$ . For membranes exchanged with  $\text{Ni}^{2+}$ ,  $\kappa$  changed almost in a linear fashion with membrane ionic composition. The most peculiar phenomena is that  $\kappa$  changed in a convex fashion with membrane ionic composition for membranes exchanged with  $\text{Cu}^{2+}$ , indicating that  $\text{Cu}^{2+}$  can enhance the movement of  $\text{H}^+$



inside the membrane. These three examples would show typically different effects about cation movements for mixed cation systems inside the membrane, i.e., retardation, no interference, and acceleration modes.

The difference in the behavior of ionic movement is more apparently seen in Figure 5, where the mobility of cations calculated using eqs 10 and 11 together with the data of ionic transference numbers (see below) is plotted as a function of membrane composition  $x_{\text{HM}}$ . The mobility of  $\text{H}^+$ ,  $\text{Fe}^{3+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Cu}^{2+}$  in the H-form, Fe-form, Ni-form, and Cu-form membranes, respectively, are  $u_{\text{H}^+} = 1.33 \times 10^{-7} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ ,  $u_{\text{Fe}^{3+}} = 5.3 \times 10^{-9} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ ,  $u_{\text{Ni}^{2+}} = 1.65 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ , and  $u_{\text{Cu}^{2+}} = 3.13 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ , respectively (mobility of  $\text{Ca}^{2+}$  was measured to be  $u_{\text{Ca}^{2+}} = 2.48 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ ).<sup>14</sup> The mobility of foreign cations changed in the order  $\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Fe}^{3+}$ , which follows the same order as in the water content (see Figure 2). Also this is in the opposite order of that of the affinity of the cation to the cation exchange site in the membrane. This means that the stronger the affinity of the cation to the sulfonic acid site, the lower the mobility of the cation involved. The mobility of foreign cations does not change very much by the presence of  $\text{H}^+$  in the membrane, but the mobility of  $\text{H}^+$  in the presence of foreign cation changes characteristically, depending on which type of foreign cation coexists in the membrane. In the presence of  $\text{Fe}^{3+}$ , the mobility of  $\text{H}^+$  decreases sharply (retardation mode), but in the presence of  $\text{Cu}^{2+}$ , the mobility of  $\text{H}^+$  increases almost linearly with the amount of  $\text{Cu}^{2+}$  (acceleration mode).  $\text{Ni}^{2+}$  is of intermediate nature, and there appears only little interaction between  $\text{H}^+$  and  $\text{Ni}^{2+}$  in the membrane, i.e., the mobility of  $\text{H}^+$  and  $\text{Ni}^{2+}$  remains almost constant when two cations coexist (no interaction mode).

A calculation is carried out to test the interaction of neighboring cations in the cation exchange sites in the membrane. For a system of monovalent cation–divalent cation in the membrane, HM and  $\text{AM}_2$  where M denotes the cation exchange site, the thermodynamic equilibrium constant  $K_{\text{th}}$  is defined for the reaction  $2\text{HCl}(\text{aq}) + \text{AM}_2 = \text{ACl}_2(\text{aq}) + 2\text{HM}$  as follows:<sup>20</sup>

$$K_{\text{th}} = \frac{a_{\text{ACl}_2} a_{\text{HM}}^2}{a_{\text{HCl}}^2 a_{\text{AM}_2}} = K' \frac{\gamma_{\text{HM}}^2}{\gamma_{\text{AM}_2}} \quad (19.1)$$

$$K' \equiv \frac{a_{\text{ACl}_2} x_{\text{HM}}^2}{a_{\text{HCl}}^2 x_{\text{AM}_2}} \quad (19.2)$$

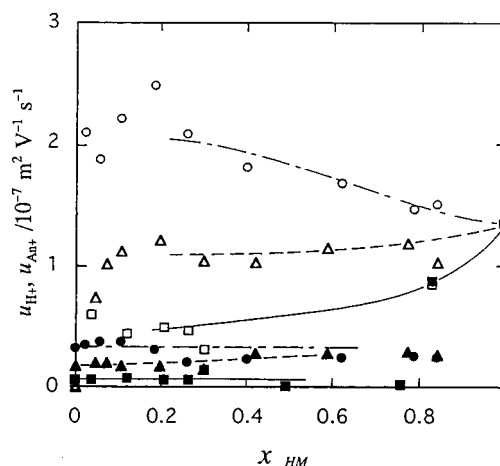
where  $a_{\text{HCl}}$  and  $a_{\text{ACl}_2}$  are the activity of HCl and  $\text{ACl}_2$  in the solution, respectively, and  $\gamma_{\text{HM}}$  and  $\gamma_{\text{AM}_2}$  are activity coefficients of HM and  $\text{AM}_2$  in the membrane, respectively. The Gibbs energy change for the exchange reaction is defined, using the chemical potential of species:

$$\Delta G = 2\mu_{\text{HM}} + \mu_{\text{ACl}_2} - 2\mu_{\text{HCl}} - \mu_{\text{AM}_2} \quad (20)$$

which is 0 at the equilibrium state. For the standard state, where the activity coefficients of all the species are 1,  $\mu_i$  becomes  $\mu_i^0$  and  $\Delta G$  becomes  $\Delta G^0$ , the latter being expressed as  $-RT \ln K_{\text{th}}$ . Then

$$2\Delta\mu_{\text{HM}} + \Delta\mu_{\text{ACl}_2} - 2\Delta\mu_{\text{HCl}} - \Delta\mu_{\text{AM}_2} = RT \ln K_{\text{th}} \quad (21)$$

where  $\Delta\mu_i \equiv \mu_i - \mu_i^0 = RT \ln a_i$ . Suppose the  $x_{\text{HM}}$  equivalent



**Figure 5.** Mobility of cationic species in the membrane plotted against membrane ionic fraction  $x_{\text{HM}}$ : (□, ■)  $u_{\text{H}^+}$  and  $u_{\text{Fe}^{3+}}$  in the H/Fe system; (Δ, ▲)  $u_{\text{H}^+}$  and  $u_{\text{Ni}^{2+}}$  in the H/Ni system; (○, ●)  $u_{\text{H}^+}$  and  $u_{\text{Cu}^{2+}}$  in the H/Cu system.

of HM and the  $x_{\text{AM}_2} = 1 - x_{\text{HM}}$  equivalent of  $\text{AM}_2$  are brought together to make a mixture of H/A-form membrane. The Gibbs energy change  $\Delta G_{\text{mix}}$  for this mixing process is given as follows:

$$\Delta G_{\text{mix}} = x_{\text{HM}} \Delta\mu_{\text{HM}} + \frac{1}{2}(1 - x_{\text{HM}}) \Delta\mu_{\text{AM}_2} \quad (22)$$

Differentiation with respect to  $x_{\text{HM}}$  results in, with the use of the Gibbs–Duhem relationship,

$$\frac{d\Delta G_{\text{mix}}}{dx_{\text{HM}}} = \Delta\mu_{\text{HM}} - \frac{1}{2} \Delta\mu_{\text{AM}_2} \quad (23)$$

which after some arrangements using eqs 19 and 21 reduces to

$$\frac{d\Delta G_{\text{mix}}}{dx_{\text{HM}}} = \frac{1}{2} RT \ln K_{\text{th}} - \frac{1}{2} RT \ln K' + \frac{1}{2} RT \ln \frac{x_{\text{HM}}^2}{x_{\text{AM}_2}} \quad (24)$$

According to the cell model of the HM and  $\text{AM}_2$  systems of cation exchange membranes, the entropy of mixing  $\Delta S_{\text{mix}}$  and the enthalpy of mixing  $\Delta H_{\text{mix}}$  are given as follows:<sup>20</sup>

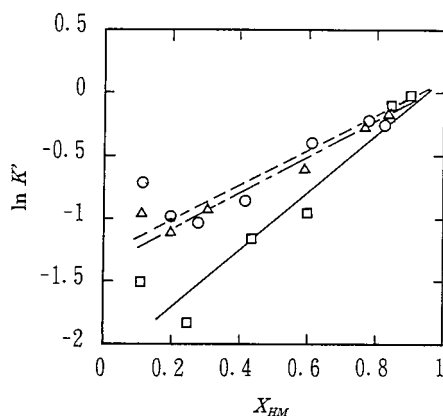
$$\Delta S_{\text{mix}} = -R \left( x_{\text{HM}} \ln x_{\text{HM}} + \frac{1}{2} x_{\text{AM}_2} \ln x_{\text{AM}_2} \right) \quad (25)$$

$$\Delta H_{\text{mix}} = b x_{\text{HM}} x_{\text{AM}_2} \quad (26)$$

where  $b$  is a constant expressing the energy change of the interaction between cation pairs by the mixing process. Here it is assumed that cation vacancy  $\text{CV}^-$  forms when  $\text{A}^{2+}$  is introduced into the lattice of the cell of HM, and this  $\text{CV}^-$  is associated with  $\text{A}^{2+}$ .<sup>20</sup> Hence

$$\begin{aligned} \frac{d\Delta H_{\text{mix}}}{dx_{\text{mix}}} &= \frac{1}{2} RT (\ln K_{\text{th}} - \ln K' - 1) \\ &= b(1 - 2x_{\text{HM}}) \end{aligned} \quad (27)$$

Equation 27 indicates that if the mixture of HM and  $\text{AM}_2$  is able to be described by a cell model of liquid mixtures, then the plot of  $\ln K'$  against  $x_{\text{HM}}$  will result in a straight line. The slope of this line will show  $b$ , the largeness of the cation–cation

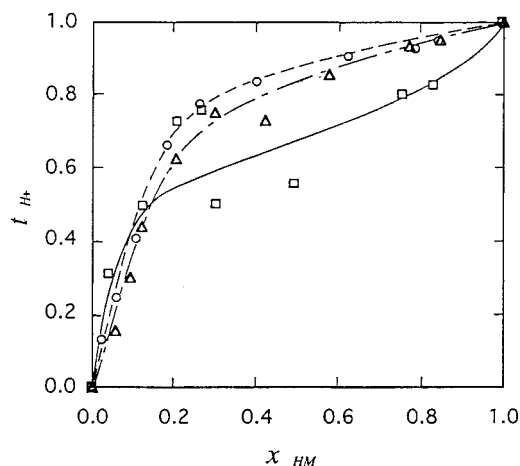


**Figure 6.** Plots of the thermodynamic function  $\ln K'$  (see text) against membrane ionic fraction  $x_{HM}$  for Nafion 117: ( $\square$ ) H/Ca system; ( $\Delta$ ) H/Ni system; ( $\circ$ ) H/Cu system. Plots for the H/Ca system are calculated from ref 14.

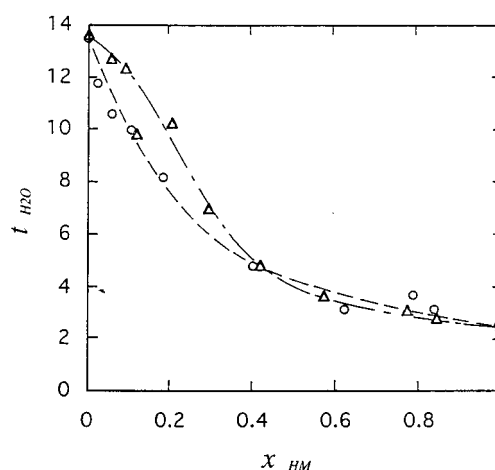
interaction. Figure 6 depicts this plot for H/Ca-, H/Ni-, and H/Cu-form membrane systems. The activities of HCl and  $\text{ACl}_2$ ,  $a_{\text{HCl}}$  and  $a_{\text{ACl}_2}$ , are calculated using activity coefficients at the same ionic strength of the solution, by the Debye–Hückel equation.<sup>19</sup> From the behavior of  $\text{H}^+$  mobility against  $x_{HM}$  in a mixture, it is classified that H/Ca and H/Ni are in the noninteraction mode while H/Cu is in the acceleration mode. The slopes in Figure 6 do not differ much among three systems, and it turns out that there is no peculiarity for cation–cation interactions in the H/Cu system as compared with the other systems. The explanation for different modes of  $u_{\text{H}^+}$  behavior in the presence of impurity cations, by the difference of direct interaction of cation–cation pairs, is thus ruled out.

The reason these different modes in  $u_{\text{H}^+}$  appear is still not clear, but it is very interesting to compare this with the results of ion exchange affinity and the water content for membranes exchanged with these cations. In membranes exchanged with  $\text{Fe}^{3+}$ , strong interaction between the cation and sulfonic acid site would cause less of a chance for  $\text{H}^+$  to find a site, and also water depletion would result in further retardation of ion transfer in the membrane because of a narrow ion cluster channel.<sup>21</sup> On the other hand, when the membrane is exchanged with  $\text{Cu}^{2+}$ , which is more hydrated than  $\text{Fe}^{3+}$ , there would exist some water that has a high self-exchange rate with the neighboring water around the cation. This, together with the loose binding between  $\text{Cu}^{2+}$  and cation exchange site, could enhance  $\text{H}^+$  hopping by favorable orientation of water around  $\text{H}^+$ .  $\text{Ni}^{2+}$  is the intermediate type and did not interfere with  $\text{H}^+$  movement. Note also that the self-exchange rate of water  $k_w$  around cations increases in the order depending on the cations:  $\text{Fe}^{3+}$  ( $k_w \approx 10^2 \text{ s}^{-1}$ ) <  $\text{Ni}^{2+}$  ( $k_w \approx 10^4 \text{ s}^{-1}$ ) <  $\text{Cu}^{2+}$  ( $k_w \approx 10^8 \text{ s}^{-1}$ ).<sup>22</sup>  $\text{H}^+$  hopping would be favored around cations, which have a high exchange rate of hydration water molecules.

**3.3. Ionic Transference Number in the Membrane.** Ionic transference number of  $\text{H}^+$  in the membrane  $t_{\text{H}^+}$  is plotted against the membrane ionic composition  $x_{HM}$  in Figure 7. The raw data are tabulated in Appendix A. In all cases,  $t_{\text{H}^+}$  decreased largely as  $x_{HM}$  became less than 0.2. The difference in the  $t_{\text{H}^+}$  vs  $x_{HM}$  dependence in Figure 7 for different cation systems in the region  $0 < x_{HM} < 0.2$  can be explained from the conductivity data in Figure 4. The ionic transference number of  $\text{H}^+$  will be larger for membranes mixed with foreign cationic species of which the conductivity is smaller, because the conduction of  $\text{H}^+$  will prevail to that of more slowly moving cations. This can be seen if the following equation for ionic transference



**Figure 7.** Ionic transference number of  $\text{H}^+$  in the membrane  $t_{\text{H}^+}$  for various cationic systems of Nafion 117, plotted against membrane ionic fraction  $x_{HM}$ : ( $\square$ ) H/Fe system; ( $\Delta$ ) H/Ni system; ( $\circ$ ) H/Cu system.



**Figure 8.** Water transference coefficient  $t_{\text{H}_2\text{O}}$  for various cationic systems of Nafion 115, plotted against membrane ionic fraction  $x_{HM}$ : ( $\Delta$ ) H/Ni system; ( $\circ$ ) H/Cu system.

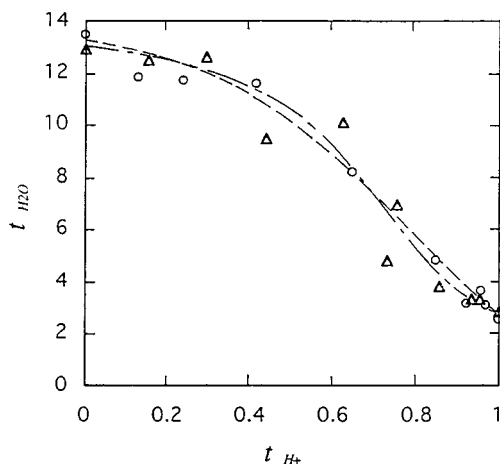
number is taken into account:

$$t_{\text{H}^+} = \frac{x_{\text{HM}} u_{\text{H}^+}}{x_{\text{HM}} u_{\text{H}^+} + x_{\text{AM}_n} u_{\text{A}^{n+}}} \quad (28)$$

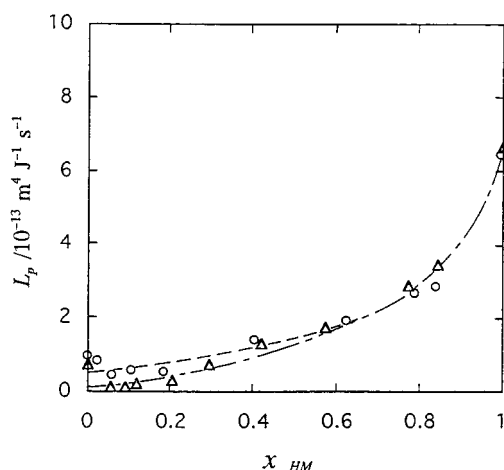
where the smaller denominator results in a larger value of  $t_{\text{H}^+}$ .

However, in the region  $0.2 < x_{HM} < 1.0$ , the trend reverses from that of the region  $0 < x_{HM} < 0.2$ , and the conduction of  $\text{H}^+$  turns smaller by coexistence of more slowly moving cations. This contradiction can be understood by considering the data of cationic mobility in Figure 5. The mobility of  $\text{H}^+$  in the presence of  $\text{Fe}^{3+}$  becomes much smaller than that in the presence of  $\text{Ni}^{2+}$  or  $\text{Cu}^{2+}$ , and this gives rise to smaller  $t_{\text{H}^+}$  because of a smaller numerator in eq 28.

**3.4. Water Transference Coefficient and Water Permeability.** In Figure 8, water transference coefficient  $t_{\text{H}_2\text{O}}$  is shown as a function of membrane ionic composition  $x_{HM}$  for H/Ni and H/Cu systems. The raw data of streaming potential measurements are displayed in Appendix B.  $t_{\text{H}_2\text{O}}$  increased abruptly when  $x_{HM}$  falls short of 0.5. Both systems H/Ni and H/Cu showed almost the same trend in  $t_{\text{H}_2\text{O}}$  vs  $x_{HM}$  curves. For the H/Fe system, the streaming potential was not properly measured due to the irregular transient of emf in the time course. This can be ascribed to the possible presence of precipitates originating from  $\text{Fe}^{3+}$  on the surface or inside the membrane. The same phenomena were observed in the H/Ca system.<sup>14</sup>



**Figure 9.** Water transference coefficient  $t_{H_2O}$  for various cationic systems, as a function of ionic transference number of  $H^+$  in the membrane  $t_{H^+}$ : ( $\Delta$ ) H/Ni system; ( $\circ$ ) H/Cu system.



**Figure 10.** Water permeability  $L_p$  of Nafion 115, plotted against membrane ionic fraction  $x_{HM}$ : ( $\Delta$ ) H/Ni system; ( $\circ$ ) H/Cu system.

Figure 9 shows the plot of  $t_{H_2O}$  against the ionic transference number  $t_{H^+}$  for H/Ni and H/Cu systems. It is interesting to note that  $t_{H_2O}$  does not change linearly with  $t_{H^+}$ , but in the convex manner. This means that the total number of water molecules carried along with cations inside the membrane in mixed cation forms becomes larger than that of the sum of the contribution from individual cations. This is in strong contrast to the case of the H/Ca system, where the total number of water molecules carried along with cations became smaller than that of the sum of the contribution from individual cations.<sup>14</sup> In fact, the former type of dependency of  $t_{H_2O}$  against  $t_{H^+}$  was observed for other membranes in monovalent–divalent mixed cation systems.<sup>23</sup> It is seen in Figure 5 that cations in the membrane interact in several ways, and so do the water molecules surrounding these cations, if these cations coexist in the membrane. The way the amount of water changes by the change in membrane composition, as seen in Figure 2, might have favorably influenced the increase in the amount of water carried along cation movements in mixed cation systems. This may also be considered as a result of the specific microscopic structure of the membrane, where channels connecting ionic cluster domains are common pathways of both water and cations.

The water permeability  $L_p$  of Nafion 115 as calculated from eq 14 is shown in Figure 10 as a function of  $x_{HM}$ .  $L_p$  decreased largely as the impurity cations entered into H-form membranes. It is shown that the diffusion coefficient of water in the

membrane  $D_{H_2O}$  is directly related to  $L_p$ ,<sup>13</sup> and in this context Figure 10 indicates that  $D_{H_2O}$  decreases almost to one-tenth when impurity cations enter into the membrane. This result, together with the increase in  $t_{H_2O}$  by the presence of impurity cations, poses a problem of membrane dehydration when the membrane is contaminated by impurity cations in the fuel cell application.<sup>24,25</sup>

In the system of H/Na and H/Ca,  $D_{H_2O}$  changed proportionally with the membrane water content.<sup>13,14</sup> In the present systems, this parallelism breaks down, as can be observed from comparison of Figures 2 and 10. The reason for this discrepancy is not clear, but it can be assumed that in the case of H/Ni or H/Cu the structure of water of hydration around cations differs from that in the H/Na or H/Ca systems. In membranes containing  $Na^+$  or  $Ca^{2+}$ , the interaction of water around these cations would not go beyond the first hydration shell because of shielding.<sup>21</sup> This would result in rather free movement of water in the membrane. On the other hand, in membranes containing  $Ni^{2+}$  or  $Cu^{2+}$ , the first hydration shell around these cations would be strongly bound with a fixed number of water coordination, and the structure of water is more or less retained beyond the first hydration shell. Then  $L_p$  reduces to a large extent due to large local viscosity when these cations enter into the membrane.

In all cases, the transport characteristics of Nafion membranes will be affected largely by the presence of impurity cations such as  $Fe^{3+}$ ,  $Ni^{2+}$ , and  $Cu^{2+}$ , and the membranes will tend to dry if operated as electrolytes in fuel cells. Because these cations will easily enter into the membrane from surroundings either through air or through stack materials, a special caution should be directed in order to avoid contamination of membranes by these cations.

#### 4. Conclusions

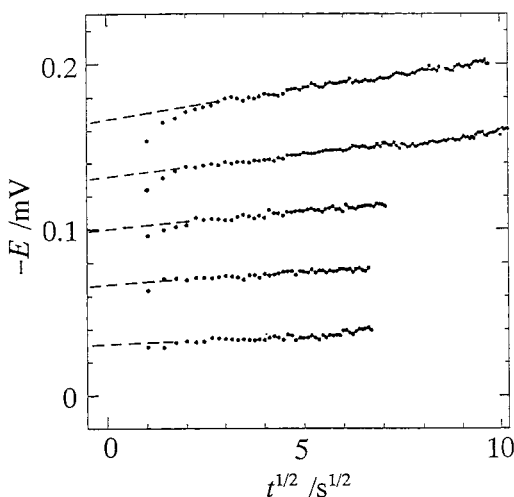
Nafion membranes were investigated for equilibrium and transport properties in the presence of  $Fe^{3+}$ ,  $Ni^{2+}$ , and  $Cu^{2+}$  as impurity cations. The following conclusions were found regarding the effects of impurities by such cations on the membrane performance.

- (1) Impurity cations have a high preference over  $H^+$  in Nafion membranes. The order of preference is  $Fe^{3+} > Ni^{2+} > Cu^{2+}$ .
- (2) The polymer electrolyte membrane is shrunk and the density increases if these multivalent cations are exchanged for  $H^+$  in the membrane.
- (3) If these impurity cations exist in solutions contacting the membrane, the water content  $\lambda$ , the ionic conductivity  $\kappa$ , the ionic transference number of  $H^+$  in the membrane  $t_{H^+}$ , and water permeability  $L_p$  decrease rapidly even if the amount of impurity is small.
- (4) Three modes of effects are found for different kinds of cation pairs in the membrane conductivity vs  $x_{HM}$  behaviors.
- (5) The higher the preference of foreign cations to the membrane, the more rapid the decrease of water content and ionic conductivity in the membrane.
- (6) The transference number of  $H^+$  in the membrane declines rapidly for  $x_{HM} < 0.2$ .
- (7) The water transference coefficient  $t_{H_2O}$  increases rapidly when the amount of impurity is increased.
- (8) Water transport that is coupled to cation transport interacts in a cooperative manner, when two kinds of cations are present in the membrane.

**TABLE 1: Membrane-Contact emf for a Pair of Membranes Contacting Solutions of Different Ionic Compositions at Both Ends<sup>a</sup>**

$x_{\text{HCl}}$	H/Fe system		H/Ni system		H/Cu system	
	$x_{\text{HM}}$	$E/\text{mV}$	$x_{\text{HM}}$	$E/\text{mV}$	$x_{\text{HM}}$	$E/\text{mV}$
0.158		-1.8 <sub>4</sub>	0.04 <sub>5</sub>	-0.8 <sub>9</sub>	0.04 <sub>3</sub>	-3.3 <sub>0</sub>
0.333		-1.7 <sub>8</sub>	0.07 <sub>3</sub>	-0.6 <sub>4</sub>	0.08 <sub>2</sub>	-2.1 <sub>3</sub>
0.529	0.06 <sub>2</sub>	-1.3 <sub>0</sub>	0.10 <sub>8</sub>	0.4 <sub>0</sub>	0.11 <sub>8</sub>	0.0 <sub>7</sub>
0.750	0.15 <sub>0</sub>	-1.0 <sub>0</sub>	0.19 <sub>6</sub>	2.6 <sub>0</sub>	0.20 <sub>6</sub>	1.8 <sub>0</sub>
0.871	0.20 <sub>5</sub>	-0.8 <sub>0</sub>	0.30 <sub>1</sub>	4.0 <sub>5</sub>	0.28 <sub>5</sub>	2.9 <sub>9</sub>
0.934	0.25 <sub>4</sub>	1.7 <sub>0</sub>	0.41 <sub>9</sub>	6.7 <sub>2</sub>	0.41 <sub>7</sub>	4.3 <sub>9</sub>
0.967	0.45 <sub>3</sub>	7.5 <sub>9</sub>	0.58 <sub>6</sub>	8.9 <sub>3</sub>	0.62 <sub>0</sub>	5.6 <sub>9</sub>
0.985	0.73 <sub>9</sub>	10.0	0.77 <sub>3</sub>	9.1 <sub>0</sub>	0.77 <sub>9</sub>	7.7 <sub>9</sub>
0.990	0.82 <sub>8</sub>	11.6	0.84 <sub>1</sub>	10.0	0.83 <sub>1</sub>	7.2 <sub>2</sub>
1.000	1.00	12.4	1.00	9.0 <sub>4</sub>	1.00	7.0 <sub>2</sub>

<sup>a</sup> Reference membrane is contacting the solution of  $x_{\text{HCl}} = 0.529$ . Errors in  $x_{\text{HM}}$ : 0.5 to 3% and errors in  $E$ :  $\pm 0.1$  to  $0.5\text{mV}$ .



**Figure 11.** emf transients at various pressures plotted against the square root of time in the streaming potential measurements. Solution:  $0.02\text{ mol dm}^{-3}\text{ NiCl}_2$ . Applied pressure  $\Delta p$  (top to bottom):  $6.67 \times 10^4$ ,  $5.33 \times 10^4$ ,  $4.00 \times 10^4$ ,  $2.67 \times 10^4$ , and  $1.33 \times 10^4\text{ Pa}$ .

**TABLE 2: Dependence of the Intercept  $a/F$  (V) and the Slope  $b/F$  ( $\text{V s}^{-1/2}$ ) on  $\Delta p$  (Pa) (See eqs 12–14)<sup>a</sup>**

$x_{\text{HCl}}$	H/Ni system		H/Cu system	
	$A/10^{-9}\text{ V Pa}^{-1}$	$B/10^{-11}\text{ V s}^{-1/2}\text{ Pa}^{-1}$	$A/10^{-9}\text{ V Pa}^{-1}$	$B/10^{-11}\text{ V s}^{-1/2}\text{ Pa}^{-1}$
0.000	2.4 <sub>4</sub>	7.2 <sub>1</sub>	2.4 <sub>2</sub>	9.3 <sub>8</sub>
0.158	2.3 <sub>8</sub>	0.93	2.0 <sub>8</sub>	6.2 <sub>8</sub>
0.333	2.3 <sub>6</sub>	0.84	2.0 <sub>7</sub>	2.7 <sub>8</sub>
0.529	1.7 <sub>6</sub>	1.0 <sub>6</sub>	2.0 <sub>8</sub>	2.7 <sub>3</sub>
0.750	1.8 <sub>8</sub>	1.0 <sub>7</sub>	1.5 <sub>3</sub>	1.7 <sub>7</sub>
0.871	1.2 <sub>5</sub>	2.2 <sub>2</sub>		
0.934	0.93	3.6 <sub>0</sub>	0.95	3.6 <sub>4</sub>
0.967	0.66	4.3 <sub>0</sub>	0.63	4.5 <sub>0</sub>
0.985	0.61	6.5 <sub>9</sub>	0.66	6.0 <sub>5</sub>
0.990	0.56	7.8 <sub>1</sub>	0.65	6.3 <sub>4</sub>
1.000	0.50	13. <sub>8</sub>	0.50	13. <sub>8</sub>

<sup>a</sup> A linear relationship exists like  $a = AF\Delta p$  and  $b = BF\Delta p$ , and  $A$  and  $B$  are listed in the table. Errors in  $A$  are 3–7%, and errors in  $B$  are 3–10%.

(9) Transitional metal cations show different behaviors as compared with alkali or alkaline earth metal cations, in their interaction with water in the membrane.

## Appendix A

Data of membrane contact emf for ionic transference number measurements for Nafion 117 membranes of H/Fe, H/Ni, and

H/Cu systems are listed in Table 1, together with membrane composition  $x_{\text{HM}}$ .

## Appendix B

emf vs  $t^{1/2}$  curves in streaming potential measurements are shown in Figure 11 for a Nafion 115 membrane contacting the solution  $0.02\text{ mol dm}^{-3}\text{ NiCl}_2$ . The dependence of the intercept and the slope on the applied pressure difference across the membrane  $\Delta p$  in the emf vs  $t^{1/2}$  curves is given in Table 2. A very good linearity was observed between the intercept or the slope and the pressure difference, in the range  $-6.7 \times 10^4\text{ Pa} < \Delta p < 6.7 \times 10^4\text{ Pa}$ .

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- (26) More precisely, the electrochemical potentials of  $\text{H}^+$  and  $\text{A}^{n+}$  are equated between the membrane and the solution phases, and this results in the additional terms of the interface potential between the membrane and the solution phases to the membrane bulk potential in eq 7. The final form is the same.