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Dissociation and Conduction of Alkali Metal Ion in Nafion/Crown Ether Composite Films

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M^+-Nafion (M=Li, Na, K)/crown ethers (15-crown-5, 18-crown-6) composite films show single ion conduction, reflecting the ion-dipole interaction between cations and crown ethers. Stable cation/crown ether complex leads to the high dissociation of M^+-Nafion but results in the low ionic conductivity.

Polymeric solid electrolytes have been studied mainly in poly (oxyethylene)/alkali metal salt complexes.[1] In these system, the migration of anion is inevitable and causes a decrease in ionic conductivity under dc polarization. We have already reported a series of polymeric solid electrolytes in which only alkali-metal ions are mobile.[2-3] Dissociated cations are surrounded by ether oxygens through ion-dipole interaction. This interaction decreases with increasing the size of cation because of its lower surface charge density.[3] Therefore, Cs^+ shows the largest ionic conductivity in all alkali metal ions. The interaction is considered to be controlled by making use of the selectivity of complex formation between cyclic ethers and alkali-metal ions. Several studies have been reported on the solid polymer electrolytes containing crown ethers.[4-9] However, in those cases, both cations and anions, ordinary, anions are carriers. On the other hand, Nafion possesses perfluorosulfonic groups and shows high single ionic conductivity by introducing oligo(oxyethylene).[10] Here we report the conduction of alkali metal ions (M^+) in M^+-Nafion/crown ethers composite films. In this system, the crown ethers are incorporated into the ionic clusters of Nafion films and make ion conduction pathway.

Crown ether (18-crown-6 or 15-crown-5) was added to a M^+-Nafion-117 solution (a 5 wt% lower aliphatic alcohols and water solution from E.I. du pont de Nemours & Co. was neutralized with LiOH, NaOH, or KOH) in equimolar amount to the perfluorosulfonic groups. The solution was completely replaced with DMF. A film was prepared by casting method at 120 °C.[11] The resulted film shows high quality such as high transparency and flexibility.

Dissociation of cation-perfluorosulfonate pair was investigated by the

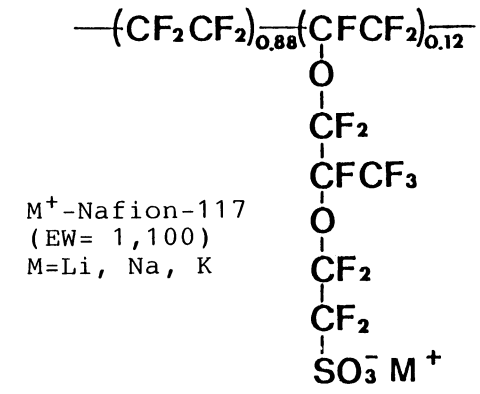
observation of peak shift of $-SO_3^-$ symmetric stretching mode (νSO_3^-) in IR transmittance spectra.[12] The νSO_3^- of Li^+, Na^+, and K^+-Nafion without containing crown ethers appeared at 1075, 1066, and 1060 cm^{-1}, respectively. This means the larger cation causes smaller degree of polarization of S-O dipole due to weaker ion-ion interaction. When Nafion was neutralized with quaternary alkyl ammonium ion, the band was confirmed at 1051 cm^{-1}, which was the smallest value. It means that ion-ion interaction in this state is estimated to be the same as that in complete dissociation of M^+-Nafion. When equimolar amount of crown ethers was incorporated into the three kinds of films, the peak shifted to the smaller wavenumber in each system. This means the dissociation of ion pairs by complexation between cation and crown ether. The rate of peak shift can be calculated according to the equation (1),

$$\text{Peak shift (\%)} = \frac{\nu_0 - \nu_1}{\nu_0 - 1051} \times 100 \qquad (1)$$

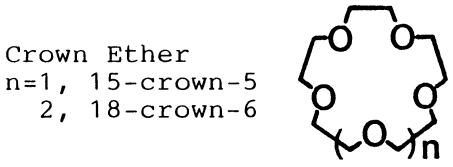
where ν_0 and ν_1 are νSO_3^- of Nafion films without and with crown ethers, respectively. Figure 1 shows the rate of peak shift of M^+-Nafion/crown ether composite films. When crown ether was 18-crown-6, it increased in the order $Li^+ < Na^+ < K^+$. On the other hand, in case of 15-crown-5, Na^+-Nafion showed the highest value. These results are identical with the well-known properties of crown ethers in solution systems.[13] Stable cation/crown ether complex is achieved when the size of cation fits the cavity of crown ether, leading to the high degree of dissociation. Larger size of K^+ than that of the cavity of 15-crown-5 also causes unstable complexation, leading to such a low rate of peak shift.

In order to make sure single ionic conduction of this system, the time dependence of the dc ionic conductivity of Li^+-Nafion/18-crown-6 composite film was measured. When a sample was sandwiched with stainless steel electrodes, rapid decrease in ionic conductivity was observed at the initial state, whereas constant ionic conductivity was confirmed for the sample sandwiched with lithium electrodes. Those results show that lithium ion is a carrier.

The cation conductivity of M^+-Nafion/crown ether composite films were measured by ac impedance technique, and are plotted in Fig. 2. The conductivity of M^+-Nafion/18-crown-6 increased in the order $Li^+ > Na^+ > K^+$. In case of a linear oligo(oxyethylene) system,[3] it increases with increasing cation diameter due to the weaker ion-dipole interaction. In a Nafion/18-crown-6 system, Li^+ ion showed the highest conductivity. Interaction between cation and oxygen of crown ether increases with increasing the



M^+-Nafion-117
(EW= 1,100)
M=Li, Na, K



Crown Ether
n=1, 15-crown-5
2, 18-crown-6

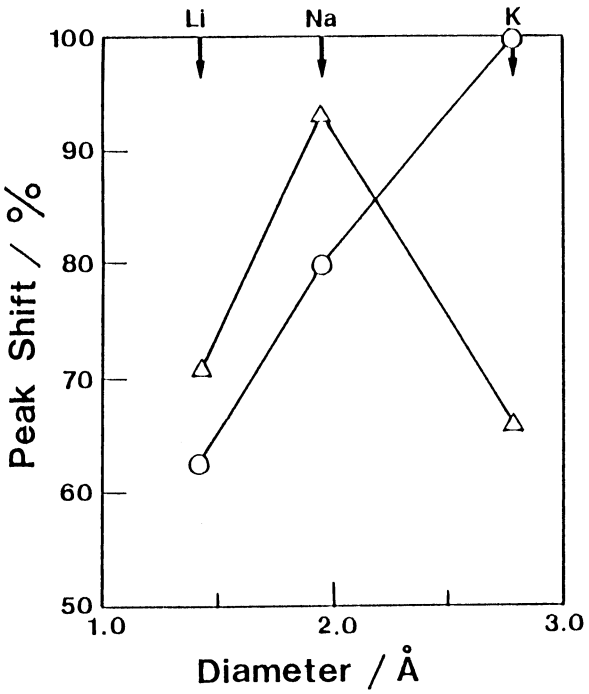


Fig. 1. Influence of cation diameter on the peak shift of νSO_3^- in M^+-Nafion/18-crown-6 (O) and 15-crown-5 (△) composite films.

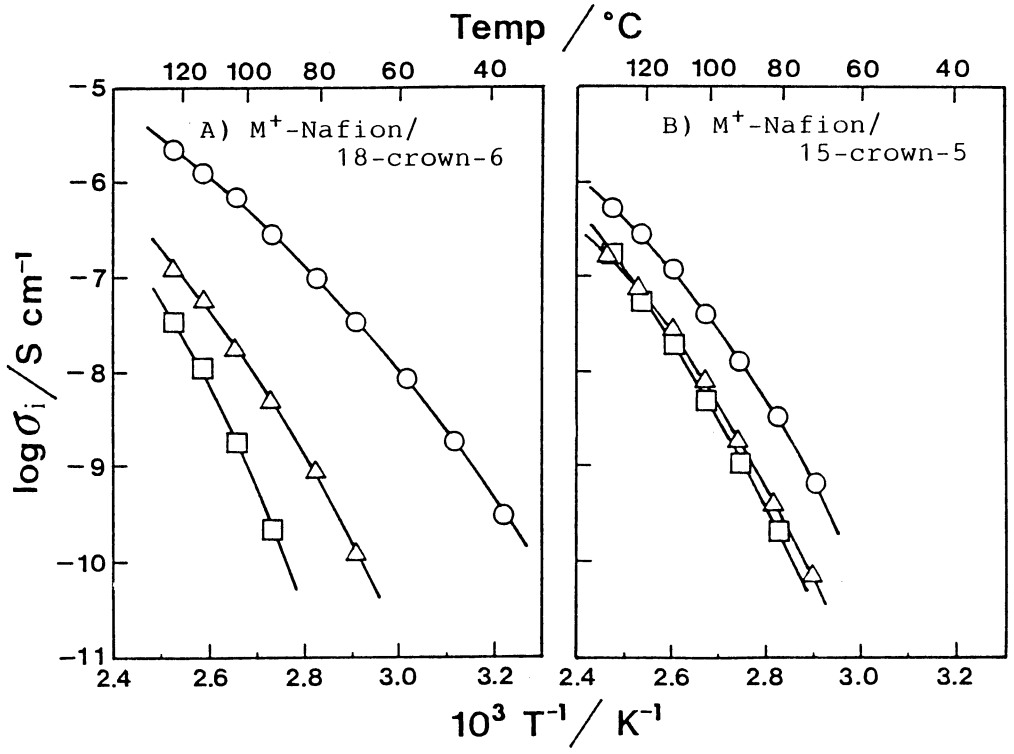


Fig. 2. Temperature dependence of the ionic conductivity of M^+-Nafion/crown ether composite films: M= Li(O), Na(△), K(□).

cation diameter from the result of IR spectrum. Therefore, it is concluded that weaker interaction causes the lower degree of dissociation, but the higher migration of dissociated ion. The cation conductivity of M^+-Nafion/15-crown-5 films also increases in the same order as the 18-crown-6 system, whereas the conductivity of lithium ion decreases significantly. It is because the smaller size of 15-crown-5 makes the stronger interaction of oxygen with Li^+. Weaker interaction between 15-crown-5 and K^+ in comparison with that of the 18-crown-6 system should explain the larger K^+ conductivity of 15-crown-5 system. The lower ionic conductivity of K^+ than that of Na^+ would mean the stabilization of intermediate state at cation exchange between crown ethers by making 2 : 1 complex.[14]

It was concluded that in solid Nafion/crown ether system high ion dissociation occurred when cation fitted to the cavity of crown ether, while high ionic conductivity was obtained when cation was smaller than the cavity and the gap between their sizes was large.

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