

# Membrane transport characteristics of binary cation systems with Li<sup>+</sup> and alkali metal cations in perfluorosulfonated ionomer

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Received 14 June 2004; received in revised form 29 October 2004; accepted 1 January 2005

Available online 10 February 2005

## Abstract

Nafion ionomer membranes were exchanged with series of pair of cation mixtures between Li<sup>+</sup> and other alkali metal cations, and investigated for equilibrium and transport characteristics of ion and water. Samples were prepared by equilibrating the membranes in the mixtures of LiCl and alkali chloride in aqueous solutions of various mixing ratios. The alkali metal cations, especially those of larger atomic number, revealed higher affinity to sulfonic acid groups than Li<sup>+</sup>, but less water content and higher density of the membrane. It was found that the mobility of cations followed the order of Li<sup>+</sup> < Na<sup>+</sup> > K<sup>+</sup>, Rb<sup>+</sup> > Cs<sup>+</sup>. Concentration of sulfonic acid group increased, when Li<sup>+</sup> was exchanged with other cations, but ionic mobility of each cation was affected differently by the other cations in the mixed state. The interaction between Li<sup>+</sup> and alkali metal cation appeared to be larger for Li/Rb and Li/Cs systems than for Li/Na and Li/K systems, but as long as the ionic transference numbers are concerned, a pair of cations moved independent of each other. The water transference coefficient (electro-osmosis drag coefficient) of Li<sup>+</sup> was ca. 15, but decreased to 10 for Na<sup>+</sup> and even less when other alkali metal cations existed. In the mixed systems, Li<sup>+</sup> and alkali metal cations showed tendency to drag more water molecules than in the individual ions, which indicated that ionic conductivity decreases when cations are coexisting in the membrane.

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**Keywords:** Ion; Water; Conductivity; Perfluorosulfonated membrane; Fuel cell

## 1. Introduction

Perfluorosulfonic acid polymer electrolyte membranes have gained a lot of research interests in the field of chlor-alkali electrolysis, water electrolysis, polymer electrolyte fuel cells, and so on [1,2]. The membranes show unique characteristics with regard to the ion and water transport, especially in binary cation systems. Binary cation systems including H<sup>+</sup> and other cations were studied extensively because these are found to provide more information than in the single cation systems [3–8]. In the membrane H<sup>+</sup> was transported mainly

by hopping mechanism (Grotthuss mechanism [9]), and the second cations affected the H<sup>+</sup> transport by way of existing water molecules [7,8].

The case of two cation mixtures where vehicle transport [10] is the major process would be very interesting because the characteristics of these systems would be strongly dependent on the size of cations and surrounding water molecules, and hence provide information about the ion–ion, ion–water and ion–polymer interactions. In this sense, the ion exchange or the membrane transport characteristics would be more relevant to the polymer structure, and such knowledge would be very useful in establishing polymer design concepts for practical applications. For example, new polymer membranes of desired characteristics would be achieved when ion transport mechanism is established.

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To this end, the transport and equilibrium properties of perfluorosulfonic acid polymer membranes are studied for Li/Na, Li/K, Li/Rb and Li/Cs binary cation systems, in a systematic way. The data are compared with those of H<sup>+</sup> and alkali cation systems, which were reported previously [8].

## 2. Experimental

### 2.1. Membrane preparation

Nafion 115 and 117 (DuPont, Polymer Products Department, Wilmington, DE, USA, nominal equivalent weight EW = 1100 g eq<sup>-1</sup>) membranes were cut into 25 mm × 25 mm pieces, pretreated first in 2% H<sub>2</sub>O<sub>2</sub> at 80 °C for 2 h, immersed in 0.1 mol dm<sup>-3</sup> HCl for 24 h, and finally rinsed with pure water.

ACl (A = Li, Na, K, Rb and Cs) were of reagent grade from Wako Pure Chemical Industries Ltd., Osaka, Japan, and used without further purification. Mixtures of LiCl and ACl solutions were prepared with various kinds of molar composition of LiCl,  $x_{\text{LiCl}} = 0.000, 0.0625, 0.158, 0.333, 0.529, 0.750, 0.871, 0.934, 0.967, 0.985, \text{ and } 1.000$ , using deionized water by Milli-Q system (conductivity < 10<sup>-7</sup> Ω<sup>-1</sup> cm<sup>-1</sup>). The total concentration was fixed to 0.03 mol dm<sup>-3</sup>. Membranes were equilibrated in LiCl/ACl solutions of various compositions at 25 °C. During equilibration, solutions were renewed at least four times.

### 2.2. Membrane cationic composition, density and water content

The ionic composition (cationic site fraction) of Li<sup>+</sup> in the membrane,  $x_{\text{LiM}}$  (where M denotes the cation exchange site), is defined by the amount of Li<sup>+</sup> ion divided by that of total cation species in the membrane. The membrane element compositions in dry state were measured using a Seiko Electric Co. model SEA2010 X-ray fluorescence spectroscopic analyzer, where spectral intensity was counted for elements A (A = K, Rb, Cs), S and Cl. Element Cl was only within the error amount, and was not further analyzed.  $x_{\text{LiM}}$  is calculated from the atomic ratio [A]/[S] in the spectra:

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

where [A] and [S] are the intensities of the elements A and S in the spectra, and the value in the denominator means the ratio [A]/[S] at  $x_{\text{LiCl}} = 0$ . For the Na<sup>+</sup> content determination in the Li/Na-form membrane, EPMA (electron probe micro-analysis) was carried out using Eq. (1). A JEOL electron probe micro-analyzer model JXA-8800M was used to obtain the energy dispersion spectra. The membrane samples were deposited with thin layer of carbon in order to prevent the electric charging.

The membrane water content  $\lambda$  was determined by measuring the weight of membrane in wet state ( $W_{\text{wet}}$ ) and dry state ( $W_{\text{dry}}$ ). For the dry state, samples were dried in vacuum at room temperature for 24 h and then in vacuum at 110 °C for 12 h. The water content was calculated as the number of water molecules per cationic site  $\lambda \equiv n_{\text{H}_2\text{O}}/n_{\text{SO}_3^-}$ :

$$\lambda = \frac{(W_{\text{wet}} - W_{\text{dry}})EW'}{18W_{\text{dry}}} \quad (2)$$

where EW' is the equivalent weight value corrected for the exchanged cations A<sup>+</sup> in place of Li<sup>+</sup> (atomic weight 6.94),  $M_{\text{A}}$  being the atomic weight of the element A:

$$EW' \equiv EW + (6.94 - 1.01) + (M_{\text{A}} - 6.94)(1 - x_{\text{LiM}}) \quad (3)$$

Original EW is defined for H-form membrane, and is 1100 for present membranes.

Volume fraction of water  $\theta$  was calculated from the equation:

$$\theta = \frac{V_{\text{wet}} - V_{\text{dry}}}{V_{\text{wet}}} \quad (4)$$

where  $V_{\text{wet}}$  and  $V_{\text{dry}}$  are the volume of the membrane sample as measured by a micrometer in wet and dry states, respectively.

The density of the membrane in wet state,  $d_{\text{wet}}$  (g cm<sup>-3</sup>) was obtained by dividing the weight of the wet membrane by its volume:

$$d_{\text{wet}} = \frac{W_{\text{wet}}}{V_{\text{wet}}} \quad (5)$$

### 2.3. Membrane conductivity

The impedance of Nafion 117 membrane was measured in the lateral direction with a Solartron S-1260 frequency response analyzer (Solartron Instruments, UK) at 25 °C, using the Teflon cell as described elsewhere [11]. This cell was similar to that used by Zawodzinski et al. [12], except that the electrode was black-platinized Pt foil contacting the membrane on each of the two sides with 10 mm width and 5 mm separation. The membrane was in contact with equilibrating solution by way of a 10 mm × 5 mm window on each side. The specific conductivity of the membrane  $\kappa$  (S cm<sup>-1</sup>) was obtained from the real part of the impedance  $R$  (Ω) of the membrane:

$$\kappa = \frac{s}{Rwl} \quad (6)$$

where  $w$  is the width of the electrode (cm),  $s$  the separation of a pair of electrodes contacting the membrane (cm) and  $l$  the thickness (cm) of the membrane.  $l$  was measured for a membrane sandwiched with two Teflon sheets, with a micrometer where the accuracy was 0.0002 cm.

#### 2.4. Ionic transference number

The ionic transference numbers  $t_{\text{Li}^+}$  and  $t_{\text{A}^+}$  of  $\text{Li}^+$  and  $\text{A}^+$  in the membrane, respectively, were determined by the membrane-contact emf (electromotive force) method [13], using a Teflon cell at 25 °C, as described before [5]:

$$t_{\text{Li}^+} = x_{\text{LiCl}} - (1 - x_{\text{LiCl}}) \frac{d \Delta \phi}{d \Delta \mu_{\text{LiCl}}} \quad (7)$$

where  $\Delta \phi \equiv EF$  ( $\text{J mol}^{-1}$ ),  $E$  is the membrane-contact emf (V),  $F$  the Faraday, and  $\Delta \mu_{\text{LiCl}}$  ( $\text{J mol}^{-1}$ ) the difference in the chemical potentials of LiCl in two solutions contacting the membranes. 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. Emfs were measured by an electrometer after steady values were reached.

Mobility of ions in the membrane  $u_i$  ( $\text{m}^2 \text{V}^{-1} \text{s}^{-1}$ ) is obtained from the following equation [6]:

$$u_{\text{Li}^+} = \frac{t_{\text{Li}^+} \kappa}{Fc_{\text{SO}_3^-} x_{\text{LiM}}} \quad (8)$$

$$u_{\text{A}^{n+}} = \frac{(1 - t_{\text{Li}^+}) \kappa}{Fc_{\text{SO}_3^-} (1 - x_{\text{LiM}})} \quad (9)$$

The concentration of sulfonic acid group in the membrane,  $c_{\text{SO}_3^-}$ , is expressed as follows:

$$c_{\text{SO}_3^-} = \frac{d_{\text{dry}}}{(\text{EW}' \chi_{\text{V}})} \quad (10)$$

where  $\chi_{\text{V}}$  is the ratio of membrane volume between wet and dry states.

#### 2.5. Water transference coefficient

Water transference coefficient  $t_{\text{H}_2\text{O}}$  was obtained from the streaming potential measurements for Nafion 115 membranes [14]. The experiments were performed for each membrane in contact with deaerated equilibrating solutions on both sides, using computer-aided homemade apparatus at 25 °C [15]. A differential pressure  $\Delta p$  was applied across the membrane, and the potential difference (emf) was measured using a pair of Ag/AgCl electrodes. Pressure source was  $\text{N}_2$  gas with a pressure control by model 250C-1-D of MKS Instruments, Inc., USA. Thereby emf was plotted against square root of time [14]:

$$EF = a - b\sqrt{t} \quad (11)$$

where the intercept of the plot is given as follows:

$$a = -(t_{\text{Li}^+} V_{\text{LiCl}} + t_{\text{A}^+} V_{\text{ACl}} + t_{\text{H}_2\text{O}} V_{\text{H}_2\text{O}} + \Delta V_{\text{el}}) \Delta p \quad (12)$$

where  $V_i$  ( $\text{cm}^3 \text{mol}^{-1}$ ) is the molar volume of species  $i$  and  $\Delta V_{\text{el}} \equiv V_{\text{Ag}} - V_{\text{AgCl}}$ . The following values were used

for calculation [16]:  $V_{\text{LiCl}} = 17.3$ ,  $V_{\text{NaCl}} = 16.9$ ,  $V_{\text{KCl}} = 27.0$ ,  $V_{\text{RbCl}} = 32.3$ ,  $V_{\text{CsCl}} = 39.5$ ,  $V_{\text{H}_2\text{O}} = 18.0$ , and  $\Delta V_{\text{el}} = -15.5$ .

#### 2.6. Analysis of membrane equilibrium parameters

The thermodynamic equilibrium constant  $K_{\text{th}}$  for the cation exchange reaction  $\text{LiCl}(\text{aq}) + \text{AM} = \text{ACl}(\text{aq}) + \text{LiM}$ , is defined as follows [17]:

$$K_{\text{th}} = \frac{a_{\text{ACl}} a_{\text{LiM}}}{a_{\text{LiCl}} a_{\text{AM}}} = K' \frac{\gamma_{\text{LiM}}}{\gamma_{\text{AM}}} \quad (13a)$$

$$K' \equiv \frac{a_{\text{ACl}} x_{\text{LiM}}}{a_{\text{LiCl}} x_{\text{AM}}} \quad (13b)$$

where  $a_{\text{LiCl}}$  and  $a_{\text{ACl}}$  are the activity of LiCl and ACl in the solution, and  $\gamma_{\text{LiM}}$  and  $\gamma_{\text{AM}}$  the activity coefficients of LiM and AM in the membrane, respectively. The chemical potential of species  $i$  is  $\mu_i = \mu_i^0 + RT \ln a_i$  and  $\mu_i^0$  is that for the standard state. Then it is written:

$$\Delta \mu_{\text{LiM}} + \Delta \mu_{\text{ACl}} - \Delta \mu_{\text{LiCl}} - \Delta \mu_{\text{AM}} = RT \ln K_{\text{th}} \quad (14)$$

where  $\Delta \mu_i \equiv \mu_i - \mu_i^0 = RT \ln a_i$ .

Consider the Gibbs energy change  $\Delta G_{\text{mix}}$  of mixing  $x_{\text{LiM}}$  moles of LiM and  $x_{\text{AM}}$  moles of AM in the standard states to make a mixture of Li/A-form membrane:

$$\Delta G_{\text{mix}} = x_{\text{LiM}} \Delta \mu_{\text{LiM}} + (1 - x_{\text{LiM}}) \Delta \mu_{\text{AM}} \quad (15)$$

Differentiating Eq. (15) with respect to  $x_{\text{LiM}}$  results in, with Eqs. (13) and (14)

$$\frac{d \Delta G_{\text{mix}}}{d x_{\text{LiM}}} = RT \ln K_{\text{th}} - RT \ln K' + RT \ln \frac{x_{\text{LiM}}}{x_{\text{AM}}} \quad (16)$$

According to the cell model of LiM and AM system 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 [18]:

$$\Delta S_{\text{mix}} = -R(x_{\text{LiM}} \ln x_{\text{LiM}} + x_{\text{AM}} \ln x_{\text{AM}}) \quad (17)$$

$$\Delta H_{\text{mix}} = b x_{\text{LiM}} x_{\text{AM}} \quad (18)$$

where  $b$  is constant expressing the energy change of interaction between cation pairs through the mixing process. Hence

$$\frac{d \Delta H_{\text{mix}}}{d x_{\text{LiM}}} = RT(\ln K_{\text{th}} - \ln K') = b(1 - 2x_{\text{LiM}}) \quad (19)$$

Plotting  $\ln K'$  against  $x_{\text{LiM}}$  would give the values of  $b$  and  $K_{\text{th}}$  [19].

### 3. Experimental results

#### 3.1. Membrane composition

Fig. 1 shows the membrane composition  $x_{\text{LiM}}$  as a function of the contacting solution composition  $x_{\text{LiCl}}$ , for membranes exchanged with four kinds of cation systems, Li/Na, Li/K, Li/Rb and Li/Cs. It is seen that  $\text{Li}^+$  in Nafion membrane was preferentially exchanged with any kind of alkali

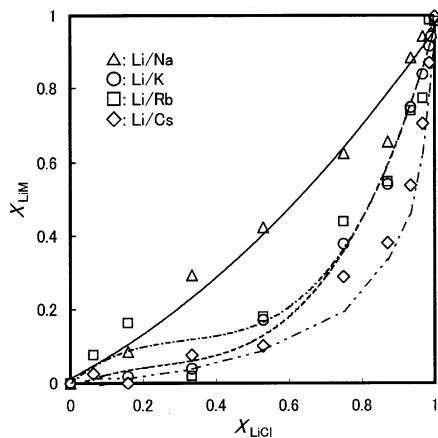


Fig. 1. Membrane ionic fraction  $x_{LiM}$  at equilibrium state vs. solution composition  $x_{LiCl}$  for Nafion 117 at 25 °C. ( $\Delta$ ) Li/Na system; ( $\circ$ ) Li/K system; ( $\square$ ) Li/Rb system; ( $\diamond$ ) Li/Cs system.

cations tested. Generally, cations of higher atomic number have higher affinity to the membrane than those of lower ones. The equilibrium constant  $K_{ex}$  of the exchange reaction between the solution phase and the membrane phase,  $LiCl(aq) + AM = ACl(aq) + LiM$  ( $A = Na, K, Rb, Cs$ ), is defined as follows:

$$K_{ex} = \frac{x_{ACl} \cdot x_{LiM}}{x_{LiCl} \cdot x_{AM}} \quad (20)$$

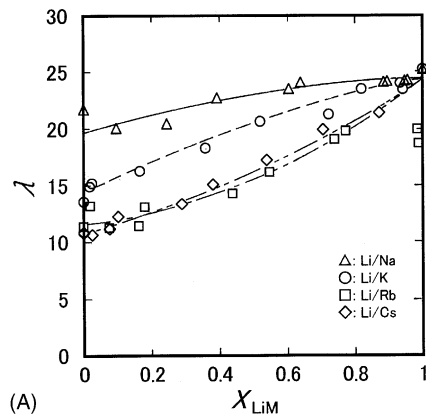
$K_{ex}$  is calculated to be  $0.46 \pm 0.16$  for Li/Na,  $0.15 \pm 0.05$  for Li/K,  $0.17 \pm 0.08$  for Li/Rb, and  $0.11 \pm 0.03$  for Li/Cs systems.

Fig. 2(A) and (B) shows the water content  $\lambda$  and volume fraction of water  $\theta$  in the membrane as a function of membrane ionic composition  $x_{LiM}$  for various kinds of cation systems. Both  $\lambda$  and  $\theta$  decreased by the presence of  $Na^+$ ,  $K^+$ ,  $Rb^+$  and  $Cs^+$  cations. Especially in the case of  $Rb^+$  and  $Cs^+$ , both parameters decreased to half of Li-form membrane. Comparison with the result of membrane cationic compositions in Fig. 1 indicates the trend, that when the membrane is exchanged with cations of higher affinity, lower water content results in.

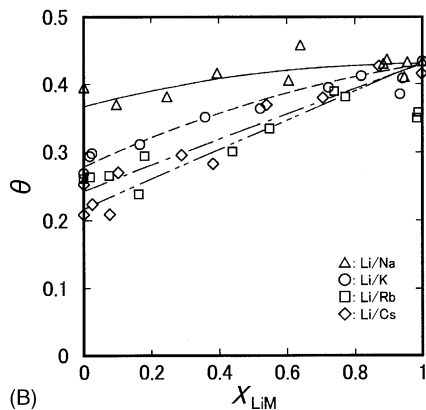
In Fig. 3, the density of the membrane in the wet state is shown against the membrane composition  $x_{LiM}$ . The density increased when the composition of  $Li^+$  decreased, and this trend was larger in the order of systems  $Li/Na < Li/K < Li/Rb < Li/Cs$ , which is just the opposite of the order in water content.

### 3.2. Membrane ionic conductivity

The membrane specific conductivity  $\kappa$  is plotted against the membrane composition  $x_{LiM}$  in Fig. 4. The membrane conductivity in pure alkali metal form was in the order:  $\kappa(Na), \kappa(K) > \kappa(Li), \kappa(Rb) > \kappa(Cs)$ . This trend was in accordance to the previous results about the single cation form membrane systems [11].



(A)



(B)

Fig. 2. (A) Membrane water content  $\lambda \equiv n_{H_2O}/n_{SO_3^-}$  and (B) the volume fraction of water  $\theta$  plotted against membrane ionic fraction  $x_{LiM}$  for Nafion 117. Symbols are the same as in Fig. 1.

The mobilities of cations calculated using Eqs. (8) and (9) together with the data of ionic transference numbers (see below) are plotted in Fig. 5(A) and (B), as a function of membrane composition  $x_{LiM}$ . The mobility of  $Li^+$  cation,  $u_{Li^+}$ , was affected differently by the presence of the other alkali metal cations in the membrane. In the presence of  $Na^+$ ,  $u_{Li^+}$  increased but in the presence of  $Rb^+$ , it decreased.  $K^+$  did not alter  $u_{Li^+}$ . For the mobilities of the other alkali metal cations,

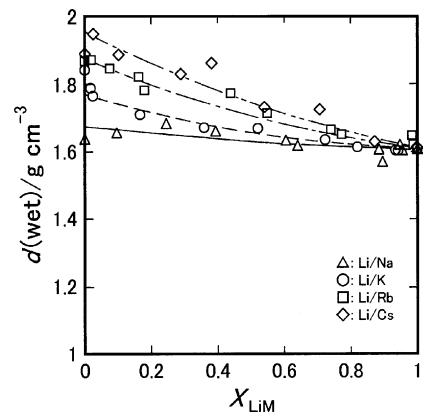


Fig. 3. Density of the Nafion 117 membrane in wet state plotted against membrane ionic fraction  $x_{LiM}$ . Symbols are the same as in Fig. 1.

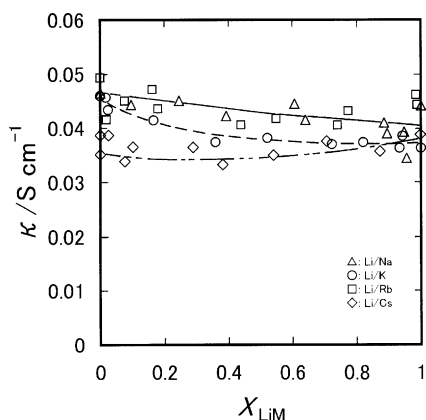
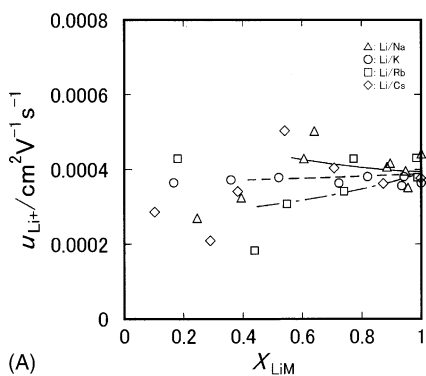


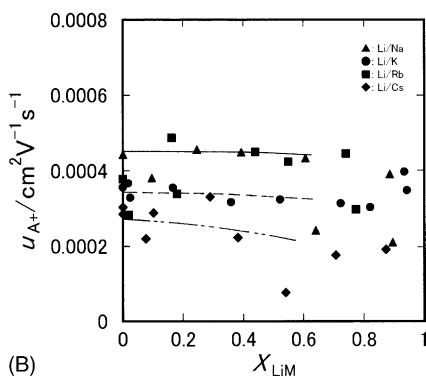
Fig. 4. Membrane ionic conductivity  $\kappa$  in fully hydrated state plotted against membrane ionic fraction  $x_{LiM}$  for Nafion 115. Symbols are the same as in Fig. 1.

those of  $Na^+$ ,  $K^+$  and  $Rb^+$  remained almost unchanged, but the mobility of  $Cs^+$  appeared to decrease slightly by the presence of  $Li^+$ .

On the other hand, the concentration of sulfonic acid groups in the membrane,  $c_{SO_3^-}$ , as calculated from Eq. (10) increased almost in all the cases as the  $Li^+$  content decreased. This result is in accordance with the density of the membrane,



(A)



(B)

Fig. 5. Mobility of cationic species in the membrane plotted against membrane ionic fraction  $x_{LiM}$ . (A) Mobility of  $Li^+$  in Li/Na system ( $\Delta$ ); Li/K system ( $\circ$ ); Li/Rb system ( $\square$ ); Li/Cs system ( $\diamond$ ). (B) Mobility of  $Na^+$  in Li/Na system ( $\blacktriangle$ );  $K^+$  in Li/K system ( $\bullet$ );  $Rb^+$  in Li/Rb system ( $\blacksquare$ );  $Cs^+$  in Li/Cs system ( $\blacklozenge$ ).

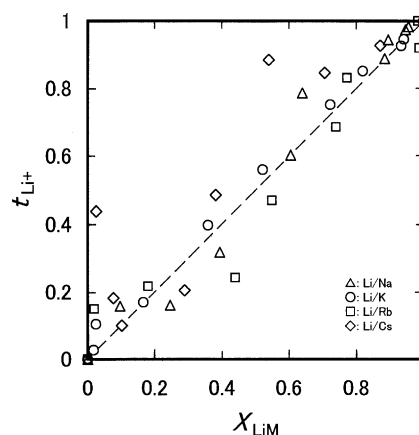


Fig. 6. Ionic transference number of  $Li^+$  in the membrane  $t_{Li^+}$  for various cationic systems of Nafion 117, plotted against membrane ionic fraction  $x_{LiM}$ . Symbols are the same as in Fig. 1.

$d_{wet}$ , indicating that the membrane shrinkage caused the increase in the anionic site density.

### 3.3. Ionic transference number in the membrane

Fig. 6 depicts the ionic transference number of  $Li^+$  in the membrane  $t_{Li^+}$ , plotted against the membrane ionic composition  $x_{LiM}$ . The difference in the  $t_{Li^+}$  versus  $x_{LiM}$  dependence for different cation systems was small, and  $t_{Li^+}$  decreased almost linearly with decreasing  $x_{LiM}$ .

### 3.4. Water transference coefficient

In Fig. 7, water transference coefficient  $t_{H_2O}$  is plotted as a function of the ionic transference number  $t_{Li^+}$ .  $t_{H_2O}$  changed in different ways with  $t_{Li^+}$ , depending on the alkali metal cations. For the Li/Na system,  $t_{H_2O}$  changed almost linearly with  $t_{Li^+}$ , but for Li/K and Li/Rb systems, convex curves appeared.

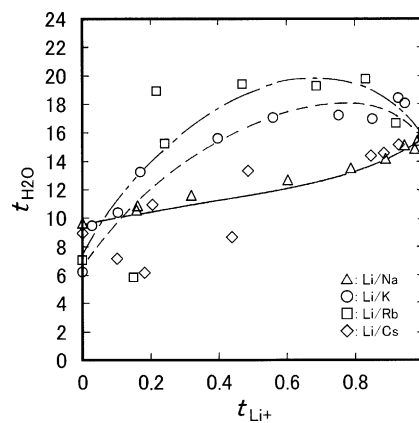


Fig. 7. Water transference coefficient  $t_{H_2O}$  vs. ionic transference number of  $Li^+$  in the membrane  $t_{Li^+}$  for various cationic systems. Symbols are the same as in Fig. 1.

Table 1  
Cation interactions in Nafion membranes

Systems	$K_{\text{ex}}$	$K_{\text{th}}$	$b$ (J mol <sup>-1</sup> )	$K_{\text{ex}}$ (calc.)	$K_{\text{th}}$ (calc.)
Li/Na	0.46	0.52	-202	0.39	0.45
Li/K	0.15	0.17	-175	0.14	0.18
Li/Rb	0.17	0.19	-768	0.11	0.12
Li/Cs	0.11	0.095	-288	0.076	0.097

$K_{\text{ex}}$ : equilibrium constant of the exchange reaction;  $K_{\text{th}}$ : thermodynamic equilibrium constant;  $b$ : constant expressing the interaction between Li<sup>+</sup> and A<sup>+</sup> (A<sup>+</sup> = Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup>) as compared with the Li<sup>+</sup>-Li<sup>+</sup> and A<sup>+</sup>-A<sup>+</sup> pairs in the membrane (see Eq. (18)).  $K_{\text{ex}}$  (calc.) and  $K_{\text{th}}$  (calc.) are calculated values from the H/A (A = Li, Na, K, Rb, Cs) systems [8].

#### 4. Discussion

It should be noted that there would be a difference in transport mechanisms between H<sup>+</sup> and other alkali metal cations. For H<sup>+</sup> Grotthuss (hopping) mechanism may prevail owing to the hydrogen bond formation, but for alkali metal cations vehicle mechanism should occur. So interesting point is that unlike the case of binary cation systems with H<sup>+</sup> and alkali metal cations [8], some specific feature would be observed for Li<sup>+</sup> and other alkali metal cation systems. The similarity of H<sup>+</sup> and Li<sup>+</sup> in terms of water content and affinity to sulfonic acid group is another interesting point to compare Li<sup>+</sup> and alkali metal cation systems in relation to H<sup>+</sup> and alkali metal cation systems [8].

The mobility of the cation may be affected by the water content or the volume fraction of water in the membrane [8]. The larger is the domain of ion conducting path, the higher will be the ionic mobility [20]. The results of water content and membrane density in Figs. 2(A) and 3 infer that membranes tend to shrink when they are exchanged with K<sup>+</sup>, Rb<sup>+</sup> or Cs<sup>+</sup> cations. These cations are less hydrophilic than Li<sup>+</sup>, and fewer amount of water molecules are brought inside the membrane, resulting in smaller volume of hydrophilic domains.

The concentration of the sulfonic acid groups  $c_{\text{SO}_3^-}$  is another factor to be considered. In almost all cases,  $c_{\text{SO}_3^-}$  increased when other alkali metal cations are added to the Li-form membrane. This may be a consequence of the decrease in water content and the membrane shrinkage, and with too low  $\lambda$  the chance of ion pair formation between cations and sulfonic acid groups may increase. Note the case of H<sup>+</sup> conductivity in membranes of different EW values, where increased ion exchange capacity did not result in the increase in  $c_{\text{SO}_3^-}$  [21]. In this case increased anionic site number brought about the increased water content, and as a result  $c_{\text{SO}_3^-}$  was almost unchanged. Here larger ion exchange capacity brought about the increase in H<sup>+</sup> conductivity, not by the increased concentration of the sulfonic acid groups but by the increased mobility of H<sup>+</sup> ions [21].

In  $K'$  is plotted against  $x_{\text{LiM}}$  in Fig. 8 for Li/Na, Li/K, Li/Rb and Li/Cs-form membrane systems, which resulted in straight lines. The slopes and intercepts in Fig. 8 give values of  $K_{\text{th}}$  and  $b$  as calculated using Eq. (19). The results are shown in Table 1.  $K_{\text{th}}$  is a measure of the interaction between

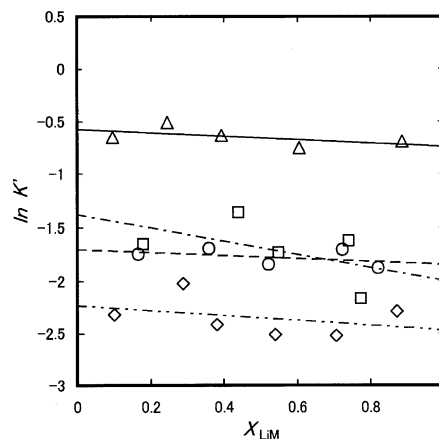


Fig. 8. Relations between  $\ln K'$  and the membrane ionic fraction  $x_{\text{LiM}}$ . Symbols are the same as in Fig. 1.

cations and sulfonic acid groups. When Li<sup>+</sup> has higher affinity to sulfonic acid group than A<sup>+</sup> does,  $K_{\text{th}}$  becomes larger, which conforms well to the results in Fig. 1. Also  $b$  is the measure of interactions between Li<sup>+</sup> and A<sup>+</sup> as compared with the Li<sup>+</sup>-Li<sup>+</sup> pairs and A<sup>+</sup>-A<sup>+</sup> pairs. From  $b$  values it is indicated that there is very little difference in interactions between Li/Na and Li/K cations. This might be accounted for by the large number of water molecules surrounding these cations.

On the other hand, for Li/Rb and Li/Cs pairs, mixed state is favored as compared with separated states of Li<sup>+</sup>-Li<sup>+</sup> pairs and A<sup>+</sup>-A<sup>+</sup> pairs. Note that the amount of water brought in the membrane by Li<sup>+</sup> cation is rather large, and the repulsive force between a pair of alkali metal cations Li<sup>+</sup>-A<sup>+</sup> would be mitigated. For the systems Li/Rb and Li/Cs, water content is low and the polymer structure tends to shrink. Fig. 1 infers repulsion of Rb<sup>+</sup> or Cs<sup>+</sup> cations when the population of Li<sup>+</sup> ion is low. In this case the repulsive force between Li<sup>+</sup> and A<sup>+</sup>, would be smaller than the force between Li<sup>+</sup>-Li<sup>+</sup> or A<sup>+</sup>-A<sup>+</sup> averaged for the mixed state because of intervening water molecules between Li<sup>+</sup> and A<sup>+</sup>.

Table 1 also shows the calculated values of  $K_{\text{ex}}$  and  $K_{\text{th}}$  using the following relationship:

$$K_{\text{ex}}(\text{Li}/\text{A}) = \frac{X_{\text{ACl}}X_{\text{LiM}}}{X_{\text{LiCl}}X_{\text{AM}}} = \frac{K_{\text{ex}}(\text{H}/\text{A})}{K_{\text{ex}}(\text{H}/\text{Li})}, \text{ etc.} \quad (21)$$

where  $K_{\text{ex}}(\text{H}/\text{A})$  represents the equilibrium constant of the exchange reaction  $\text{HCl}(\text{aq}) + \text{AM} = \text{ACl}(\text{aq}) + \text{HM}$  (A = Li, Na, K, Rb, Cs), and is obtained from the previous results for H/Li, H/Na, H/K, H/Rb and H/Cs systems [8]. The discrepancy between values of  $K_{\text{ex}}$  or  $K_{\text{th}}$  in the present system and the calculated values would come from the difference in environments, especially the water content, because in the present case the change in  $\lambda$  is larger in the middle range of  $x_{\text{LiM}}$  as compared to the previous systems.

It seems that there exist some interactions between cations and water molecules in the membrane. Fig. 7 reveals that in the case of Li/K and Li/Rb systems, the amount of water dragged is larger in the mixed state than in the single cation

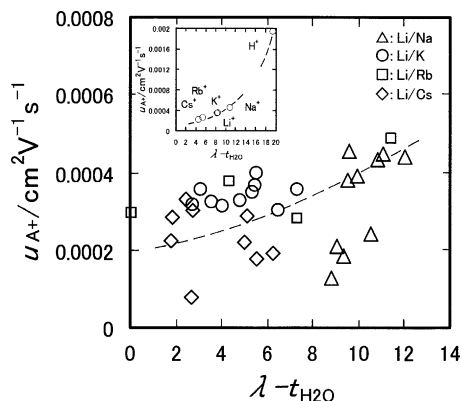


Fig. 9. Cation mobilities in the membrane plotted as a function of the parameter  $\lambda - t_{\text{H}_2\text{O}}$  obtained for various cation mixtures. The inset shows the plots calculated from Table 2 of Ref. [8].

form, in contrast to the case of Li/Na system. The concave curve in the membrane conductivity against the membrane composition for Li/K, as seen in Fig. 4, would thus be explained by the amount of dragged water in relation to the membrane water content. The reason why the interaction of water with cations in the mixed state is enhanced needs further investigation, because this is a rather rare case [7].

Fig. 9 expresses the relationship between the cation mobility and the parameter  $\lambda - t_{\text{H}_2\text{O}}$  obtained for various cation mixtures. The inset shows the similar plots as obtained separately in H-form and alkali metal cation form membranes [8]. There is observed a good correlation in the figure, which means that it is mainly the amount of water not moving with cations that determines the membrane conductivity [20]. Previous results with the  $\text{H}^+$  and alkali metal cation systems show that the size of hydrated cations in relation to the size of ionic channel determines the ionic mobility of cations in the membrane [8]. The mobility of alkali metal cations in Fig. 5 changed in the following order:  $\text{Li}^+ < \text{Na}^+ > \text{K}^+$ ,  $\text{Rb}^+ > \text{Cs}^+$ , which was just the order of the largeness of the parameter  $\lambda - t_{\text{H}_2\text{O}}$  [8]. Larger amount of water not moving with cations means the easiness of ion path formation [20], and this would result in the higher mobility of the cation.

The same tendency is observed for the system where membranes of different EW value are used [21]. In the case where cations move by vehicle mechanism through channel structure, it appears that the friction force acting on cations would be the factor together with electrostatic force between cations and sulfonic acid groups that determines the cation mobility.

## 5. Conclusions

The equilibrium and transport characteristics of Nafion membranes were investigated with the binary cation systems of  $\text{Li}^+$  and several kinds of alkali metal cations. The followings were found regarding the effects of interactions by such

cations and water molecules on the membrane characteristics:

- (1) Alkali metal cations have higher preference over  $\text{Li}^+$  in Nafion membranes.
- (2) The polymer electrolyte membrane shrinks and the density increases if the alkali metal cations  $\text{Rb}^+$  and  $\text{Cs}^+$  are exchanged for  $\text{Li}^+$  in the membrane.
- (3) When less hydrophilic cations like  $\text{Rb}^+$  or  $\text{Cs}^+$  are mixed with  $\text{Li}^+$ , repulsion between cations will be mitigated because  $\text{Li}^+$  has a large amount of water sheath. Then these cations have a tendency to mix with  $\text{Li}^+$  rather than to be separated each other.
- (4) The cationic conductivity in the membrane is determined by two major factors: one is the amount of residing water in the ionic channel, and the other is the interaction between cations and sulfonic acid groups. These factors should be of significant criteria in considering the microstructural designing of high performance polymer membranes.

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