Pergamon

Electrochimica Acta, Vol. 43, No. 24, pp. 3741–3747, 1998

Printed in Great Britain
PII: S0013-4686(98)00132-7
0013–4686/98 $19.00 + 0.00

Ion and water transport characteristics of Nafion membranes as electrolytes

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(Received 15 October 1997; in revised form 2 January 1998)

Abstract—Transport characteristics of Nafion membranes, that have been published earlier, are re-evaluated. It is found that the specific conductivity of the membranes is not only determined by the mobility of the ions, but largely also by the interaction of ions with water and with microscopic membrane channel structures. Similarly, the water transference coefficient, defined as the number of moles of water transported per Faraday through the membrane, is governed by two effects: an electrostatic effect between ion and water dipoles, and an effect due to the size of the cation. Contributions to electro-osmotic water transfer are water of hydration to cations and hydrodynamically pushed water molecules. The size of the ion compared to the channel diameter, has a major impact on the electric conductivity, but also on water transport. It is shown that hydrophilic cations can promote an enlarged hydrophilic domain in the membrane, that is accompanied by a lower membrane resistance. Criteria for designing high performance ion conducting membranes are given based on this basis. © 1998 Elsevier Science Ltd. All rights reserved

Key words: polymer electrolyte fuel cell, membrane, transport, ion, water.

INTRODUCTION

Perfluoro-sulfonated cation exchange membranes have been used as electrolyte in polymer electrolyte fuel cells, because of their high ionic conductivity as well as mechanical, thermal and chemical stability [1, 2]. The membrane ionic conductivity is especially important: it should be as high as possible to keep small the resistance losses and to maintain high output power density in the cell [3–5]. The membrane specific conductivity is strongly influenced by the water content [6], so water management is also a crucial problem for fuel cell operation [7–13].

The membrane state of hydration is determined by the flux equation of water in the membrane. When the direction of transport across the membrane is the x-direction, we have [13]:

$$j_{H_2O} = -D_{H_2O}\frac{\partial c_{H_2O}}{\partial x} + \frac{I t_{H_2O}}{F} \qquad (1)$$

Here j_{H_2O} is the water flux, I the electric current density, c_{H_2O} the concentration of water, D_{H_2O} the diffusion coefficient of water, t_{H_2O} the water transference coefficient and F is Faraday's constant. Experimental determination of the transport parameters, D_{H_2O} and t_{H_2O}, has been considered of major importance for fuel cell operations, and many efforts have been devoted to their determination [14–21].

In this paper, published data of D_{H_2O} and t_{H_2O}, are re-evaluated together with recent data of ionic mobility and equilibrium results. Nafion membranes exchanged with single and with binary cation systems have been studied, for various kinds of cations. Elucidation of some general rules for the mechanism of ion transport is attempted, especially with the emphasis on the interaction with water in the polymer microscopic structures. The amount of

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*Author to whom correspondence should be addressed. Fax: +81 29 8544678; E-mail: tokada@ccmail.nimc.go.jp water present in the channels seems more important for good ionic conductivity, than earlier believed. On the background of this result we are able to give better criteria for the design of new polymer electrolytes with high performances.

The overview of equations which describe membrane transport was given in Ref. [22], and an evaluation of methods for the determination of transport coefficients will be published elsewhere [23]. Only data analyses are presented here.

CALCULATIONS AND DATA

Equilibrium studies

The data used in the calculations and analyses are taken from our studies on Nafion 115 and 117 membranes of DuPont Polymer Products Department, Wilmington, DE, U.S.A. (equivalent weight 1100). Membrane treatment procedures and analyses of membrane compositions are described elsewhere [24, 25]. The membranes were all studied in solutions containing 0.03 kequiv. m^{-3} electrolyte. The electrolytes, which will exchange only their cations with the membrane at this concentration [18] were HCl, alkali and alkaline earth metal chlorides, and ammonium salt chlorides ($NH_{4-n}R_nCl$, where R = H, CH_3, C_2H_5, C_3H_7, C_4H_9, and n = 1–4). The alkali and alkaline earth metal chlorides were studied also in binary mixtures with HCl.

Membrane water content, defined as the number of moles of water per mole of ion exchange site, $\lambda \equiv H_2O/SO_3^-$, was:

$$\lambda = \frac{M(W_1 - W_2)}{18.0 W_2} \tag{2}$$

where M is the equivalent weight of the membrane, and W_1 (g) and W_2 (g) are the weights of a membrane piece before and after drying *in vacuo* at 110°C.

Membrane conductivity

Membrane conductivity data were taken from measurements of the AC impedance in the lateral direction of the membrane at 25 ± 1°C (hereafter, the data are all at this temperature) [21, 24, 25]. The specific conductivity κ was expressed by:

$$\kappa = \sum_{A} F c_S x_{AM} u_A \tag{3}$$

where c_S is the cationic site concentration, x_{AM} is the membrane ionic equivalent fraction, and u_A is the mobility of species A.

Ionic transference number in binary cationic systems

The transference numbers of ions in the membrane were taken from *emf* (electromotive force) studies of concentration cells [24, 25], based on the theoretical formulation [26, 27]. The ionic transference number of H^+ in the membrane is expressed by ionic mobility as:

$$t_{H^+}(m) = \frac{x_{HM} u_H}{\sum_{A} x_{AM} u_A} \tag{4}$$

Combination of equation (3) and equation (4) then gives:

$$u_A = \frac{\kappa t_A(m)}{F c_S x_{AM}} \tag{5}$$

Water transference coefficient and water permeability

The water transference coefficient t_{H_2O} is defined as the number of moles of water transported per Faraday through the membrane:

$$t_{H_2O} = \left(\frac{j_{H_2O}}{I/F}\right)_{\Delta c=0} \tag{6}$$

The water transference coefficient t_{H_2O} used in this study was obtained by accurate streaming potential measurements [18–20, 24, 25]. The same measurements yielded water permeability L_p, if the diffusion coefficients of salts in the adjacent, electrolyte were known [27, 28]

$$L_p = -\left(\frac{j_{H_2O} V_{H_2O}}{\Delta p}\right)_{I=0} \tag{7}$$

where V_{H_2O} is the partial molar volume of water.

Diffusion coefficient of water in the membrane

If the mechanism for water diffusion is the same whether there is a pressure difference or a concentration difference across the membrane, and the activity coefficient of water is constant in the membrane, there is a relationship between the water permeability and the diffusion coefficient:

$$D_{H_2O} = \frac{L_p l}{V_{H_2O} K_{H_2O}(p)} \tag{8}$$

where l is membrane thickness and $K_{H_2O}(p) = \Delta c_{H_2O}/\Delta p$ is the partition coefficient of water between membrane and solution at pressure p. We use the factor $K_{H_2O}(p)$ to estimate D_{H_2O} from the measured value of L_p [24, 25].

RESULTS AND DISCUSSION

Cationic mobility in single cation-form membranes

Single cation mobility in Nafion 117 membranes of various cationic forms, calculated from equation (3), is compared with the mobility of the same cation in infinitely dilute aqueous solutions. The results are shown in Fig. 1. The mobility does not vary in the same manner in the two cases, and the value is smaller in the membrane by a factor ranging from 1.3 to 4. The membrane polymer must influence the relative ionic velocities, and alter

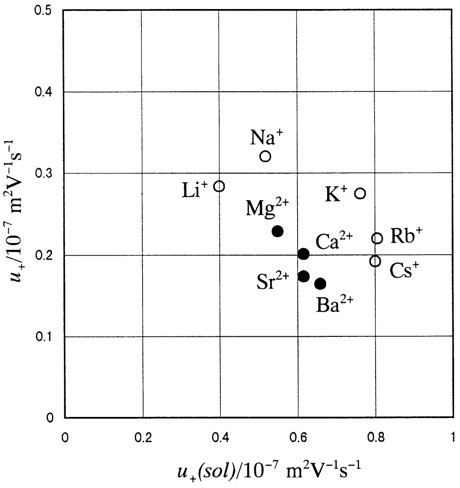

Fig. 1. Cationic mobility u_+ inside Nafion 117 membranes of various cation forms plotted as a function of cationic mobility in aqueous solution u_+(sol).

the friction force on the ion. In Nafion polymer, a cation migrates along the restricted path through channels of hydrophilic domains (cluster network model) [29]. In the solution, a cation moves with larger freedom against the viscous force of the surrounding medium.

According to the cluster network model of Nafion structure, the diameter of the channel is estimated to be 1 nm [29]. The data for the ammonium derivative cations gave a clear effect of ion size on the membrane conductivity. When the size of the cation approached 1 nm, i.e. the diameter of the channel, the membrane resistance increased enormously (a "plugging effect") [19]. This supports the Gierke estimate of channels of a finite size.

Water transference coefficient in single cation-form membranes

Figure 2 shows that the water transference coefficient can be grouped in three different classes for different kinds of cations exchanged in Nafion membranes.

With a single alkali or alkaline earth metal cation in the membrane, t_{H_2O} increases with cation hydrophilicity, and so does also the membrane water content, λ. When plotted against the ionic radius of the cations, t_{H_2O} increases when the radius becomes smaller. The water transference coefficient for these cations also correlates with the hydration enthalpy of water (see Fig. 3, also Ref. [18]), where the water transference coefficient multiplied by the number of valence of the cation, zt_{H_2O}, is shown in the membrane. We see that the number of water molecules carried by a cation, zt_{H_2O}, can be larger than the water of hydration in aqueous solutions.

For hydrophobic ammonium derivative cations, t_{H_2O} changes largely, although λ is constantly close to 10. The value of t_{H_2O} now increases with the radius of the ion.

The membrane in the H-form (the fuel cell membrane) has an exceptionally high water content, and a low water transference coefficient ($t_{H_2O} = 2.6$) [18, 30].

It is noted that ion transport promotes simultaneous water transport in two ways. The first effect is an electrostatic effect where charge–dipole interaction is dominant, and which keeps a certain amount of water located around a cation at any time. The second effect results from ionic size: water can be "pushed" along the membrane chan-

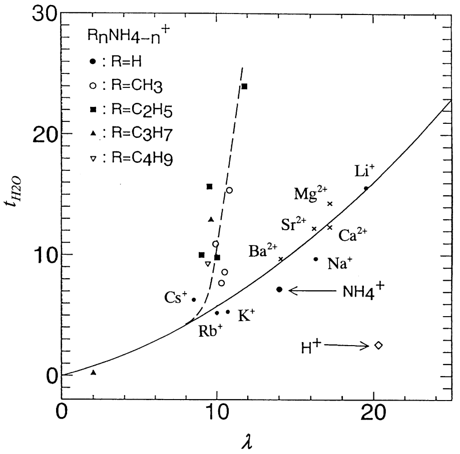

Fig. 2. Water transference coefficient t_{H_2O} in Nafion 115 membranes of various kinds of cation forms plotted against the membrane water content λ in full hydration state. ———: hydrophilic cations, - - -: hydrophobic cations.

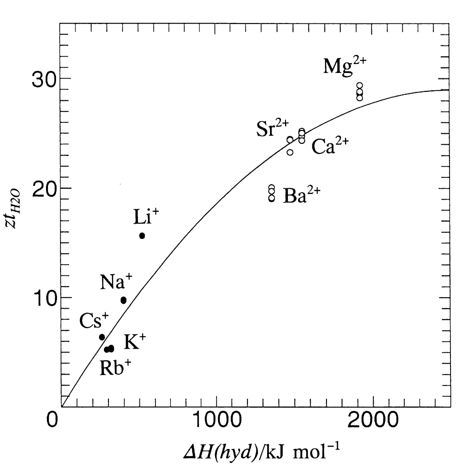

Fig. 3. Water transference coefficient t_{H_2O} multiplied by cationic valence z in Nafion 115 membranes of various kinds of cation forms plotted against the hydration enthalpy of cations ΔH(hyd), recalculated from Ref. [18].

nel as the cation is transported [31]. The larger the cation is, the more water it can push by a volume exclusion. This simultaneous transport of ions and water must take place along hydrophilic paths in the membrane.

A model for electro-osmotic water transport in the channels of Nafion membranes is therefore: $t_{H_2O} = t_{H_2O}(\mathrm{hyd}) + t_{H_2O}(\mathrm{vol})$ [31], where $t_{H_2O}(\mathrm{hyd})$ is water of hydration and $t_{H_2O}(\mathrm{vol})$ stands for the water beyond the water of hydration that accompanies the cation (pushed water by volume exclusion). The water of hydration was assumed to be the same as that in the solution [31]. A strict superposition, as suggested by the formula, may not be true, and it may not be appropriate to allocate certain water molecules to an ion. When pushed water, $t_{H_2O}(\mathrm{vol})$, was plotted against the radius of the hydrated ion, however, a similar behavior was seen for both hydrophilic and hydrophobic cations [20].

Ion transport in relation to water transport

The relation between ion and water transport was also studied by plotting the membrane specific resistance towards the water transference coefficients, t_{H_2O}, for hydrophilic as well as hydrophobic cations exchanged in the membrane (Fig. 4). The membrane conductivity data gave smaller mobility for the hydrophobic ions than for the hydrophilic ions. It is likely that larger ions migrate slower than smaller ones.

On this background it is interesting to see that there are two kinds of trends in Fig. 4. The membranes containing the bulky hydrophobic cations, have a resistance that increases parallel to an increase in the water transference coefficients (the size effect in t_{H_2O}). The membranes containing hydrophilic cations, on the other hand, have a resistance that has a maximum around $t_{H_2O} = 10$. The hydrophilic cations like H^+, alkali and alkaline earth metal cations, bring more water into the membrane than the hydrophobic ones (which have $\lambda = 10$). This means that hydrophilic cations can promote an enlarged hydrophilic domain in the membrane, that is accompanied by a lower membrane resistance.

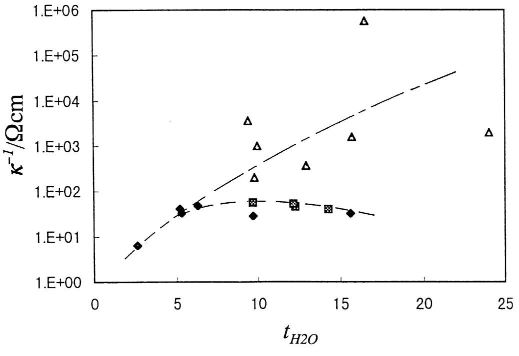

Fig. 4. Membrane specific resistance $1/\kappa$ plotted against the water transference coefficient t_{H_2O} in Nafion 117 membranes of various kinds of cation forms. △: ammonium derivative cations, ◆: H^+ and alkali metal cations, ■: alkaline earth metal cations.

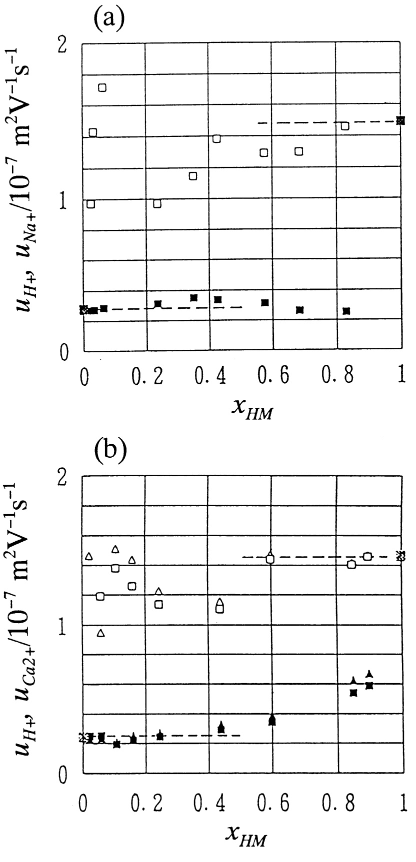

Fig. 5. Mobility of cations in (a) H/Na and (b) H/Ca mixed form Nafion 117 membranes plotted against the cationic equivalent fraction of H^+ in the membrane x_{HM}. △, □: u_{H^+}, ▲, ■: u_{Na^+} and $u_{Ca^{2+}}$.

Mobility of cation pairs

With cation mixtures of H^+/Na^+ and H^+/Ca^{2+}, the membrane conductivity changed almost linearly with the equivalent fraction of H^+ [24, 25], see Fig. 5 where the mobility of species as calculated from equation (5) is depicted. This means that a model that assumes constant ionic mobility in equation (3) and equation (4) is reasonable. The fact that the mobility of one ion is affected very little by the presence of the other ion is surprising, considering the high concentration of ionic sites (1–2 kmol m^{-3}) and the membrane preference for one of the ions to the other (according to equilibrium constants for ion exchange equilibria) [24, 25].

The apparent disagreement can be resolved by assuming strong shielding of the fixed negative sites of the polymer by water and by cation association. Such a shielding has been reported for charged

Table 1.
Attributed number per cationic site of water molecules of different states in Nafion membranes exchanged with various kinds of cations (a = b + c + d)

Membrane form	LiM	NaM	KM	RbM	CsM
a. Water content λ	19.5	16.5	10.8	10.1	8.6
b. Hydrated water to cation	5.5	2.8	1.4	1.2	1.0
c. Bound water to SO_3^- site and hydrophilic/hydrophobic region interface	4.7	5.9	4.9	5.8	4.1
d. Semi-free water	9.3	7.8	4.5	3.1	3.5
e. Ratio d/a	0.47	0.47	0.41	0.30	0.40

polymers. This finding is also in agreement with the behavior of cation mixtures in membranes, which appeared as regular mixtures [23, 32].

Water transference coefficients in binary cation-form membranes

There is a non-linear relation between the water transference coefficient and the ionic transference number in Nafion membranes of cation systems H^+/Na^+ and H^+/Ca^{2+} [24, 25], while the relationship was linear for H^+/K^+ for a crosslinked sulfonated copolymer membranes [28]. A deviation from a straight line indicates that the amount of water that is associated with the transport of one ion is not constant, and some water interferes when water is being dragged by binary cation systems. Since the results in Section 3.4 shows that the ions do not interact strongly, the main cause of deviation must be the interaction between the ions and the membrane. Another possibility is that water in the channel is affected by the presence of two kinds of cations. In Section 3.2 it is suggested that some water molecules are pushed by the cation movement inside the hydrophilic channel, and these water molecules would interfere when two kinds of cations coexist.

The state of water in the membrane

The equilibrium state of water in the membrane was investigated by differential scanning calorimetry (DSC) [21]. The results are summarized in Table 1, together with additional calculations. By DSC it was distinguished between water that freezes around −20°C, and water that remains unfrozen down to −120°C. The first type of water is more bulk-like than the other water: it is "semi-free". The second type of water can be associated with cations and sulfonic acid groups in hydrophilic domains. Water molecules associated with various ionic types are shown in Table 1. The rest might be associated with regions between hydrophilic and hydrophobic domains, having a disordered structure.

The amount of semi-free water in Table 1, about 50% of the total, was calculated from the peak area in the DSC curves. The amount decreased as the hydrophilicity of the cation in the membrane decreased. The DSC peak also shifted towards more negative temperatures as the hydrophilicity of the cation decreased. This is interpreted by the water becoming less bulk-like or interacting more with the membrane [21]. The total amount of water also decreases, suggesting that the water becomes more confined when it depletes the membrane. FT–IR spectra support this result: less hydrophilic cations in the membrane result in a smaller extent of hydrogen bonding and less water [21, 33].

An interesting feature is that the number of pushed water molecules by cations in the channel is similar to the amount of freezing water (semi-free water) as illustrated in Fig. 6. It can be anticipated that during ion migration inside the channel, semi-free water which resides in the channel and is almost bulk-like can be pushed by moving cations.

Ionic transport pathways and water diffusion

The transference coefficient is a direct measure of how water transport is coupled to ion transport. The water permeability, however, is a measure of water flow that takes place independent of ion transport. If water is always transferred along the hydrophilic sites in the membrane, there should be a correlation also between ionic mobility (ionic conductivity) and water permeability. The diffusion coefficient, D_{H_2O}, was therefore correlated with water content (Fig. 7(a)) and with membrane conductivity (Fig. 7(b)).

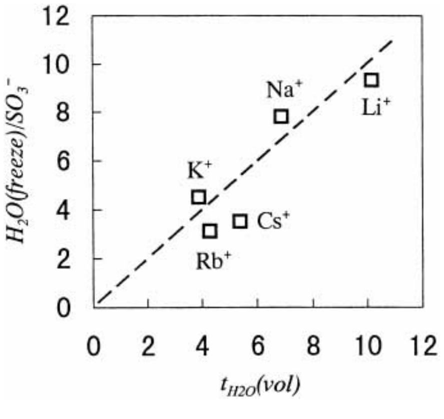

Fig. 6. Number of freezing water molecules per cationic site plotted against the number of water molecules "pushed" by hydrated cations in Nafion membranes of various cation forms.

A surprisingly parallel relationship can be seen from these figures. The similar behavior indicates that the ions and water indeed move along the same (narrow) hydrophilic paths in the membrane, whether it diffuses (pressure diffusion or normal diffusion), or is transported by electro-osmosis. Furthermore, the water content of these paths, seems to be crucial for the membrane conductivity.

Correlation of the membrane structure and transport properties

The following picture emerges for the state of water in the membrane from the above data correlations. It is seen that the ion transport is coupled to water transport in a way that may enlarge or reduce the hydrophilic domains in the membrane, depending on the nature of the ion. This means that the ion influences the channel structure and/or diameter. The fact that the amount of semi-free water in the membrane decreased as the hydrophilicity of the membrane cation decreased, supports the idea that there is some water especially associated with the fixed charges and the cations in the membrane. This further supports our model for the water transference coefficient.

The correlations between κ, D_{H_2O} and water content λ supports the idea of a common path for transport of water and ions. It is found that high membrane conductivity is linked to high water content in the hydrophilic domains of the membrane. The membrane conductivity and the diffusion coefficient of water, which showed a correlation in Fig. 7(a) and Fig. 7(b) was also plotted against the channel cross section in Fig. 8. The channel cross section was calculated from the streaming potential data [18]. The tendency is that the rate of transfer of particles is uniquely determined by the largeness of the path of those particles. This simple rule, in a membrane which can be specified by a channel structure like Nafion, will be useful as a first order approximation.

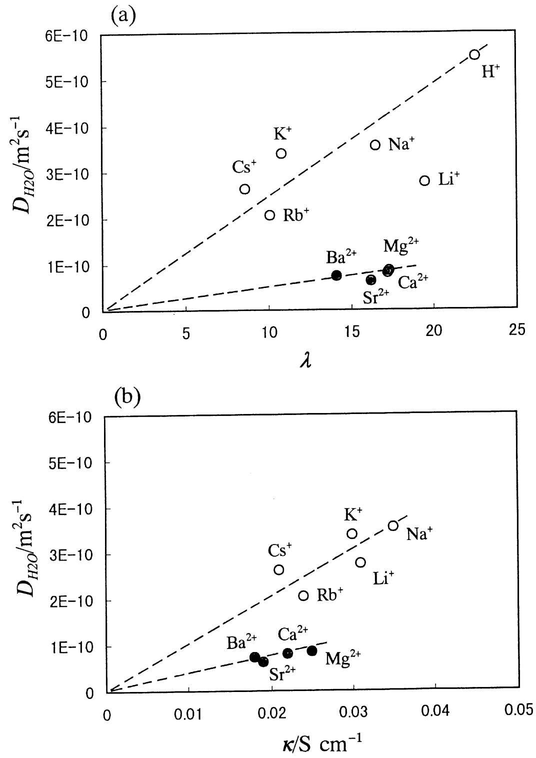

Fig. 7. (a) Diffusion coefficient of water D_{H_2O} in Nafion 117 membranes of various cation forms plotted against the membrane water content λ in full hydration state. (b) Relationship between the diffusion coefficient of water D_{H_2O} and the membrane specific conductivity κ.

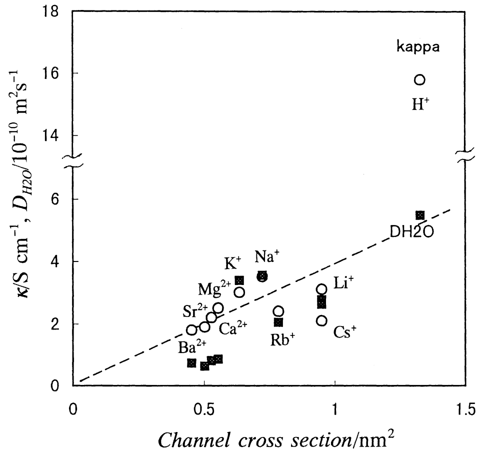

Fig. 8. Membrane specific conductivity κ and diffusion coefficient of water D_{H_2O} in Nafion 117 membranes of various cation forms, plotted as a function of the cross section of the channel calculated from Ref. [18]. ○: κ, ■: D_{H_2O}.

One system which falls outside is the membrane with H^+. This system has clearly a higher conductivity than the one expected from the trend of the other ions. H^+ and water transport is less coupled than that of the normal cation and water, and t_{H_2O} is low.

These findings are of practical importance for the design of membranes with higher performance in electrochemical systems. According to the conclusions above we can say that a strategy for membrane synthesis is to aim at [34]:

(1) a high concentration of sulfonic acid groups to increase the ionic site density in the hydrophilic domains,

(2) a high water content to enlarge hydrophilic domains in the membrane,

(3) alignment of channel structures to ease ion (and water) transport.

CONCLUDING REMARKS

Water and ion transport must be understood from the microstructure of the membrane. In this study, the water transference coefficient t_{H_2O} is related to the channel structure of Nafion, where water pushed by cations with volume exclusion is a plausible mechanism in this kind of hydrophilic/hydrophobic domain separated polymers with "reverse micelle" structures [29]. In total, the volume of ion and accompanying water molecules, in comparison to the volume of the channel structure will determine the mobility of the ion in the membrane.

The mechanism of ionic conduction in the membrane is totally different from that in the bulk solution. In the former case ions move in the environment of hydrophilic channels which are formed in the membrane, while in the latter case ions move freely in the environment characterized by the local viscosity of the solution. It is shown that increasing the water content will improve the transport characteristics of the membrane by increasing hydrophilic domains through which ions move. On the other hand, water is inevitably transported by the moving cations, and the amount of water accompanied will limit the rate of cations travelling along the ion exchange sites inside the narrow channel structure. Water can be regarded as an "obstacle" for ion movement in one sense, but as a "lubricant" in another sense.

In spite of the high concentration of ions in the membrane, the mixture of counterions can be regarded as a "regular mixture", and can be described by a simple model. This fact indicates that ions in the membranes are strongly shielded by ions of the opposite sign and by water molecules, and ion–ion interaction will not go beyond next-neighbor distance.

The conduction of H^+ in the membrane is different from other cations, and the Grotthus mechanism can be assumed like in aqueous solutions. Also the small value of t_{H_2O} in H-form membranes ($t_{H_2O} = 2.6$) indicates the easiness of H^+ to move in the membrane phase. This small value turns out to be a favorable fact in view of water management, for the application of the membrane to fuel cell technology. The strategy of designing new membranes of higher performances for polymer electrolyte fuel cells is proposed based on the proposed model [34].

ACKNOWLEDGEMENTS

The authors express their deep respect and hearty thanks to late Professor Tormod Førland and also to Professor Kristine Seip Førland, for many indications and helpful discussions for this work.

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