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Investigation of Ion and Water Transport Mechanisms in Perfluorosulfonated Ionomer Membranes for Fuel Cells

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Introduction

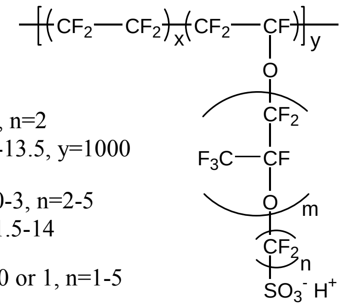
Perfluorosulfonic acid polymer electrolyte membranes have attracted much attention in the past decade because of their wide applications in chlor-alkali electrolytes, water electrolysis, polymer electrolyte fuel cells (PEFC), and so on. [1,2] Especially, their application to the PEFC has been recently focused in view of energy and environmental demands. However, they are still expensive for practical purposes and new advanced membranes with lower cost and higher performances, especially higher H^+ conductivity, are strongly desired. In order to design advanced polymer membranes with new concepts, at first, clarification of the mechanisms of ion and water molecule transports in the membrane having high performances like Nafion might be greatly valuable. In this study, we utilize two Aciplex and four Flemion membranes having various EW values along with Nafion 117 and prepare H-form, Li-form and Na-form samples for each membrane, to investigate the membrane properties in more detail.

Experimental

Nafion 117 of DuPont (Wilmington, DE), Aciplex S-1112 and S-1008 of Asahi Kasei Corp. (Kawasaki, Japan), and Flemion LSH-180, MSH-200, MSH175 and SH-120 of Asahi Glass Co., Ltd. (Yokohama, Japan) were utilized as perfluorosulfonated ionomer membrane samples. The structures of the membranes are shown in Fig. 1. After the pretreatment with 2 % H_2O_2 aqueous solution, the membranes were immersed in 0.03 M HCl, LiCl and NaCl aqueous solutions to exchange the counter cation in the membranes. For each membrane, water content and density were determined by the gravimetric method. The ionic conductivity of the membranes was measured by a.c. impedance spectroscopy. The water transference coefficient and water permeability for the membranes were estimated by using a streaming potential method. [3-5] The self-diffusion coefficients of the water (^{1}H) and the Li^+ cation (^{7}Li) in the membranes were measured by the pulsed-gradient spin-echo (PGSE) NMR method. [5]

Results and discussion

Figure 2 shows the water content λ and ionic conductivity κ for the membranes in the fully hydrated state. The water content increased with decreasing the EW value of the membranes, independent of not only the type of membranes but also the counter cation species and the ionic conductivity increased with increasing the water content. These facts indicate that the membrane having higher concentration of ionic exchange group can absorb larger amount of water molecules in the membranes and form larger ionic cluster regions in which the carrier cations can move. Considering the cation species, the order of the water content was $Li^+ > H^+ > Na^+$ for all of the membranes. It suggests that the water content depends on the cation species and Li-form membranes can form the largest ionic cluster regions in the membranes. However, the ionic conductivity showed that the order is $H^+ >> Na^+ \geq Li^+$. This fact means that H^+ is transported by Grotthuss (hopping) mechanism and Li^+ and Na^+ by vehicle mechanism. In addition, as shown in Fig. 3, Li^+ and Na^+-form membranes exhibited higher water transference coefficient t_{H2O}. This suggests that Li^+ and Na^+ interact with the water molecules more strongly than H^+ and the mobilities of these cations and the water molecules become lower. In fact, the water permeability L_p of these cation-form membranes also shows the lower values than H-form ones. All of the results of the self-diffusion coefficient D for water molecule and Li^+ cation measured by the PGSE-NMR method were in good agreement with the above results.



Nafion®: m≥1, n=2
x=5-13.5, y=1000

Aciplex®: m=0-3, n=2-5
x=1.5-14

Flemion®: m=0 or 1, n=1-5

Figure 1. Structures of polymer membrane matrix of Nafion®, Aciplex® and Flemion® in H-from state.

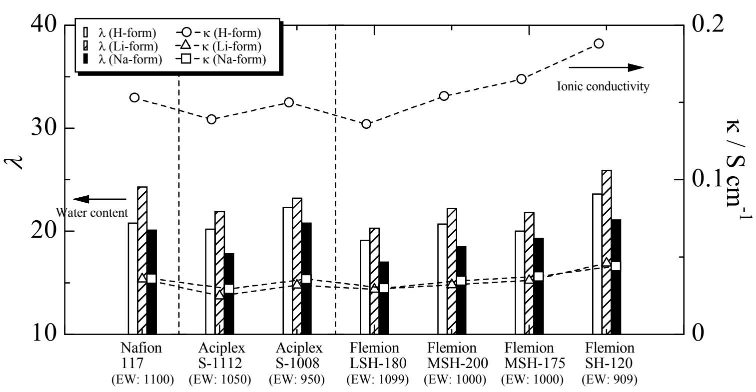


Figure 2. Water content $\lambda \equiv n_{H2O}/n_{SO3-}$ and ionic conductivity κ for perfluorinated membranes in the fully hydrated state.

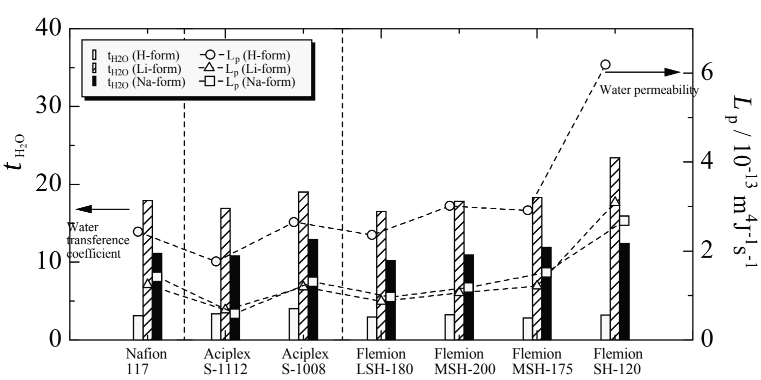


Figure 3. Water transference coefficient t_{H2O} and water permeability L_p for perfluorinated membranes in the fully hydrated state.

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