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Description	

OH^- Conductive Properties and Water Uptake of Anion Exchange Thin Films

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Abstract: Several investigations have indicated that proton conduction and hydration properties of acidic ionomers differ from those of membranes. However, relations between the OH^- conductivity and water uptake in thin film forms of anion exchange membranes have not been reported yet. For this study, new in situ measurements were established to elucidate the OH^- conductivity and water uptake without allowing any influence of CO_2 from the air. Poly[(9,9-bis(6′-(N,N,N-trimethylammonium)-hexyl)-9H-fluorene)-alt-(1,4-benzene)], denoted as PFB^+, was synthesized as a model ionomer. The highest OH^- conductivity of 273-nm-thick PFB^+ film is 5.3×10^{-2} S cm^{-1} at 25°C under 95% relative humidity (RH), which is comparable to the reported OH^- conductivity of PFB^+ membrane. Reduced OH^- conductivity was found in the thinner film at 95% RH. The decreased OH^- conductivity is explainable by the reduced number of water molecules contained in the thinner film. The OH^- conductivity was reduced only slightly under the same water uptake.

Fuel cells, electrochemical devices that produce electrical energy from chemical reactions, have potentially higher electrical efficiency than conventional power-generating systems. Because of their alkaline operating conditions, anion exchange membrane fuel cells (AEMFCs) offer advantages of using non-precious metal catalysts and higher oxygen reduction reaction (ORR) kinetics than proton exchange membrane fuel cells (PEMFCs). [1]

Anion exchange membranes (AEMs) are a key component of AEMFCs: they allow hydroxyl ions to migrate from the cathode to the anode. In fact, OH^- ion conduction and hydration properties of bulk AEMs have been investigated widely.[2–8] At the electrodes, the electrochemical reactions of fuel cells occur on the triple-phase interface, which comprises ion conductive ionomer, catalyst, and fuel/oxidant. The ionomer, which serves as a binder and ion conduction channel in this triple-phase interface, is crucially important for enhancing the electrochemical performance of fuel cells. Therefore, understanding the OH^- ion transport properties and water uptake in the thin film form of AEMs is important.

It is particularly interesting that the proton transport properties and water uptake in thin film are completely different from bulk membrane properties. Thin-film confinement can affect water uptake and proton conductivity by changing ionic-domain morphology through polymer–substrate interaction.[9–13] High proton conductivity can be achieved by the organized structure in alkyl sulfonated polyimide (ASPI) thin films with humidity-induced lyotropic liquid crystalline (LC) property.[14,15] Several studies have examined anion (F^-, Cl^-, Br^-, and HCO_3^-) transport properties of anion conducting ionomers.[16,17] Shrivastava et al. demonstrated that anion conductivity of FAA3 thin film in F^-, Br^-, and HCO_3^- forms is higher than that of FAA3 bulk membrane.[16] Kimura et al. studied the interface between hydrated BAF-QAF (Cl^- form) anion exchange ionomer on SiO_2 and Pt substrates using neutron reflectometry.[17]

Elucidating the OH^- conductive properties of thin films is important. However, experiments to assess OH^- conductivity measurement are more challenging than other anion conduction experiments in thin films because they must be shielded from the influence of CO_2 from the air in all processes from film preparation to measurement. No report of the relevant literature has described a study of OH^- conductive properties in the thin film form of anion conductive polymers. For this study, we established in situ OH^- conductivity and water uptake measurements in thin film form.

Diverse backbones and cationic groups were developed to obtain high anion conductivity and good alkaline stability AEMs.[18–25] Recently, fluorene-based polymers have been used extensively as AEMs.[26–31] Lee et al. reported poly[(9,9-bis(6′-(N,N,N-trimethylammonium)-hexyl)-9H-fluorene)-alt-(1,4-benzene)] (PFB^+) (Figure 1) as a high-performance AEM. PFB^+ bulk membrane displayed high OH^- conductivity at 30°C in water and good chemical stability (1 M NaOH at 80°C).[26] Consequently, for this study, the OH^- form of PFB^+ was used as a model ionomer. The objective of this study is clarification of the OH^- conductive properties and water uptake in thin film forms. In situ quartz crystal microbalance (QCM) and impedance spectroscopy measurements were established under different RH. All processes including transfer of samples and measurements were conducted in N_2 atmosphere. Higher OH^- conductivity than Br^- conductivity in the thin film form of AEM was confirmed. The OH^- conductivity of 273-nm-thick PFB^+ film shows a comparable value to the reported value of PFB^+ bulk membrane. Both reduced OH^- conductivity and water uptake were observed in the thinner PFB^+ film.

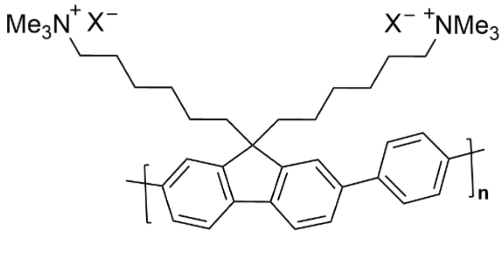

Figure 1. Chemical structure of PFB^+X^- (X=Br and OH).

The synthetic route of monomer and polymers is shown in Scheme S1. Briefly, poly[(9,9-bis(6-bromohexyl)-9H-fluorene)-alt-(1,4-benzene)] (PFB) was synthesized using a Pd-catalyzed Suzuki cross-coupling reaction. The weight-average molecular weight (M_w) of PFB was found to be 32 kDa, as estimated using gel permeation chromatography (GPC). The Br$^-$ form of PFB$^+$ was obtained after the quaternization reaction of PFB. The chemical structures of PFB and PFB$^+$ were confirmed from ^{1}H NMR and FTIR spectra (Figures S2 and S3).

Water uptake of the OH$^-$ form of anion conductive polymers is known to be higher than that of Br$^-$ form of bulk membrane. [32,33] Nevertheless, no report describes thin film forms of AEMs. The water uptake of PFB$^+$ thin films in both Br$^-$ and OH$^-$ forms was confirmed using our RH-controlled in situ QCM. Figure 2 depicts the RH dependence of water uptake of PFB$^+$ thin films in Br$^-$ and OH$^-$ forms at 25°C. Actually, λ (number of water molecules per functional group) has been used widely to describe the water uptake. For both Br$^-$ and OH$^-$ forms of PFB$^+$ thin films, the water uptake increased concomitantly with increasing RH. The water uptake increased slowly at lower RH. Sharp enhancement is visible in the range of higher RH (>80%). The water uptake of PFB$^+$ thin film in OH$^-$ form was higher than that of PFB$^+$ thin film in Br$^-$ form, especially for 80–95% RH. The water content of PFB$^+$ thin film in OH$^-$ form at 95%RH was 77 wt%, which is comparable to that of bulk membrane (71 wt% at 30°C in water).[26]

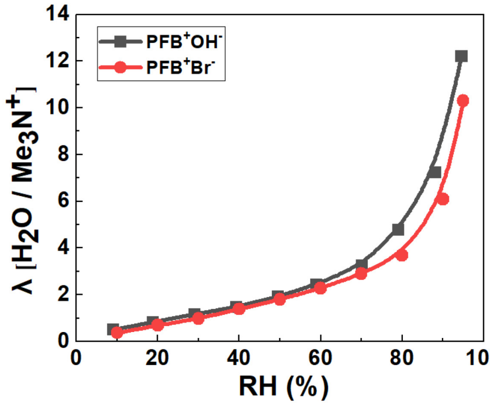

Figure 2. Water uptake of 273 nm thick PFB$^+$ films as a function of RH at 25°C.

Figure 3 portrays the Br$^-$ and OH$^-$ conductivity of PFB$^+$ thin films as a function of water uptake at 25°C: Br$^-$ and OH$^-$ conductivity increased concomitantly with increasing water uptake. The Br$^-$ and OH$^-$ conductivities respectively reached 2.2 × 10^{-2} and 5.3 × 10^{-2} S cm^{-1} at 25°C under 95%RH. The OH$^-$ conductivity of PFB$^+$ thin film was much higher than Br$^-$ conductivity at high hydration conditions. Because of the higher mobility in dilute aqueous solutions and higher dissociation degree of OH$^-$, higher OH$^-$ conductivity than Br$^-$ conductivity was observed.[33,34]

The OH$^-$ ions are converted easily to CO_3^{2-} and HCO_3^- ions during the conductivity measurement process.[35] Therefore, the RH dependence of HCO_3^- conductivity at 25°C was also investigated (Figure S6). Results show that the conductivity of PFB$^+$ thin film was lower in its HCO_3^- form than in its OH$^-$ form within the RH range of conductivity measurement. The highest HCO_3^- conductivity is 1.7 × 10^{-2} S cm^{-1} at 95%RH, which is much lower than OH$^-$ conductivity. These results indicate successful measurement of the OH$^-$ conductivity of PFB$^+$ thin film in this study. We confirmed that OH$^-$ conductivity is higher than Br$^-$ conductivity in the thin film form by developing the RH in situ measurement. Lee et al. reported that the OH$^-$ conductivity of PFB$^+$ bulk membrane is 5.0 × 10^{-2} S cm^{-1} at 30°C in water.[26] Our OH$^-$ conductivity of PFB$^+$ thin film is comparable to the reported OH$^-$ conductivity of PFB$^+$ bulk membrane. For the transport of F$^-$, Br$^-$, and HCO_3^- ions, thin films have higher ionic conductivity than that reported for bulk membranes.[16] This report is the first demonstrating that, through transport of OH$^-$ ions, a thin film can have comparable OH$^-$ conductivity to that of a bulk membrane.

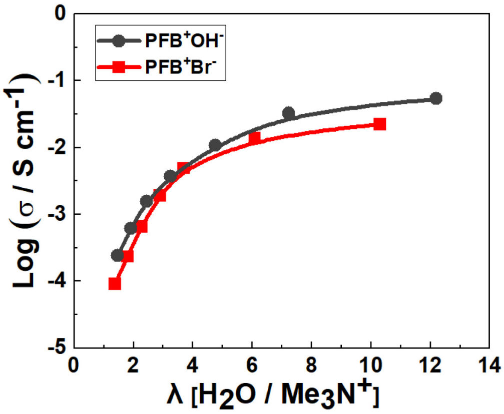

Figure 3. Anion conductivity of 273 nm thick PFB$^+$ films as a function of water uptake at 25°C.

To illustrate the relations between OH$^-$ conductivity and water uptake, a thinner, 30-nm-thick film in OH$^-$ from was newly prepared. Figure 4 presents the RH dependence of OH$^-$ conductivity of PFB$^+$ thin films at each thickness at 25°C. The OH$^-$ conductivity of 30-nm-thick film was lower than that of 273-nm-thick film in the RH range of conductivity measurements. The highest OH$^-$ conductivity of 30-nm-thick film was 3.5 × 10^{-2} S cm^{-1} at 95%RH.

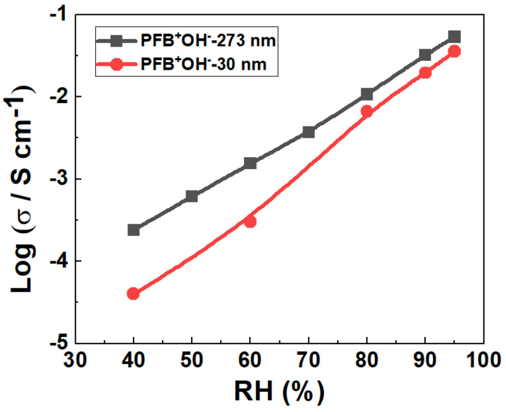

Figure 4. OH$^-$ conductivity of PFB$^+$ thin films in different thicknesses as a function of RH at 25°C.

Figure 5 presents the water uptake of PFB$^+$ thin films of the OH$^-$ form with different thicknesses as a function of RH. Compared to the 273-nm-thick film, a lower water uptake result was observed for 30-nm-thick PFB$^+$ thin film. The reduced ionic conductivity in thinner films is also apparent in the proton conduction of acidic ionomers. The decreased conductivity of acidic ionomers in thinner film can be derived from the reduced water uptake.[36] For further clarification of the relation between OH$^-$ conductivity and water uptake, the OH$^-$ conductivities of PFB$^+$ thin films for the respective thicknesses are shown in Figure 6 as a function of water uptake. Similar curves were obtained for both 273-nm-thick and 30-nm-thick films. As one might expect, the 273-nm-thick PFB$^+$ film included more water molecules than the 30-nm-thick PFB$^+$ film. As the number of water molecules contained increased, the OH$^-$ conductivity of PFB$^+$ thin film also increased. Given the same water content amount, the OH$^-$ conductivity was barely reduced with decreasing film thickness. The results presented above indicate clearly that the lower water uptake is directly responsible for the reduced OH$^-$ conductivity in thinner PFB$^+$ films, as reported also for acidic ionomers.

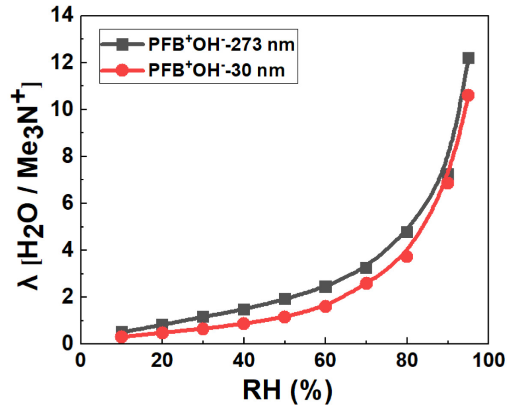

Figure 5. Water uptake of PFB$^+$ thin films in different thicknesses as a function of RH at 25°C.

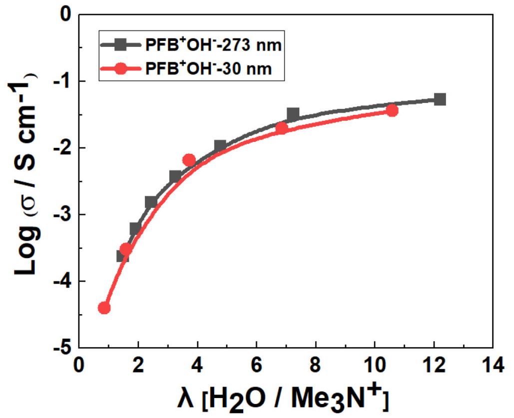

Figure 6. Water uptake dependence of OH$^-$ conductivity for PFB$^+$ thin films in different thicknesses at 25°C.

In summary, this report is the first time to demonstrate the OH$^-$ conductivity and water uptake in the thin film form of AEM. For this work, PFB$^+$ was chosen as a model ionomer. The OH$^-$ conductivity and water uptake of PFB$^+$ thin films were investigated at 25°C under various RH using newly established in situ measurements. Results confirmed the higher OH$^-$ conductivity than Br$^-$ conductivity in the thin film form of PFB$^+$. The 273-nm-thick PFB$^+$ film showed a comparable OH$^-$ conductivity value to the reported value of PFB$^+$ bulk membrane. As the PFB$^+$ thin film thickness decreased from 273 nm to 30 nm, the OH$^-$ conductivity decreased from 5.3×10^{-2} S cm^{-1} to 3.5×10^{-2} S cm^{-1}. Moreover, a lower water uptake result was observed in the thinner PFB$^+$ film. Results revealed that the decreased OH$^-$ conductivity in thinner PFB$^+$ film is explainable by the reduced number of water molecules contained in the thinner film. The OH$^-$ conductivity was reduced only slightly under the same number of water molecules.

Acknowledgments

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Keywords: OH$^-$ conductivity • Water uptake • Thin film

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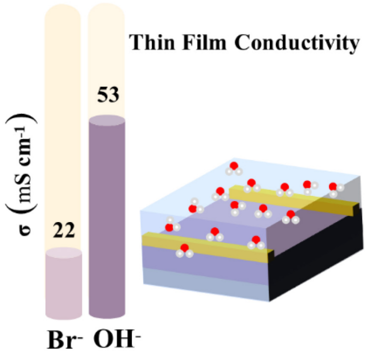

Poly[(9,9-bis(6′-(N,N,N-trimethylammonium)-hexyl)-9H-fluorene)-alt-(1,4-benzene)] (PFB$^+$) was used as a model ionomer to investigate the OH$^-$ conductivity and water uptake in thin film form. Reduced OH$^-$ conductivity was observed in the thinner film at 95% relative humidity, which can be attributed to the decreased amount of water content. The OH$^-$ conductivity was only slightly reduced under the same water uptake.

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