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| Title | OH^- Conductive Properties and Water Uptake of Anion Exchange Thin Films |
| Author(s) | Wang, Fangfang; Wang, Dongjin; Nagao, Yuki |
| Citation | Chemsuschem, 14(13): 2694-2697 |
| Issue Date | 2021-04-29 |
| Type | Journal Article |
| Text version | author |
| URL | http://hdl.handle.net/10119/18096 |
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# $OH^-$ 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 $5.3 \times 10^{-2}$ 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.

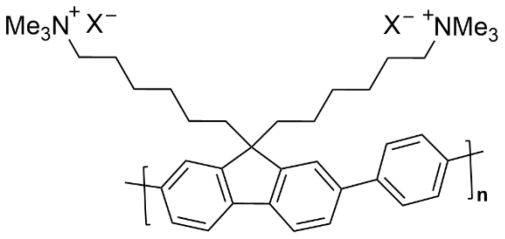


**Figure 1.** Chemical structure of $PFB^+X^-$ (X=Br and OH).

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 $^1H$ 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]

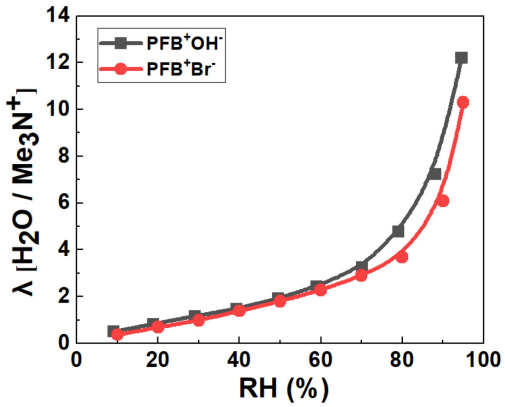


**Figure 2.** Water uptake of 273 nm thick $PFB^+$ films as a function of RH at 25°C.

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.

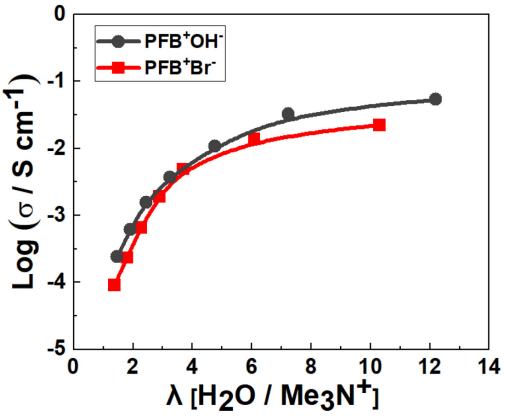


**Figure 3.** Anion conductivity of 273 nm thick $PFB^+$ films as a function of water uptake at 25°C.

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.

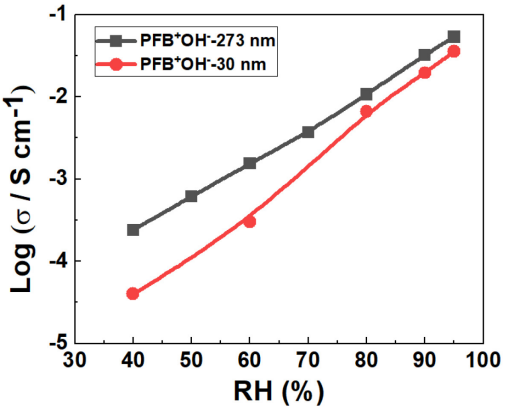


**Figure 4.** $OH^-$ conductivity of $PFB^+$ thin films in different thicknesses as a function of RH at 25°C.

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.

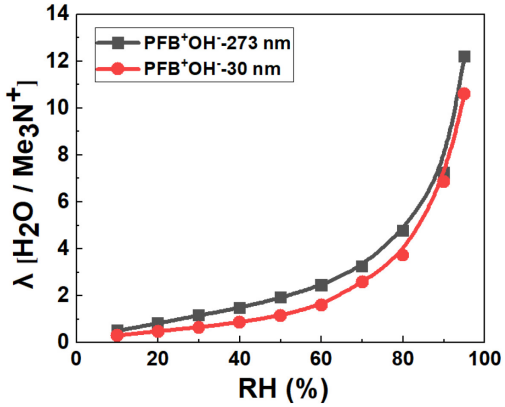


**Figure 5.** Water uptake of $PFB^+$ thin films in different thicknesses as a function of RH at 25°C.

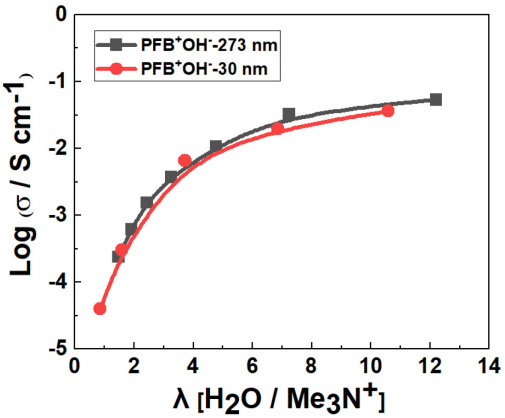


**Figure 6.** Water uptake dependence of $OH^-$ conductivity for $PFB^+$ thin films in different thicknesses at 25°C.

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 $5.3 \times 10^{-2}$ S $cm^{-1}$ to $3.5 \times 10^{-2}$ 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

This work was supported by research funding from JSPS KAKENHI Grant Number JP18K05257, 21H00020, and 21H01997.

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

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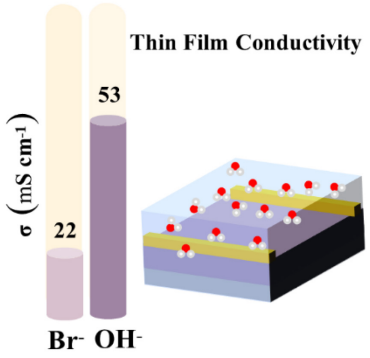


Poly[(9,9-bis(6′-(N,N,N-trimethylammonium)-hexyl)-9H-fluorene)-alt-(1,4-benzene)] ($PFB^+$) was used as a model ionomer to investigate the $OH^-$ conductivity and water uptake in thin film form. Reduced $OH^-$ conductivity was observed in the thinner film at 95% relative humidity, which can be attributed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

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