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Japan Advanced Institute of Science and Technology

Doctoral Dissertation

Hydration and Anion Conductive Properties of Anion Exchange Thin Films

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General Abstract

Anion exchange membrane fuel cell (AEMFC) provides the advantages of lower cost due to the possible utilization of non-noble metal catalysts and faster oxygen reduction reaction kinetics under alkaline conditions. Anion exchange thin films serve as binders and ion conduction channels in the triple-phase interface, which is related to the electrochemical performance of AEMFC. Hence, the investigation of anion exchange thin film is important. This research is mainly focused on the hydration and anion conduction properties of anion exchange thin films, especially the properties of OH⁻ form thin films.

Firstly, in situ OH⁻ conductivity and quartz crystal microbalance (QCM) measurements were newly established to investigate the OH⁻ conductivity and water uptake of thin films under a CO₂-free atmosphere. Poly[(9,9-bis(6'-(N,N,N-trimethylammonium)-hexyl)fluorene)-alt-(1,4-benzene)] (PFB-TMA) was chosen as a model anion conductive polymer. At 25 °C under 95% relative humidity (RH), the OH⁻ conductivity of 273 nm-thick PFB-TMA-OH thin film was 5.3×10^{-2} S cm⁻¹, which is similar to that of the membrane in the literature. Film thickness dependence of water uptake and OH⁻ conductivity were observed in PFB-TMA-OH thin films.

Secondly, to systematically observe OH^- conduction and hydration properties of thin films, fluorenethiophene-based anion conductive polymers with different cations were synthesized and investigated as thin film form. Furthermore, in situ temperature dependence of OH^- conductivity measurement process was newly established to obtain the activation energy (E_a) of OH^- conduction in thin films. Similar E_a of $OH^$ conduction between the cationic groups of trimethylammonium (TMA) and N-methylpiperidinium (Pip), indicated that higher IEC, less hydrophobicity, and smaller size of TMA contributed to the higher $OH^$ conductivity of TMA-based thin films.

Finally, the effect of side chain length on the properties of anion exchange thin films was investigated. Poly[(9,9-bis(3'-(N,N,N-trimethylammonium)propyl)fluorene)-alt-(3,3'-dihexyl-2,2'-bithiophene)] (PFT3-TMA) was synthesized and investigated as thin film form. Under high hydration conditions, similar OH⁻ conductivity was observed in fluorene-thiophene-based thin films with n-propyl alkyl spacer and nhexyl alkyl spacer. While higher OH⁻ conductivity was found in fluorene-thiophene-based thin film with npropyl alkyl spacer than that of thin film with n-hexyl alkyl spacer under the low number of water molecules which provided new insight into the OH⁻ conduction properties of anion conductive polymers with different side chain lengths under low number of water molecules.

Keywords: Anion exchange thin film, Fuel cell; OH⁻ conductivity, Water uptake, Activation energy

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Chapter 1 General Introduction

1.1 Introduction of Fuel Cell

A fuel cell is a type of electrochemical energy converter that can produce electrical energy from chemical energy. Although fuel cells have certain similarities to combustion engines and batteries, they outperform combustion engines efficiently. Furthermore, unlike batteries, fuel cells do not require charging.^{1,2} According to the electrolyte of fuel cells, fuel cells can be divided into five types: phosphoric acid fuel cell (PAFC), polymer electrolyte membrane fuel cell (PEMFC), alkaline fuel cell (AFC), molten carbonate fuel cell (MCFC), and solid-oxide fuel cell (SOFC).³

PEMFC is thought to be a suitable next-generation power source. PEMFC provides several advantages over other types of fuel cells, including increased power density, low performing temperature, and rapid start-up. The utilization of an expensive platinum catalyst, on the other hand, is a significant roadblock to the commercialization of PEMFC. Anion exchange membrane fuel cell (AEMFC) provides higher oxygen reduction reaction (ORR) kinetics than PEMFC.⁴ Moreover, non-noble metal catalysts can be employed in the electrode of AEMFC, reducing the cost of fuel cells.⁵ The schematic diagram of AEMFC is illustrated in Figure 1-1. The anode, cathode and overall reactions in the AEMFC are shown below:

Anode: $2H_2+4OH^-=4H_2O+4e^-$

Cathode: $O_2+2H_2O+4e^-=4OH^-$

Overall reaction: $2H_2 + O_2 = 2H_2O$



Figure 1-1. Schematic diagram of anion exchange membrane fuel cell.

The Membrane electrode assembly (MEA) is a critical component for the electrochemical performance of fuel cells. The MEA is placed between the anode and the cathode in a single AEMFC. The gas diffusion layer (GDL), catalyst layer, and anion exchange membrane (AEM) make up the MEA.⁶ AEM is used as a gas barrier and an OH⁻ conductive channel in the MEA. The electrochemical reactions happen at the triple-phase interface. The triple-phase interface of AEMFC is shown in Figure 1-2, which is composed of the electron conduction phase, ion conduction phase, and gas phase. MEA's interfacial resistance can be reduced using anion exchange thin film as a binder and OH⁻ conductive channel in the triple-phase interface. AEM and anion exchange thin film are anion conductive polymer which are vital parts for the electrochemistry performance of AEMFC.^{7–11} The properties of AEM have been investigated intensively.^{12–14} Nevertheless,

the properties of anion exchange thin film are still unclear. Hence, the investigation and design of anion exchange thin film are essential.



Figure 1-2. Triple-phase interface of AEMFC.

1.2 Anion Exchange Membranes (AEMs)

1.2.1 AEMs with Different Backbones

AEMs and anion exchange thin film are solid polymer electrolytes. In 1970s, the concept of solid polymer electrolyte was established.^{15,16} In 2001, Agel and Fauvarque prepared KOH-doped poly(ethylene oxide) (KOH-PEO) SPE to solve the problem caused by liquid electrolyte in AFC. A hydrophobic polymer backbone and a hydrophilic cationic group make up the AEM.¹⁷ After that, a wide variety of cationic groups and polymer backbones have been employed in the preparation of AEMs. High OH⁻ conductivity, superior mechanical performance, and good chemical stability at high pH are desirable characteristics for AEM.¹⁸

Various polymer backbones and cationic groups have been created over a lengthy period.^{19–28} Two essential polymer backbones for AEM are aromatic-based polymers and aliphatic-based polymers. Figure 1-3 shows the chemical structures of commonly used polymer backbones. As shown in Figure 1-3, poly(aryl ethers),²⁹ poly(phenylenes),³⁰ poly(aryl benzimidazoles),³¹ and poly(aryl imides)³² are the commonly used aromatic-based backbone. On the other hand, polyolefins are the main aliphatic-based backbone which consist of polyethylene,³³ polystyrene,³⁴ polynorbornene,³⁵ and polytetrafluoroethylene.³⁶



Figure 1-3. Chemical structures of various polymer backbones.¹⁴

Poly(aryl ethers), such as poly(aryl ether sulfones) and poly(aryl ether ketones), was initially investigated for AEM application in terms of mechanical and thermal properties. However, aryl ether (C-O) bond is present in poly(aryl ethers)-based anion conductive polymers. In 2012, Fujimoto and co-authors found the cleavage of aryl-ether bond under alkaline conditions firstly.³⁷ When OH⁻ ions attack poly(aryl ethers)-based anion conductive polymers, the aryl ether (C-O) bonds can be broken, especially if electron-withdrawing substituents are present. Electron-withdrawing groups (such as the sulfone linkage) can remove electrons from the benzene ring of the poly(aryl ethers) backbone, allowing for nucleophilic aromatic substitution under alkaline conditions.³⁸ Figure 1-4 portrays the chemical structure of quaterinized poly(arylene ether sulfone) and the polymer backbone degradation mechanism under alkaline conditions.



Figure 1-4. Chemical structure of quaterinized poly(arylene ether sulfone) and polymer backbone degradation mechanism under the alkaline condition.¹³

The poly(aryl ethers) based-AEM are not suitable for long-term AEMFC due to the facile cleavage of aryl-ether bonds under alkaline conditions. In 2014, the stable anion conductive aryl ether-free based polymer backbone such as polyolefins and polyphenylenes were developed.³⁹ In 2015, Lee and co-authors synthesized highly stable fluorene-based AEM.⁴⁰ The synthesized fluorene-based AEM can be stable in NaOH solution (1M) over one month and displayed high OH⁻ conductivity. Furthermore, over 0.1 S cm⁻¹ OH⁻ conductivity was found in the synthesized poly[9,9-bis(6'-(N,N,Ntrimethylammonium)-hexyl)fluorene)-alt-(1,4-benzene)] (PFB-TMA) AEM in water at 80 °C. In 2017, Ono and co-authors prepared anion exchange membrane based on fluorene and perfluoroalkylene (QPAF-4). The QPAF-4 AEM exhibited excellent mechanical properties and superior OH⁻ conductivity. Moreover, QPAF-4 AEM can be stable in 1 M KOH at 80 °C for 1000 h.41 Figure 1-5 shows the chemical structure of reported fluorene-based AEM. In 2020, Salma and co-authors prepared fluorene-based AEM carrying piperidinium (Pip) cation. The synthesized anion conductive polymer was stable in alkaline conditions and exhibited high OH⁻ conductivity.⁴² In this study, fluorene-based polymer was designed as polymer backbone.



Figure 1-5. Chemical structure of reported fluorene-based anion conductive polymers.^{40,41}1.2.2 AEMs with Different Cations

Quaternary ammoniums (QA), which are the most thoroughly explored cationic groups in AEMFC, have the advantages of relatively high conductivity, low cost, adequate alkaline stability, and easy functionalization.⁴³ Figure 1-6 shows the chemical structure of various cations. Among the various QA cationic groups, trimethylammonium (TMA) was the most used cation in the AEM. Besides, TMA cation, cyclic ammonium is another commonly used cation with good alkaline stability. Imidazolium, benzimidazolium, pyridinium, guanidinium, sulfonium, phosphonium, pyrrolidinium, and metal cations are being explored as part of the novel cationic groups.^{44–48} Pyridinium, sulfonium, and phosphonium-based cations, on the other hand, are unstable under alkaline conditions.⁴³ The alkaline stability of metal-based cations was good, but the functionality procedure was problematic.^{49,50}



Figure 1-6. Various cationic groups of AEM.^{14,18,51}

Marino and co-authors investigate the alkaline stability of some model quaternary ammonium cationic groups at 160 °C in 6 mol L⁻¹ NaOH solution.⁵² Table 1-1 shows the half-life of some model quaternary ammoniums at 160 °C in 6 M NaOH. Results suggested that 6-azonia-spiro[5.5]undecane (ASU), piperidinium (Pip) and tetraalkylammonium (TMA) show relatively high alkaline stability than other cations. The synthesis process of ASU is complicated. Besides, the bulkiness and more hydrophobic ASU usually result in much lower OH⁻ conductivity than that of TMA and Pip cations. Considering the alkaline stability properties, OH⁻ conductive properties, cost, and functionalization process, TMA and Pip was chosen as cationic groups in this thesis.

Quaternary ammonium	Abbreviation	Half-life (h)
N⊕	ASU	110
(⊕ N ∕	DMP	87
N N I	ТМА	62
(The second sec	DMPy	37
N⊕ N⊕	BMP	7.2
	BTM	4.2

Table 1-1. Half-life of quaternary ammoniums at T=160 °C in 6 M NaOH.⁵²

1.2.3 Side Chain Type AEMs

One critical issue in applying AEMs is the alkaline stability of cationic group.^{7,14,26, 38,58–62,52–57} Benzyltrimethylammonium-based AEMs has been investigated intensively. In the case of benzyltrimethylammonium cation, several degradation mechanisms can be observed under alkaline solution. The degradation mechanisms are shown in Figure 1-7. Nucleophilic substitution and Hofmann elimination from the OH⁻ attack are the principal degradation mechanisms for ammonium cations. Besides, Sommelet-Hauser rearrangement, Stevens rearrangement, and ylide degradation were also found to decompose ammonium cations under alkaline conditions.



Figure 1-7. Detailed degradation mechanisms of bezyltrimethylammonium under

alkaline condition.65

To overcome the alkaline stability problem of bezyltrimethylammonium cation, side chain type AEMs was developed. As shown in Figure 1-8, the alkyl spacer was placed between the polymer backbone and the cationic group in side chain type AEMs to improve the alkaline stability of the quaternary ammonium-based AEMs.^{40,64–77} Tomoi and co-authors were one of the earliest groups to investigate the effect of alkyl spacer on the stability of TMA in polystyrene-based AEM.⁸⁰ The alkaline stability of TMA was improved after the introduction of n-alkyl spacers. After that, some literature also investigated the effect of side chain on the alkaline stability of TMA-based AEM. After tethered TMA cation to an aromatic ring by a long alkyl chain the alkaline stability of TMA cation appears to have significantly improved when compared to benzylic trimethylammonium. Furthermore, side chain type AEM exhibited improved OH⁻ conductivity.^{66,69,70,75,76,79–88} Li and co-authors compared the water uptake, swelling ratio and OH⁻ conductivity of side chain type and main chain type AEM. Side chain type AEM exhibited lower water uptake and swelling ratio, but enhanced OH⁻ conductivity.⁹¹ In this study, side chain type anion exchange thin films were designed.



Figure 1-8. Schematic illustration of side chain type anion conductive polymers.⁹²

1.2.4 The Effect of CO2 on Anion Exchange Membranes

The reaction between OH^- and CO_2 converts OH^- into HCO_3^- and CO_3^{2-} when the OH^- form AEM contact with air, as shown in Equations (4) and (5).⁹³

$$OH^- + CO_2 \rightleftharpoons HCO_3^-(4)$$

$$1.6$$
 OH^{-}
 1.2 OH^{-}
 0.8 OH^{-}

 $HCO_3^- + OH^- \rightleftharpoons CO_3^{2-} + H_2O(5)$

Figure 1-9. The OH^- , HCO_3^- , and CO_3^{2-} concentration changes when OH^- form Tokuyama A201 anion conductive polymer contacted with air.⁹⁴

Yanagi and Fukuta examined the content of OH^- , CO_3^{2-} , and HCO_3^- in OH^- form Tokuyama A201 AEM after contact with air.⁹⁴ As shown in Figure 1-9, CO_2 has a negative effect on the conduction of AEM. The concentration of OH^- dropped significantly after the OH^- form Tokuyama A201 AEM was exposed to air. There is almost no OH^- remained after half an hour. OH^- conductivity of AEM is higher than their CO_3^{2-} and HCO_3^{-} conductivity due to the superior mobility of OH^- . As a result, the OH^- conductivity measurement of AEM should be conducted in a CO_2 -free atmosphere. Understanding the properties of OH⁻ form anion exchange thin films is important, however, one of the major obstacles in the evaluation process is that the CO_2 of ambient air react with OH⁻ to form HCO_3^{-}/CO_3^{-2} and significantly affect the properties of OH⁻ form thin films. In this study, in situ OH⁻ conductivity and water uptake measurement process of OH⁻ form thin films were established under the N₂ atmosphere.

1.3 Anion Exchange Thin Films

Compared to the AEM, the literature about anion exchange thin films is limited. So far, the detailed understanding of the properties of anion exchange thin films is insufficient. Although the same chemical structure between AEM and anion exchange thin film, the hydration, anion conduction, and morphology of AEM and anion exchange thin film may be different.

1.3.1 Hydration Properties of Anion Exchange Thin Films

Water uptake is a crucial parameter for the anion conduction in anion conductive polymers.^{95,96,105–108,97–104} However, the literature about the hydration properties of anion exchange thin films is limited.^{109–117} Only a few works have investigated the hydration properties of anion exchange thin films. Kushner and co-authors investigated the water content of 100 nm-thick quaternized poly(2,6-dimethyl-1,4-phenylene oxide) (QA-PPO, in Br⁻ form) thin films with several side chains.¹¹⁷ Figure 1-10 shows the water uptake result of Br⁻ form QA-PPO anion exchange thin films exhibited lower water uptake than that of QA-PPO anion exchange thin film without side chain, as illustrated in Figure 1-10. Similar water uptake was obtained for Br⁻ form QA-PPO anion exchange thin films with different side chain lengths.



Figure 1-10. Number of water molecules of Br⁻ form QA-PPO anion exchange thin films with different side chain lengths as a function of RH. QA-PPO anion conductive polymers with carbon atom number 0, 6, 10, and 16 are denoted as BTMA40, C6D40,

C10D40 and C16D40.117

The hydration properties of commercial Fumasep Fumion FAA3 thin films in F⁻, Br⁻ and HCO₃⁻ forms were reported.¹¹⁴ The F⁻ form FAA3 thin film exhibited the highest water uptake, whereas the water uptake of the Br⁻ form FAA3 thin film was the lowest. The water content of anion exchange thin films with different backbones, side chains, and counter-anion was investigated systematically. The chemical structures of the studied anion conductive polymers were shown in Figure 1-11.¹¹⁰ The counter-anion significantly impacts the water adsorption properties of anion exchange thin films. In comparison to thin films in other anion forms, anion exchange thin film in I⁻ form exhibited the lowest water uptake result. Aliphatic-based anion exchange thin films adsorbed more water than aromatic-based anion exchange thin films with the same film thickness. With the increase of side chain length of QA-PPO in Br⁻ form, the water uptake decreased in the thin film

form. Buggy and co-authors designed block copolymer functionalized with TMA and Pip and investigated as anion exchange thin film.¹¹³ Compared to the anion exchange thin film functionalized with TMA, anion exchange thin film with Pip cationic group exhibited higher water uptake. Bharath and co-authors investigated the water adsorption behaviors of Tokuyama anion exchange thin films. Compared to Nafion thin film, lower water uptake was obtained in the same thickness Tokuyama anion exchange thin films.¹¹⁶



Figure 1-11. The chemical structure of various anion exchange thin films.¹¹⁰

In summary, the available water uptake investigation literature focused on the halide and HCO_3^- forms anion exchange thin films. Furthermore, there is a limitation in investigating thin films in OH⁻ form.

1.3.2 Anion Conductive Properties of Anion Exchange Thin Films

A few of literature focused on the anion conductive properties of anion exchange thin film. The anion conductivity of 50 nm-thick FAA3 thin films in F⁻, Br⁻, and HCO₃⁻ forms was reported. Under the same RH, F⁻ conductivity of FAA3 thin film than Br⁻ conductivity and HCO₃⁻ conductivity. The correlation between water uptake and anion conductivity in FAA3 thin films was illustrated. Under the same number of water molecules, higher Br⁻ and HCO₃⁻ conductivity was observed than F- conductivity in the FAA3 thin film.¹¹⁴

1.3.3 Morphology of Anion Exchange Thin Films

Previous studies illustrated different morphology in thin films compared to the bulk proton exchange membranes due to the confinement effects and interfacial interactions caused by thin film and substrate.^{118–120} As a result, investigating the morphology of anion exchange thin films is crucial. Luo and co-authors investigated the morphology of various anion exchange thin films using grazing-incidence small-angle X-ray scattering (GI-SAXS).¹¹⁰ The chemical structure of anion conductive polymers is shown in Figure 1-13. The phase separation in PF-AEM anion exchange thin film was relatively poor. No nanophase separation was found in other anion exchange thin films. Shrivastava and coauthors investigated the phase separation morphology of FAA3 thin film using GI-SAXS.¹¹⁴ However, there is no nanophase separation existed in the FAA3 thin film. Kushner and co-authors compared the morphology of QA-PPO polymers in the thin film form on the silicon substrate.¹¹⁷ Smaller domains and very weak scattering were found in the Br⁻ form QA-PPO anion exchange thin film. Buggy and co-authors reported a perpendicularly oriented structure of neutral block copolymer thin film on the silver substrate. Figure 1-12 shows the schematic illustration of neutral block copolymer and quaternized block copolymer. After quaternization, the organized structure disappeared due to the effect of cations. Very weak nanophase separation was existed in quaternized bloke copolymer.¹¹³ In summary, most of the reported anion exchange thin films were amorphous.



Figure 1-12. Schematic illustration of neutral block copolymer and quaternized block copolymer.¹²¹

Besides the properties of anion exchange thin films, understanding the interface between ionomer and catalyst is also critical for the high performance and stability of AEMFC. Kimura and co-authors investigated the BAF-QAF/substrate (SiO₂ and Pt) interface by neutron reflectometry (NR) at 60 °C under various relative humidity (RH). A Hydrophilic interface was observed between BAF-QAF ionomer and SiO₂ substrate.¹¹² Matanovic and co-authors investigated the interaction between the catalyst surface and the alkaline ionomers used in AEMFC by density functional theory (DFT) calculations. In the case of the same anode catalyst surface, the interaction energies between ionomer and catalyst surface decrease in the following order: p-terphenyl \geq m-terphenyl >biphenyl > diphenyl ether > benzene \geq o-terphenyl > 9,9-dimethyl fluorene which is consistent with the fuel cell performance by using the corresponding ionomer in the AEMFC.¹²² Cao and co-authors regulate the interaction between catalyst and ionomers by changing the alkyl spacer length between backbone and cation. The ionomer with the suitable alkyl spacer length reduced the toxicity of catalyst due to the strong adsorption of the ionomer backbone on the catalyst surface.¹²³
1.4 Research objectives

Anion exchange thin film is critical for the electrochemical performance of AEMFC. Nevertheless, the understanding of hydration and ion conductive properties of thin films in OH^- form is limited. This is due to the conductivity and hydration properties measurements of anion exchange thin films in the OH^- form should be conducted in a CO_2 -free atmosphere. The literature mainly studied the anion conductive and hydration properties of anion exchange thin films in halide and HCO_3^- forms rather than OH^- form. Hence, the author focused on the systematically understanding of hydration and ion conductive properties of thin films in OH^- form in this thesis. The research objectives were summarized as follows:

- (1) To establish the in situ OH⁻ conductivity and water uptake measurements of thin films in OH⁻ form and investigate the film thickness dependence OH⁻ conductivity and water uptake of reported anion conductive polymer.
- (2) To establish the in situ temperature dependence OH⁻ conductivity measurement process under the N₂ atmosphere. To synthesize new anion conductive polymers and systematically investigate the effect of counter-anion and cationic groups on the anion conductive and hydration properties of fluorene-thiophene-based anion exchange thin films.
- (3) To investigate the effect of side chain length on the anion conductive and hydration properties of fluorene-thiophene-based anion exchange thin films.

1.5 Outline of thesis

In chapter 1, the general introduction of this thesis summarized the recent advancement of AEMs and emphasized the state-of-the-art anion exchange thin films.

In chapter 2, the in situ OH⁻ conductivity and water uptake measurements of thin films in OH⁻ form were established. In addition, the film thickness dependence of OH⁻ conductivity and water uptake of thin films were investigated.

In chapter 3, fluorene-thiophene-based anion exchange thin films with different cations were newly synthesized. In situ temperature dependence OH^- conductivity measurement under the N₂ atmosphere was established. Furthermore, the effect of counter-anion and cationic groups on the anion conductive and hydration properties of fluorene-thiophene-based anion exchange thin films were systematically demonstrated.

In chapter 4, fluorene-thiophene-based anion conductive polymer with a shorter npropyl alkyl spacer between backbone and cationic group was newly synthesized. The effect of side chain length on the anion conductive and hydration properties of fluorenethiophene-based anion exchange thin films was demonstrated.

In chapter 5, the general conclusion of this research was summarized. The findings provide new insights for understanding the OH⁻ conductive and hydration properties of anion exchange thin films under various RH conditions. Besides, the operation of AEMFC under low RH conditions provides the advantages of lower cost and high performance. However, the alkaline stability of ionomer under low RH differs from that under high RH conditions. The in situ OH⁻ conductivity measurement method which was

established in this study can be used to investigate the alkaline stability of anion conductive polymers under different RH, which is beneficial for developing highperformance AEMFC.

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Chapter 2

Anion Conductive Properties and Water Uptake of Fluorene-based Anion Exchange Thin Films

Abstract

Several studies exhibited different water content and proton conductive properties between proton exchange thin film and membrane. The water uptake and OH⁻ conduction properties of anion exchange membrane have been studied extensively. Nevertheless, there is no literature investigating OH⁻ conductivity and water uptake of anion exchange thin films. In situ OH⁻ conductivity and quartz crystal microbalance (QCM) measurements were newly established to investigate the OH⁻ conductivity and water uptake of thin film under a CO₂-free atmosphere. Poly[(9,9-bis(6'-(N,N,Ntrimethylammonium)-hexyl)fluorene)-alt-(1,4-benzene)] (PFB-TMA) was chosen as a model anion conductive polymer in this chapter. At 25 °C under 95% relative humidity (RH), the OH⁻ conductivity of PFB-TMA-OH (273-nm-thick) thin film was 5.3×10^{-2} S cm⁻¹, which is similar to that of the membrane in the literature. Under the same RH, decreased OH⁻ conductivity and water uptake were observed in the PFB-TMA-OH (30nm-thick) film. The decreased water uptake of a thinner film is contributed to the reduced OH⁻ conductivity. Under the same number of water molecules, only slightly decreased OH⁻ conductivity was found in the thinner film. Compared with bulk membrane, similar OH⁻ conductivity was observed in PFB-TMA-OH thin film, which differs from acidic ionomer. Film thickness dependent OH⁻ conductivity and water uptake was newly observed in PFB-TMA-OH thin films.

2.1 Introduction

Environmental pollution and global warming have become critical due to pollutant gas emissions. Conventional power generating systems commonly used in factories and vehicles are the main source of pollutant gas. Therefore, there is an urgent need to develop environment-friendly power generation systems. The fuel cell is a clean, highly efficient, mobile, and noise-free operation power generation system.¹ Among the various types of fuel cells, proton exchange membrane fuel cells (PEMFCs) are an active research area. However, one of the most challenging hurdles for the large-scale use of PEMFCs is the employment of precious metal catalysts in acidic environments. Compared to PEMFCs, anion exchange membrane fuel cells (AEMFCs) provide a lower cost by using non-precious metal catalysts and faster oxygen reduction reaction (ORR) kinetics in alkaline conditions.²

There are two kinds of anion conductive polymers in AEMFCs. Anion exchange membranes (AEM) are installed between two electrodes and serves as a gas barrier and ion conduction channel. Alkaline ionomer acts as a binder and ion conduction channel in the catalyst layer in the electrode. The suitable alkaline ionomer can improve the electrochemical performance of AEMFCs by forming an effective triple-phase interface in the electrode. Hence, it is important to investigate the anion conductive and hydration properties of anion exchange thin films. The OH⁻ conduction and hydration properties of anion exchange thin films are in halide and HCO₃⁻ forms. Kushner and co-

authors investigated the water uptake of quaternized poly(2,6-dimethyl-1,4-phenylene oxide) (QA-PPO, in Br⁻ form) containing various alkyl side chain lengths in both membrane and 100-nm-thick thin film. Compared to the QA-PPO membrane, all the 100nm-thick QA-PPO films exhibited higher % mass water content.¹⁵ The hydration and anion conductive properties of commercial Fumasep Fumion FAA3 thin film in F⁻, Br⁻, and HCO_3^- forms under various RH were revealed. Less water uptake was obtained in the FAA3 thin film than that of the FAA3 membrane. Interestingly, superior anion conductivity was found in FAA3 thin films under the same hydration conditions.¹⁶ Luo and co-authors investigated the water uptake of anion exchange thin film with different structures (halide and HCO₃⁻ forms). Different hydration properties can be observed between membranes and these thin film form.¹⁷ However, the investigation of anion exchange thin films in the OH⁻ form is insufficient because the whole process must be conducted in a CO₂-free atmosphere.¹⁸ To overcome this problem, in situ measurements were established for measuring OH⁻ conductivity and water content of thin film in this chapter.

Fluorene-based anion conductive polymers have been studied widely due to their high chemical stability.^{7,19–26} Poly[(9,9-bis(6'-(N,N,N-trimethylammonium)hexyl)fluorene)-alt-(1,4-benzene)] (PFB-TMA) membrane showed superior OH⁻ conductivity with good chemical stability.²¹ Hence, PFB-TMA was synthesized and investigated as anion exchange thin film in this chapter. A new in situ measurement process was developed to create a CO₂-free measurement environment under different RH. Besides the measurement process, the sample transfer process was also carried out under the N_2 atmosphere. The objective of this work is to understand the OH⁻ conductivity and water uptake of OH⁻ form thin films.

2.2 Experimental Section

2.2.1 Materials

1,4-Benzenediboronic acid bis(pinacol) ester, tetrabutylammonium bromide (TBAB), 2,7-dibromofluorene, 1,6-dibromohexane, and tetrakis(triphenylphosphine) palladium (0) (Pd (PPh₃)₄) were used as received from Tokyo Chemical Industry, Japan. Sodium hydroxide, sodium chloride, magnesium sulfate, dichloromethane, sodium bicarbonate, anhydrous, methanol, toluene, chloroform, hexane, tetrahydrofuran (THF), potassium carbonate, 30% trimethylamine solution and diethyl ether were obtained from Fujifilm Wako Pure Chemical Corp., Japan.

2.2.2 Synthesis of monomer and polymer

The synthetic route of 2,7-dibromo-9,9-bis(6'-bromohexyl)fluorene (DBF6), poly[9,9-bis(6-bromohexyl)fluorene)-alt-1,4-benzene] (PFB), and poly[9,9-bis(6'-(N,N,N-trimethylammonium)-hexyl)fluorene)-alt-(1,4-benzene)] (PFB-TMA) is shown in Scheme 2-1.^{21,25}



Scheme 2-1. Synthetic Route of DBF6, PFB and PFB-TMA.

DBF6

65 mmol of 1,6-dibromohexane, 2 mmol of TBAB, 8 mmol of 2,7-dibromofluorene, 30 mL of sodium hydroxide solution (50 wt%) were added together to the 100 mL threeneck flask. The reaction temperature was controlled at 60 °C. During the 8 h reaction period, the mixture was protected by argon. To obtain the organic layer, CH₂Cl₂ was used to extract the mixture. Next, water and brine were added to remove the residual NaOH and catalyst in the organic layer. After that, the organic layer was dried with MgSO₄. Subsequently, the surplus 1,6-dibromohexane was evaporated by vacuum distillation. Finally, the product was produced with a 71% yield by column chromatography. (Hexane as eluent).

PFB

The Suzuki cross-coupling process was used to synthesize PFB. Firstly, a 50 mL three-necked flask was filled with 2 mmol of 1,4-benzenediboronic acid bis(pinacol) ester, 2 mmol of DBF, 15 mL of toluene, and 5 mL of 2 M K₂CO₃ solution. Secondly, the mixture was degassed for five times and saturated with argon for half an hour. Finally, the catalyst Pd (PPh₃)₄ was added into the flask under argon atmosphere. The reaction temperature was controlled at 100 °C. During the 60 h reaction period, the mixture was protected by argon. The rotary evaporator was used to remove the remaining solvent after reaction. CHCl₃ was used to dissolve the crude polymer, and hexane was used to precipitate the polymer. This procedure was repeated several times. After drying the polymer in a vacuum oven for 12 h, PFB was obtained finally. (Yield: 53%)

PFB-TMA

PFB-TMA was obtained after the quaternization of PFB. 2 mL of THF was employed to dissolve 200 mg of PFB in a vial. 2 mL of 30% TMA solution was added once the PFB completely dissolved. 2 mL of DI water was added to the vial after the appearance of precipitation. To achieve complete quaternization, the mixture solution was stirred at room temperature for 2 days. The rotary evaporator was used for the removal of solvent after the reaction process. MeOH was used to dissolve the crude product, and diethyl ether was used to precipitate the product. After centrifugation and overnight drying under vacuum, pure PFB-TMA was obtained. (Yield: 79%)

2.2.3 Characterization

¹H NMR spectra of monomer and polymers were recorded on (400 MHz) Bruker Avance III spectrometer (Bruker Analytik GmbH). CDCl₃ or MeOD- d_4 was used as a solvent. ATR-FTIR spectra were obtained by a FTIR spectrometer (Nicolet 6700; Thermo Fisher Scientific Inc.) with a wavenumber ranging of 400-4000 cm⁻¹. The weight average molecular weight (M_w), number average molecular weight (M_n), and polydispersity index (PDI, M_w/M_n) of PFB were estimated using gel permeation chromatography (GPC). THF was applied as eluent. On a thermogravimetric analyzer, the thermal decomposition of PFB-TMA was measured in the temperature range 40-600 °C with a heating rate of 10 °C min⁻¹ under N₂ flow. The polymer was dried overnight at 40 °C under vacuum before being measured.

2.2.4 Ion Exchange Process

To get OH⁻ form PFB-TMA, PFB-TMA was immersed in 1 M NaOH solution for 2 days under the protection of Ar. Within 2 days, the 1 M NaOH solution was changed three times. After that, degassed ultra-pure water was used to wash PFB-TMA (in OH⁻ form) until the pH was neutral. All the process for OH⁻ form anion conductive polymers was performed under Ar or N₂ atmosphere. The HCO₃⁻ form PFB-TMA was done by immersing PFB-TMA in 1M NaHCO₃ solution for 2 days. Within 2 days, the 1 M NaHCO₃ solution was changed three times. After that, degassed ultra-pure water was used to wash PFB-TMA (in HCO₃⁻ form) until the pH was neutral. The Br⁻, OH⁻ and HCO₃⁻ forms of PFB-based anion conductive polymers were denoted as PFB-TMA-Br, PFB-TMA-OH, and PFB-TMA-HCO₃.

2.2.5 Preparation of Thin Films

The spin-coating (ACT-200; Active Co. Ltd.) of thin films were done on SiO₂ substrates and Au-coated quartz crystal microbalance (QCM) substrates (Seiko EG&G Co. Ltd.). The substrates were cleaned using 2-propanol and vacuum plasma (Cute-MP; Femto Science Inc., Korea) before spin-coating. For the preparation of PFB-TMA-OH thin films, the PFB-TMA-OH dispersion preparation and spin-coating processes were performed under a N₂ atmosphere to remove the effect of CO₂. The thickness of PFB-TMA thin films was measured by white light interference microscope after conductivity measurement. 273 nm and 30 nm thick PFB-TMA films were used in this study.

2.2.6 Scanning Electron Microscope and Energy Dispersive X-ray Spectroscopy (SEM-EDX)

TM3030Plus miniscope (Hitachi) was used to perform scanning Electron Microscope and Energy Dispersive X-ray Spectroscopy (SEM-EDX). 15 kV was used as the accelerating voltage.

2.2.7 RH-controlled In Situ Grazing-Incidence Small-Angle X-ray Scattering Measurements (GI-SAXS)

On an X-ray diffractometer (FR-E; Rigaku Corp.) with an R-AXIS IV twodimensional detector, RH controlled GI-SAXS was performed. Source of Cu-K α X-rays (wavelength = 0.1542 nm). The thin film was held in a humidity-controlled cell on the goniometer and vertical stage (ATS-C316-EM/ALV-3005-HM; Chuo Precision Industrial Co. Ltd.). The RH was controlled using nitrogen gas and water vapor. Lumirror windows are kept in the humidified cell. The camera's focal length was 300 mm, and the incidence angle was 0.20°-0.22°.

2.2.8 Water Uptake Measurement of Anion Exchange Thin Films

Under controlled 0-95% RH conditions, the water uptake of PFB-TMA-Br and PFB-TMA-OH thin films was obtained using an in situ quartz crystal microbalance (QCM) system. Figure 2-1 shows the schematic diagram of in situ QCM system. QCM substrates were coupled to a frequency counter and a DC power source in an oscillation circuit (53131 A; Agilent Technologies, Inc.). QCM substrates with or without thin film were held in a home-made small chamber with a high-resolution RH sensor to monitor the
temperature and RH. Humidity controller (BEL Flow; Mirrorable Corp.) was utilized to create 0-95% RH conditions through modulating the N_2 and water vapor. The frequencies of substrates with or without thin film were measured under 0% RH. The mass of dry thin film mass can be got by the following Sauerbrey equation,

$$\Delta m = \frac{S \times \sqrt{\rho \mu}}{2 \times F^2} \times (-\Delta F) \quad (1)$$

Where S is the surface area of the electrode; ρ is quartz density; μ is the quartz shear modulus respectively and F is the fundamental frequency of QCM substrate.

Water uptake λ was calculated by the following equation:

$$\lambda = \left(\frac{m}{m_0} - 1\right) \times \frac{EW}{M_{H_2O}} \quad (2)$$

Where *m* is the mass of the film under each RH, m_0 represents the mass of film at the dry condition, M_{H_2O} represents the molecular weight of water molecules, and *EW* is equivalent weight of PFB-TMA.



Figure 2-1. Schematic illustration of QCM measurement system.

2.2.9 Impedance Spectroscopy at Various Relative Humidity (RH)

The conductivity of PFB-TMA-Br, PFB-TMA-OH, and PFB-TMA-HCO₃ thin films spin-coated on quartz substrates was measured at 25 °C by impedance spectroscopy. A frequency response analyzer (SI1260; Solartron Analytical) equipped with a highfrequency dielectric interface (SI1296; Solartron Analytical) was used to perform the impedance spectroscopy measurement. Figure 2-2 shows the schematic diagram of in situ OH⁻ conductivity measurement system. Humidity-temperature chamber (SH-221; Espec Corp.) was used to generate the 40-95% RH which was the condition for the conductivity measurement of PFB-TMA-Br and PFB-TMA-HCO₃ thin films. For conductivity measurement of PFB-TMA-OH thin films, the thin film electrodes were placed in a sealed box with a high-resolution RH sensor. The temperature was controlled by humiditytemperature chamber (SH-221; Espec Corp.). Precise dew point generator (me-40DP-2PW; Micro equipment) was used to generate the 40-95% RH under a N₂ atmosphere which was the condition for the conductivity measurement of PFB-TMA-OH thin films.

$$\sigma = \frac{d}{Rlt} \qquad (3)$$

where d denotes the distance between the Au electrodes, R represents the resistance of thin film from impedance, l, and t stand for the length of the contact electrodes and the film thickness, respectively.



Figure 2-2. Schematic illustration of in situ OH⁻ conductivity measurement process.

2.3 Results and Discussions

2.3.1 Characterization of Monomer and Polymer

The chemical structure of DBF6 was confirmed by ¹H NMR. Figure 2-3 shows the ¹H NMR spectrum of DBF6. All proton signals can match the chemical structure of DBF6 well. The proton signals that emerged around 7.4-8.0 ppm are assigned to the protons of the aromatic ring, as seen in Figure 2-3. It is noticeable that side chain proton signals occurred at 0.4-3.4 ppm. The chemical structure of DBF6 was confirmed by ¹H NMR spectrum.



Figure 2-3. ¹H NMR spectrum of DBF6.

In this chapter, PFB was synthesized via a Suzuki cross-coupling reaction catalyzed by Pd, which is similar with the previous literature.^{21,27} ¹H NMR was used to determine the chemical structures of PFB. Figures 2-4 exhibits the ¹H NMR spectrum of PFB. The proton signals seen at 7.3-8.0 ppm in PFB are attributed to the aromatic rings. The proton signal of terminal -CH₂ groups adjacent to Br was found around 3.3 ppm. The signals around 0.4-3.4 ppm correspond to the protons of alkyl side chains. Quaternization reaction of PFB (weight-average molecular weight (Mw)=32 kg mol⁻¹) was performed to obtain PFB-TMA. Figures 2-5 shows the ¹H NMR spectrum of PFB-TMA. The proton signals seen at 7.3-8.0 ppm in PFB-TMA are attributed to the aromatic ring of the PFB backbone. Proton signals associated with the TMA group showed at 2.9-3.1 ppm for PFB-TMA-Br. The newly discovered peak at 2.9-3.1 ppm indicates the presence of quaternary ammonium. As a result, the ¹H NMR results reveal that PFB and PFB-TMA-Br were successfully synthesized.



Figure 2-4. ¹H NMR spectrum of PFB.



Figure 2-5. ¹H NMR spectrum of PFB-TMA.

Thermogravimetric analysis (TGA) was utilized to demonstrate the thermal stability of PFB-TMA. The TGA curve of PFB-TMA is shown in Figure 2-6. Three stages of weight reduction were discovered, as depicted in Figure 2-6. The removal of absorbed water caused the first weight loss step, which occurred below 100 °C. The decomposition of the quaternary ammonium group caused the second weight loss step, which occurred between 250 and 350 °C. The degradation of the polymer backbone could be responsible for the third step of weight loss above 400 °C. The thermal decomposition temperature of PFB-TMA was higher than the common working temperature of anion exchange membrane fuel cells, according to thermal study.



Figure 2-6. TGA curve of PFB-TMA.

Figure 2-7 exhibits the EDX spectra of PFB-TMA-Br and PFB-TMA-OH. The EDX spectra indicated that Br⁻ ions decreased sharply after immersed in degassed 1 M NaOH solution for 48 h. Most of Br⁻ ions have been exchanged by OH⁻ ions.



Figure 2-7. EDX spectra of PFB-TMA-Br and PFB-TMA-OH.

2.3.2 Morphology

RH-controlled GI-SAXS was used to examine the morphology of the PFB-TMA-Br thin film at 0% and 95% RH. The 2D GI-SAXS spectra of PFB-TMA-Br thin film at 0% and 95% RH are shown in Figure 2-8. PFB-TMA-Br thin film has no distinguishable scattering peak, implying that PFB-TMA-Br thin film has an amorphous structure. Anion exchange thin films with an amorphous structure have been reported.^{15,16,28} Amorphous structure was documented in a variety of hydrocarbon-based anion exchange thin films in the literature.²⁸ Nanophase separation in anion exchange thin films is substantially weaker than in proton exchange thin films. The fact that quaternary ammonium groups are less hydrophilic than sulfonic acid groups is one of the possible explanations for the poor nanophase separation observed in anion exchange thin films. Furthermore, it may be caused by an insufficient electron density contrast.



Figure 2-8. 2D GI-SAXS spectra of PFB-TMA-Br at dry and 95% RH.

2.3.3 Water Uptake and Anion Conductivity

The water content of anion conductive polymers in thin film form is critical for the anion conduction. Higher OH⁻ water uptake than Br⁻ was observed in AEM.^{29,30} Nevertheless, there is no study to elucidate the water adsorption amount of thin films in OH⁻ form. In situ QCM was developed to investigate the water uptake of PFB-TMA-OH thin films under different RH conditions. Figure 2-9 shows the water uptake result of PFB-TMA-Br and PFB-TMA-OH thin films with 273 nm thickness as a function of RH. λ (number of H₂O per functional group) was used to represent the water adsorption of anion exchange thin film. As shown in Figure 2-9, the water uptake of PFB-TMA-Br and PFB-TMA-OH thin films increased along with RH. The water content of PFB-TMA-OH thin film is much higher than that of PFB-TMA-Br thin film. The higher water affinity and dissociation degree of OH⁻ cause higher water uptake of PFB-TMA-OH thin film than that of PFB-TMA-Br thin film.³¹ Results reveal that the counter-anion affects the water uptake of PFB-TMA thin films.



Figure 2-9. Water uptake of PFB-TMA-Br and PFB-TMA-OH thin films at 25 °C. (Film thickness: 273 nm)

The water uptake of PFB-TMA-OH thin film at 25 °C under 95% RH was 77 wt%. Lee and Co-authors demonstrated that the water uptake of PFB-TMA-OH bulk membrane is 71 wt% at 30 °C in water, suggesting the comparable water uptake result between membrane and thin film. ²¹

The OH⁻ conduction in anion exchange thin film is still unclear due to the requirement of a CO₂-free atmosphere. In situ OH⁻ conductivity measurement process for thin film form was developed. Figure 2-10 summarizes the RH dependence of anion conductivity of PFB-TMA-Br and PFB-TMA-OH thin films spin-coated on quartz substrates. As shown in Figure 2-10, the anion conductivity increased with increasing RH. The increased water uptake and mobile anion are contributed to the increased anion conductivity with increasing RH. In the entire RH range, PFB-TMA-OH thin films had

higher OH⁻ conductivity than the Br⁻ conductivity of PFB-TMA-Br thin film. Lower Br⁻ conductivity than OH⁻ conductivity was confirmed in PFB-TMA thin films by the established in situ conductivity measurement process. The Br⁻ conductivity and OH⁻ conductivity of PFB-TMA thin films under 95% RH are 2.2×10^{-2} and 5.3×10^{-2} S cm⁻¹, respectively. Lee and co-authors demonstrated that the OH⁻ conductivity of PFB-TMA membrane is 5.0×10^{-2} S cm⁻¹ at 30°C in water.²¹ The result reveals that comparable OH⁻ conductivity was found in thin film form.



Figure 2-10. Anion conductivity of PFB-TMA-OH and PFB-TMA-Br thin films as a function of RH at 25 °C. (Film thickness: 273 nm)

To deeply understand the relationship between anion conductivity and water uptake, the anion conductivity was plotted as number of water molecules. As shown in Figure 2-11, much higher OH⁻ conductivity was obtained than Br⁻ conductivity due to the high dissociation degree and superior OH⁻ mobility under high number of water molecules.^{29,30}



Figure 2-11. Anion conductivity of PFB-TMA-Br and PFB-TMA-OH thin films as a function of number of water molecules at 25 °C. (Film thickness: 273 nm)

The OH⁻ ions are easily converted to HCO_3^- and CO_3^{2-} in the air, leading to the reduction of OH⁻ conductivity of anion conductive polymers. To avoid this situation, the OH⁻ conductivity measurement process in this chapter was conducted under N₂ atmosphere. To confirm the accuracy of the OH⁻ conductivity measurement, the HCO_3^- conductivity of PFB-TMA-HCO₃ thin films was measured under various RH. Figure 2-12 shows the comparison of OH⁻ conductivity and HCO_3^- conductivity as a function of RH. As shown in Figure 2-12, much higher OH⁻ conductivity than HCO_3^- conductivity under various RH. At 95% RH, the HCO_3^- conductivity of PFB-TMA-HCO₃ is $1.7 \times 10^-$ ² S cm⁻¹, which is substantially lower than the conductivity of PFB-TMA-OH. The above findings suggest that OH⁻ conductivity in thin films can be measured successfully.



Figure 2-12. Anion conductivity of PFB-TMA-OH and PFB-TMA-HCO₃ thin films as a function of RH at 25 °C. (Film thickness: 273 nm)

2.3.4 Film Thickness Dependence OH⁻ Conductivity and Water Uptake

To elucidate the film thickness dependence water uptake and OH⁻ conductivity in anion exchange thin film, a PFB-TMA-OH film with thickness 30 nm was prepared. Figure 2-13 compares the OH⁻ conductivity of PFB-TMA-OH thin films at each thickness as a function of RH. As shown in Figure 2-13, lower OH⁻ conductivity in PFB-TMA-OH (30 nm) thin film than that of PFB-TMA-OH (273 nm) thin film was observed under the same RH. At 95% RH, the OH⁻ conductivity of PFB-TMA-OH (30 nm) thin film is 3.5×10^{-2} S cm⁻¹.



Figure 2-13. OH⁻ conductivity of PFB-TMA-OH with different film thickness as a function of RH at 25 °C.

Water uptake can provide a deep understanding of the properties of the thinner PFB-TMA-OH thin film. The water adsorption of PFB-TMA-OH (30 nm) was also measured under the N₂ atmosphere. The water uptake comparison of PFB-TMA-OH (273 nm) and PFB-TMA-OH (30 nm) films as a function of RH was shown in Figure 2-14. As seen from Figure 2-14, lower water uptake in PFB-TMA-OH (273 nm) thin film than that of PFB-TMA-OH (273 nm) thin film was also found.



Figure 2-14. Water uptake of PFB-TMA-OH with different film thickness as a function of RH at 25 $\,$ °C.

The thinner proton exchange thin film exhibited decreased proton conductivity was reported. The lower water uptake in the thinner proton exchange film is contributed to the decreased proton conductivity.³² To deeply clarify the relation between water uptake and OH⁻ conductivity of PFB-TMA-OH thin films. The OH⁻ conductivity of PFB-TMA-OH (273 nm) and PFB-TMA-OH (30 nm) thin films were compared as a function of the number of water molecules. Figure 2-15 shows the number of water molecules dependence of OH⁻ conductivity of PFB-TMA-OH (273 nm) and PFB-TMA-OH (30 nm) thin films. With the increase of water uptake, the OH⁻ conductivity also increased in PFB-TMA-OH thin films. As discussed in the water uptake part, PFB-TMA-OH (30 nm) thin film contains less water than PFB-TMA-OH (273 nm) thin film. Under the same number of water molecules, the OH⁻ conductivity was barely decreased in the PFB-TMA-OH (30

nm) thin film. As the literature of proton exchange thin films, the above results suggest that the reduced OH⁻ conductivity in PFB-TMA-OH (30 nm) thin film is related to the decreased water uptake.



Figure 2-15. Number of water molecules dependence of OH⁻ conductivity of PFB-TMA-OH with different film thickness as a function of RH at 25 °C. The lines were used to guideline the eyes.

Both interfacial OH⁻ transportation and internal OH⁻ transportation might be existed in the OH⁻ form thin films. To distinguish the internal conduction or interfacial conduction in PFB-TMA-OH thin films, the normalized resistance (R') was obtained according to equation (4).

$$R' = \frac{Rl}{d} \ (4)$$

where d denotes the distance between the Au electrodes, R represents the resistance value from impedance, 1 stands for the length of the contact electrodes. The interfacial OH⁻

conduction can occur at both the air-film interface and substrate-film interface. If the interfacial OH⁻ conduction mainly occurs in PFB-TMA-OH thin film, the film thickness will not affect the normalized resistance. However, if the internal OH⁻ conduction occurs in the thin film, then the normalized resistance depends on the film thickness. The normalized interfacial resistance of PFB-TMA-OH thin films with different film thicknesses as a function of RH was shown in Figure 2-16. As shown in Figure 2-16, the normalized resistance of PFB-TMA-OH as a function of RH depends on the film thickness. Therefore, internal OH⁻ conduction mainly occurs in PFB-TMA-OH thin films.



Figure 2-16. RH dependence of the normalized interfacial resistance for PFB-TMA-

OH-273 nm and PFB-TMA-30 nm.

2.4 Conclusions

In conclusion, this is the first time to elucidate the OH⁻ conductivity and water content of anion exchange thin films. PFB-TMA was used as a model anion conductive polymer. Newly developed in situ measurements were used to observe the OH⁻ conductivity and water uptake of PFB-TMA thin films under different RH which is created by N₂ and water vapor. Superior OH⁻ conductivity than Br⁻ conductivity was confirmed in PFB-TMA thin films. Similar OH⁻ conductivity was observed in PFB-TMA-OH (273 nm) film and reported membrane. The OH⁻ conductivity of PFB-TMA-OH (273 nm) and PFB-TMA-OH (30 nm) thin films was 5.3×10^{-2} S cm⁻¹ and 5×10^{-2} S cm⁻¹, respectively. Besides, decreased number of water molecules adsorbed was found in the PFB-TMA-OH (30 nm) thin film under the same RH. The deceased water adsorption in the thinner film results in reduced OH⁻ conductivity. Under the same amount of water uptake, only slightly decreased OH⁻ conductivity was observed in thinner PFB-TMA-OH thin film.

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Chapter 3

Anion Conductive and Hydration Properties of Fluorene-Thiophene-Based Anion Exchange Thin Films with Different Functional Groups

Abstract

fluorene-thiophene-based anion conductive polymers carrying with New trimethylammonium (TMA) and N-methylpiperidinium (Pip) were synthesized in this chapter. The anion conductive and hydration properties of anion exchange thin films with different counter-anion and cations were studied. TMA-based anion exchange thin film exhibited superior OH⁻ conductivity than that Pip-based anion exchange thin film, 1.8×10⁻ ² S cm⁻¹ at 25 °C under 95% relative humidity (RH), because of high ion exchange capacity (IEC), less hydrophobicity and smaller size of TMA. The number of water molecules strongly affects the anion conductive properties of thin films. The high dissociation degree of ion-pairs and high mobility are contributed to the superior OHconductivity under high hydration conditions. In contrast, low number of water molecules can result in higher Br⁻ conductivity than OH⁻ conductivity. Newly established homemade in situ measurement was used to investigate the temperature dependence OH⁻ conductivity under CO₂-free atmosphere at 90% RH. The activation energy of anion conduction is determined by the counter-anion. The influence of counter-anion and cationic groups on the water uptake and anion conduction in the anion exchange thin films has been comprehensively revealed, which is crucial for the design and development of anion exchange thin films.

3.1 Introduction

As discussed in chapter 2, anion exchange thin film is a critical part that can dictate the electrochemical performance of AEMFC. Understanding the water uptake, anion conductive properties, and morphology of anion exchange thin film are important but still unclear.¹⁻⁴ Because all procedures from OH⁻ form thin film preparation to conductivity and water uptake measurements should be performed under a CO₂-free atmosphere. In the second chapter, a CO₂-free measurement technique for the OH- form thin films was established. The OH⁻ conductivity of reported anion conductive polymer poly[(9,9-bis(6'-(N,N,N-trimethylammonium)-hexyl)fluorene)-alt-(1,4-benzene)] (PFB-TMA) in thin film form was reported. Film dependence of water uptake and OH⁻ conductivity of PFB-TMA thin films have been revealed.⁵ Nonetheless, there is still a large gap to systematically understand the OH⁻ form thin films, particularly the OH⁻ conductivity as a function of temperature in thin film form. Anion exchange membranes (AEMs) with different cationic groups have been revealed. Different water uptake and OH⁻ conductivity were observed in AEMs with different cationic groups. Buggy and co-authors synthesized trimethylammonium (TMA) and N-methylpiperidinium (Pip)-based anion exchange thin films. Higher water content was obtained in Pip-based anion exchange thin film in halide form.² However, there is no information about the OH⁻ form thin film with different cationic groups. To systematically understand the properties of anion exchange thin films, anion conductive polymers with different cationic groups were newly synthesized in this chapter. In addition, an in situ temperature dependence of the OH⁻ conductivity

measurement using in-house constructed equipment was established in this chapter. The effect of counter-anion and functional groups on the properties of anion exchange thin films were systematically investigated.

Anion conductive polymer is composed of backbone and cationic group. The design of chemical stable backbone and suitable cationic group is crucial. Various fluorene-based anion conductive polymers with superior alkaline stability have been reported.^{6–14} Conjugated polymers based on fluorene-thiophene exhibit good film-forming characteristics and chemical stability. As a result, in this chapter, the poly(fluorenethiophene) was chosen as the backbone. High OH⁻ conductivity and enhanced alkaline stability were observed for side chain type anion conductive polymers.^{9,15–22} TMA and Pip has been investigated extensively in the anion conductive polymer due to the relatively high anion conduction and easy functionalization.²³ Hence, side chain type poly(fluorene-thiophene)-based anion conductive polymers functionalized with TMA and Pip were designed in this chapter.

The objective of this chapter is to explore the hydration properties, anion conductive properties, and morphology of fluorene-thiophene-based anion exchange thin films with the different cationic groups and counter-anion. The hydration and anion conductive properties of anion exchange thin films were investigated by in situ quartz crystal microbalance (QCM), in situ Fourier transform infrared spectroscopy (FTIR), and in situ impedance spectroscopy measurements under different RH. RH-controlled grazingincidence small-angle X-ray scattering (GI-SAXS) was used to analyze the morphology of anion exchange thin films. TMA functionalized fluorene-thiophene-based anion exchange thin film exhibited high OH⁻ conductivity. Water uptake results reveal that counter-anion hydration is the dominant factor for the water uptake of fluorenethiophene-based anion exchange thin film other than cations. The relation between anion conductivity and water uptake of fluorene-thiophene-based anion exchange thin films suggests that the OH⁻ conduction is strongly dependent on the number of water molecules. PFT6-TMA and PFT6-Pip thin films exhibited similar anion conduction activation energy in Br⁻ and OH⁻ forms. The activation energy of OH⁻ conduction is higher than Br⁻ conduction in the prepared thin films.

3.2 Experimental Section

3.2.1 Materials

2,7-Dibromofluorene, bis(pinacolato)diboron, tetrabutylammonium bromide (TBAB), 1,6-dibromohexane, [1,1-bis(diphenylphosphino)ferrocene] dichloro palladium (II) $(PdCl_2)$ (dppf), 5, 5'-dibromo-3, 3'-dihexyl-2, 2'-bithiophene and tetrakis(triphenylphosphine) palladium (0) (Pd (PPh₃)₄) were obtained from Tokyo Chemical Industry Co. Ltd., Japan. NaOH, CH₂Cl₂, NaCl, NaHCO₃, magnesium sulfate anhydrous, dioxane, hexane, methanol, CHCl₃, tetrahydrofuran (THF), toluene, K₂CO₃, 30% trimethylamine solution, N-methylpiperidine, and diethyl ether were used as received from Fujifilm Wako Pure Chemical Corp., Japan.

3.2.2 Synthesis of monomer and polymers

Scheme 3-1 shows the synthetic route of 2,7-dibromo-9,9-bis(6'bromohexyl)fluorene (DBF6) and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis(6'-bromo hexyl)fluorene (TDBF6) by following the reported literature.^{24,25}



Scheme 3-1. Synthetic route of DBF6 and TDBF6.

DBF6

65 mmol of 1,6-dibromohexane, 2 mmol of TBAB, 8 mmol of 2,7-dibromofluorene, 30 mL of sodium hydroxide solution (50 wt%) were added to the 100 mL three-neck flask. The mixture was reacted at 60 °C for 8 h under the protection of argon. The organic layer was obtained after extracting the reaction mixture with dichloromethane. After washing with water and brine, the organic layer was dried with MgSO₄. Subsequently, the surplus 1,6-dibromohexane was evaporated by vacuum distillation. Finally, the product was produced with a 71% yield by column chromatography using hexane.

TDBF6

2.5 mmol of DBF, 6.0 mmol of bis(pinacolato)diboron, 15 mmol of potassium acetate, and 25 mL of dioxane was added to the 100 mL round-bottom flask. The mixture was degassed three times by using freeze–pump–thaw cycles. Next, 100 mg of PdCl₂(dppf) was added to the reaction mixture. The reaction was conducted at 85 °C for 12 h under the protection of argon. After reaction, the solvent was removed by rotary evaporator. Then, the mixture was extracted with dichloromethane, washed with water and brine, and dried by magnesium sulfate. Finally, the product was obtained by column chromatography using hexane and ethyl acetate (20:1) with a 77% yield.

Poly[(9,9-bis(6-bromohexyl)fluorene)-alt-(3,3'-dihexyl-2,2'-bithiophene)] (PFT6)

According to the reported literature, PFT6 was synthesized by a Suzuki crosscoupling reaction catalyzed by Pd (PPh₃)₄.^{6,12} A mixture of 1.0 mmol of TDBF, 15 mL of toluene and 4 mL of 2 M potassium carbonate aqueous solution were added into 50 mL three-neck flask. After two time's degas through freeze–evacuate–thaw cycles, 1.0 mmol of 5, 5'-Dibromo-3, 3'-dihexyl-2, 2'-bithiophene was added to the mixture. After another three time's degas, 0.10 mmol of [Pd (PPh₃)₄] was added into the reaction mixture under argon atmosphere. The mixture was stirred at 95 °C for 48 h under the protection of argon. The polymer was precipitated from the mixture of methanol and deionized water. The crude polymer was purified by Soxhlet extraction using a mixture of methanol, hexane, and acetone (1:1:1 v/v/v). After dried under reduced pressure, yellow solid was obtained with a 66% yield.

Poly[(9,9-bis(6'-(N,N,N-trimethylammonium)hexyl)fluorene)-alt-(3,3'-dihexyl-2,2'bithiophene)] (PFT6-TMA-Br)

Following the quaternization of PFT6, PFT-TMA-Br was obtained. (Scheme 3-2) To dissolve 200 mg of PFT6 in a vial, 2 mL of THF was employed. 1 mL of 30% TMA solution was added once the polymer had completely dissolved. 2 mL of DI water was added after the appearance of precipitate inside the vial. To achieve complete quaternization, the mixture was stirred at room temperature for 2 days. The rotary evaporator was used to remove the solvent after the process. 5 mL of MeOH was used to dissolve the crude product and precipitated in diethyl ether. After centrifugation and overnight drying under vacuum, pure PFT-TMA-Br was obtained. (Yield: 88%)

Poly[(9,9-bis(6'-(N-methylpiperidinium) hexyl)fluorene)-alt-(3,3'-dihexyl-2,2'bithiophene)] (PFT6-Pip-Br)

To dissolve 200 mg of PFT6 in a vial, 5 mL of THF was employed. 8 mL of Nmethylpiperidine was added to the solution. The mixture was stirred at 60 °C for 4 days under the protection of Ar. Afterward, the solvent was evaporated. Diethyl ether was used to precipitate the concentrate after it was dissolved in MeOH. The product was dried under vacuum overnight to obtain PFT6-Pip-Br. (Yield 80%)



Scheme 3-2. Synthetic route of PFT6-TMA-Br and PFT6-Pip-Br.

3.2.3 Characterization

¹H NMR spectra of monomer and polymers were recorded on (400 MHz) Bruker Avance III spectrometer (Bruker Analytik GmbH). CDCl₃ or MeOD- d_4 was used as a solvent. ATR-FTIR spectra were obtained by a FTIR spectrometer (Nicolet 6700; Thermo Fisher Scientific Inc.) with a wavenumber ranging of 400-4000 cm⁻¹. The weight average molecular weight (M_w), number average molecular weight (M_n), and polydispersity index (PDI, M_w/M_n) of PFT6 were estimated using gel permeation chromatography (GPC) (GPC, LC-2000plus; Jasco Inc.) equipped with Shodex GPC KF-805L column. using THF was used as mobile phase and polystyrene as standards. The polymer solution was filtered before injection into the column. On a thermogravimetric analyzer, the thermal decomposition of PFT6-TMA-Br and PFT6-Pip-Br was measured in the temperature range 40-600 °C with a heating rate of 10 °C min⁻¹ under N_2 flow. The polymer was dried overnight at 40 °C under vacuum before being measured.

3.2.4 Ion Exchange Process

To get OH⁻ form PFT6-TMA and PFT6-Pip thin films, PFT6-TMA-Br (or PFT6-Pip-Br) was immersed in 1 M NaOH solution under the protection of argon at room temperature for 2 days. The 1 M NaOH solution was changed three times within 2 days. After that, PFT6-TMA and PFT6-Pip (in OH⁻ form) were washed by degassed ultra-pure water until the pH was neutral. All the process for OH⁻ form anion conductive polymers was performed under N₂ atmosphere. To get HCO₃⁻ form PFT6-TMA and PFT6-Pip thin films, PFT6-TMA-Br (or PFT6-Pip-Br) was immersed in 1 M NaHCO₃ solution. The 1 M NaHCO₃ solution was changed three times within 2 days. After that, PFT6-TMA and PFT6-Pip (in HCO₃⁻ form) were washed by ultra-pure water until the pH was neutral. The OH⁻ and HCO₃⁻ forms of PFT6-TMA-based anion conductive polymers were denoted as PFT6-TMA-OH and PFT6-TMA-HCO₃. The OH⁻ and HCO₃⁻ forms of PFT6-Pip-based anion conductive polymers were denoted as PFT6-Pip-OH and PFT6-Pip-HCO₃

3.2.5 Preparation of Anion Exchange Thin Films

The spin-coating (ACT-200; Active Co. Ltd.) of thin films were done on Si, SiO₂, and Au-coated quartz crystal microbalance (QCM) substrates (Seiko EG&G Co. Ltd.). The substrates were cleaned using 2-propanol and vacuum plasma (Cute-MP; Femto Science Inc., Korea) before spin-coating. For the preparation of PFT6-TMA-OH and PFT6-Pip-OH thin films, the dispersion preparation and spin-coating process were performed under a N₂ atmosphere.

3.2.6 White Light Interferometric Microscopy

The white-light interferometric microscope (BWsingle bondS506; Nikon Corp.) was used to measure the thickness of thin film. 480 nm-thick films were used for the in situ FTIR, pMAIRS, water uptake and conductivity measurements. In addition, 505 nm-thick film was used for the RH-controlled in situ grazing-incidence small-angle X-ray scattering (GI-SAXS) measurements.

3.2.7 Scanning Electron Microscope and Energy Dispersive X-ray Spectroscopy (SEM-EDX)

TM3030Plus miniscope (Hitachi) was used to perform scanning Electron Microscope and Energy Dispersive X-ray Spectroscopy (SEM-EDX). 15 kV was used as the accelerating voltage.

3.2.8 RH-controlled In Situ FTIR Spectroscopy

Si substrate with thin film was placed in a small home-made chamber. To obtain transmission IR spectra, an FTIR spectrometer (Nicolet 6700; Thermo Fisher Scientific Inc.) with deuterium triglycine sulfate (DTGS) detector was used. Precise dew point generator (me-40DP-2PW; Micro equipment) was used to generate various RH conditions. The number of smooth points is 13.499 cm⁻¹.

3.2.9 RH-controlled In Situ Grazing-Incidence Small-Angle X-ray Scattering Measurements (GI-SAXS)

RH controlled GI-SAXS was conducted on a X-ray diffractometer (FR-E; Rigaku Corp.) with an R-AXIS IV two-dimensional detector. Cu-K α X-ray source (wavelength = 1.54 Å). Humidity-controlled cell on the goniometer and vertical stage (ATS-C316-EM/ALV-3005-HM; Chuo Precision Industrial Co. Ltd.) was used to hold the thin film. Nitrogen gas and water vapor were used to control the RH. The humidified cell holds Lumirror windows. The camera length was 300 mm, and the incidence angle was set in the range of 0.20°–0.22°.

3.2.10 Water Uptake Measurement of Anion Exchange Thin Films

Under controlled 0-95% RH conditions, the water uptake of PFT6-TMA-Br, PFT6-TMA-OH, PFT6-Pip-Br and PFT6-Pip-OH thin films was obtained using an in situ quartz crystal microbalance (QCM) system. Figure 3-1 shows the schematic diagram of in situ QCM system. QCM substrates were coupled to a frequency counter and a DC power source in an oscillation circuit (53131 A; Agilent Technologies, Inc.). QCM substrates with or without thin film were held in a small home-made chamber with a high-resolution RH sensor to monitor the temperature and RH. Humidity controller (BEL Flow; Mirrorable Corp.) was utilized to create 0-95% RH conditions through modulating the N₂ and water vapor. The frequencies of substrates with or without thin film were measured under 0% RH. The mass of dry thin film mass can be obtained by the following Sauerbrey equation,
$$\Delta m = \frac{S \times \sqrt{\rho \mu}}{2 \times F^2} \times (-\Delta F) \quad (1)$$

Where S is the surface area of the electrode; ρ is quartz density; μ is the quartz shear modulus respectively and F is the fundamental frequency of QCM substrate.

Water uptake λ was calculated by the following equation:

$$\lambda = \left(\frac{m}{m_0} - 1\right) \times \frac{EW}{M_{H_2O}} \quad (2)$$

Where *m* is the mass of the film under each humidity, m_0 represents the mass of film at the dry condition, M_{H_20} is the molecular weight of water molecules, and *EW* is equivalent weight of PFT6-TMA and PFT6-Pip.



Figure 3-1. Schematic illustration of QCM system.

3.2.11 Impedance Spectroscopy at Various Relative Humidity (RH)

The conductivity of PFT6-TMA-Br, PFT6-TMA-OH, PFT6-TMA-HCO₃, PFT6-Pip-Br, PFT6-Pip-OH, and PFT6-Pip-HCO₃ thin films spin-coated on quartz substrates was measured by impedance spectroscopy using a frequency response analyzer (SI1260; Solartron Analytical) equipped with a high-frequency dielectric interface (SI1296; Solartron Analytical). Figure 3-2 shows the schematic diagram of in situ OH⁻ conductivity measurement system. Humidity-temperature chamber (SH-221; Espec Corp.) was used to generate the 40-95% RH which was the condition for the conductivity measurement of thin films in Br⁻ and HCO₃⁻ forms. For conductivity measurement of PFT6-TMA-OH and PFT6-Pip-OH thin films, the thin film electrodes were placed in a sealed box with a highresolution RH sensor. The temperature was controlled by humidity-temperature chamber (SH-221; Espec Corp.). Precise dew point generator (me-40DP-2PW; Micro equipment) was used to generate the 40-95% RH under a N₂ atmosphere which was the condition for the conductivity measurement of PFB-TMA-OH thin films. Anion conductivity (σ) was calculated as follows,

$$\sigma = \frac{d}{Rlt} \qquad (3)$$

where d denotes the distance between the Au electrodes, R represents the resistance value from impedance, l, and t stand for the length of the contact electrodes and thickness of the film, respectively.

The temperature dependence anion conductivity of PFT6-TMA and PFT6-Pip thin films were measured from 20 °C to 50 °C under fixed RH=90%. The estimated activation energy of anion conduction was estimated according to the Arrhenius equation.

$$\sigma T = \sigma_0 ex \, p\left(\frac{-E_a}{RT}\right) \quad (4)$$

where R denotes the gas constant, T represents the temperature, and σ_0 represent pre-

exponential factor.



Figure 3-2. Schematic illustration of OH⁻ conductivity measurement system.

3.2.12 p-Polarized Multiple Angle Incidence Resolution Spectrometry (pMAIRS)

The molecular orientation of PFT6-TMA-Br and PFT6-Pip-Br thin films was studied by pMAIRS. Then pMAIRS measurements were conducted on a Fourier-transform infrared (FTIR) spectrometer (Nicolet 6700; Thermo Fisher Scientific Inc.) equipped with a mercury cadmium telluride (MCT) detector. Single-beam spectra were recorded at angles of incidence ranging from 38° to 8° in 6° steps.

3.3 Results and Discussions

3.3.1 Characterization of Monomers and Polymers

The chemical structure of DBF6 was confirmed by ¹H NMR. (Figure 3-3a) The proton signals that can be seen at 7.4-8.0 ppm are assigned to the aromatic protons of DBF6. The protons of side chains appeared at 0.4-3.4 ppm. The chemical structure of monomer was characterized by ¹H NMR. Figure 3-3b shows the ¹H NMR spectrum of TDBF6. As shown in Figure 3-3b, the proton signals that appeared at 7.4-8.0 ppm are assigned to the aromatic protons of DBF6. The protons of side chains appeared at 0.4-3.4 ppm. The peak that was arising at 1.4 ppm correspond to the proton signals of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane. The results of ¹H NMR spectra suggest that DBF6 and TDBF6 were synthesized successfully.



Figure 3-3. ¹H NMR spectra of (a) DBF6 and (b) TDBF6.

The chemical structure of PFT6 was analyzed through ¹H NMR. Figure 3-4 shows the ¹H NMR spectra of PFT6. The chemical shift of protons from the fluorene ring in the main chain was observed at 7.40-7.80 ppm. The signal of the thiophene ring protons was seen at 7.24 ppm. The peaks at around 0.40-3.40 ppm demonstrated the existence of alkyl side chain. The results of ¹H NMR spectrum confirmed the chemical structure of PFT6.



Figure 3-4. ¹H NMR spectrum of PFT6.

PFT6-TMA-Br was obtained by reacting PFT6 ($M_W = 22 \text{ kg mol}^{-1}$ and PDI = 2.1) with TMA. PFT6-Pip-Br was formed via Menshutkin reaction which can convert Nmethylpiperidine and trimethylamine into quaternary ammonium by reaction at the Br position of alkyl side chains, of PFT6 with Pip. The successful quaternization of PFT6 was confirmed by ¹H NMR. Figure 3-5 shows the ¹H NMR spectra of PFT6-TMA-Br and PFT6-Pip-Br. For PFT6-TMA-Br, a new peak ascribed to TMA appeared at 3.00 ppm, confirming the successful quaternization reaction. For PFT6-Pip-Br, a new peak assigned to the -CH₃ of Pip appeared at 2.90 ppm, revealing the introduction of Pip. The ion exchange capacity (IEC) values of PFT6-TMA-OH and PFT6-Pip-OH obtained from ¹H NMR were 2.34 and 2.11 meq q⁻¹, respectively.



Figure 3-5. ¹H NMR of PFT6-Pip-Br (a) and PFT6-TMA-Br (b).

The chemical structure of prepared anion conductive polymers was characterized by FTIR spectroscopy. Figure 3-6 shows the ATR-FTIR spectra of PFT6-TMA-Br and PFT6-Pip-Br. As shown in Figure 3-6, the symmetric and asymmetric vibrations of -CH₂ were observed at 2854 and 2927 cm⁻¹. The stretching vibration of -CH₃ group occurred at 3016 cm⁻¹. The band that appeared at 1463 cm⁻¹ is associated with the stretching vibration of aromatic rings. Additionally, the broad and strong band at 3400 cm⁻¹ was attributed as the v(O-H) of water, corresponding to the high hydrophilicity of PFT6-TMA-Br and PFT6-Pip-Br.



Figure 3-6. ATR-FTIR of PFT6-Pip-Br and PFT6-TMA-Br. (a) Wavenumber range from 2600 to 3800 cm⁻¹, (b) wavenumber range from 500 to 2000 cm⁻¹.

TGA was performed to investigate the thermal stability of prepared anion conductive polymers under the N₂ atmosphere. Figure 3-7 shows the TGA curves of PFT6-TMA-Br and PFT6-Pip-Br. Three distinct weight loss steps were observed in Figure 3-7. The first weight loss step was observed below 100 °C, which can be ascribed to the removal of residual water. The second weight loss step was obtained between 200 and 300 °C which can be attributed to the decomposition of quaternary ammonium of PFT6-TMA-Br and PFT6-Pip-Br. The third weight loss step, the degradation of polymer backbone occurred above 400 °C. The thermal stability results clearly implied that the degradation temperature of prepared anion conductive polymers was above the normal operating temperature of AEMFCs.



Figure 3-7. TGA curves of PFT6-Pip-Br and PFT6-TMA-Br.

Figure 3-8 exhibits the EDX spectra before and after ion exchange of (PFT6-TMA-Br and PFT6-TMA-OH). The EDX spectra indicated that Br⁻ ions decreased sharply after immersed in degassed 1 M NaOH solution for 48 h. Most of Br⁻ ions have been exchanged by OH⁻ ions.



Figure 3-8. EDX spectra of PFT6-TMA-Br and PFT6-TMA-OH.

Figure 3-9 exhibits the EDX spectra before and after ion exchange of (PFT6-Pip-Br and PFT6-Pip-OH). The EDX spectra indicated that Br⁻ ions decreased sharply after immersed in degassed 1 M NaOH solution for 48 h. Most of Br⁻ ions have been exchanged by OH⁻ ions.



Figure 3-9. EDX spectra of (A) PFT6-Pip-Br and (B) PFT6-Pip-OH.

3.3.2 Water Uptake

Water uptake is an important parameter for the anion conduction of anion exchange thin film. The water uptake of PFT6-TMA and PFT6-Pip thin films was measured by RHcontrolled in situ QCM. Figure 3-10 summarizes the number of water molecules per functional group of prepared thin films under different RH. As shown in Figure 3-10, the water uptake of PFT6-TMA-OH and PFT6-Pip-OH thin films is much higher than that of PFT6-TMA-Br and PFT6-Pip-Br thin films, especially in the high RH region. Results reveal that the water uptake of anion exchange thin films is strongly affected by counteranion. The intricate interaction between hydrophilic functional group, hydrophobic polymer matrix, and water molecules determines the water uptake of ion conduction polymers.²⁶ The water uptake of anion exchange thin film is mainly governed by the hydration properties of cation-anion pair at low RH region. The higher hydration energy and hydration number are contributed to the higher water uptake of OH⁻ form anion exchange thin films.^{27–29} At high RH range, the water uptake of anion exchange thin films in OH⁻ form increased sharply, suggesting more free water existence in the anion exchange thin films. As mentioned in the RH-controlled in situ FTIR result, the dissociation degree of anions increased along with RH. The dissociation properties of ion-pairs will dominate the water uptake at the high RH region. According to Pearson's HSAB (hard and soft acid-base) theory, the large (soft) cation prefers binding to large (soft) anion.³⁰ The large TMA (Pip) cations bind strongly with large Br⁻ ions. While the small OH⁻ ions are more easily dissociated from the cation under the high RH range, causing enhanced osmotic pressure and as a result high water uptake.^{31,32}

PFT6-TMA and PFT6-Pip thin films exhibited similar water content at high RH region in the identical anion form. Under the high RH range, the cation-anion pairs dissociated, cations will not affect the water uptake. The only difference between PFT6-TMA and PFT6-Pip is the cationic group. Hence, similar osmotic pressure can be expected for the identical anion form of PFT6-TMA and PFT6-Pip in the high RH range, corresponding to a similar number of water molecules absorption.



Figure 3-10. Water uptake of PFT6-TMA and PFT6-Pip thin films.

3.3.3 Hydration Properties of Thin Films

The hydration properties of ion conductive polymers can be obtained using IR.^{33,34} RH-controlled in situ FTIR measurements were performed to investigate the hydration properties and proton dissociation of proton exchange thin films in our previous work.³⁵ Here, the RH-controlled in situ FTIR measurement was conducted to evaluate the hydration properties and anion dissociation of anion exchange thin films. Figure 3-11 shows the RH-dependent FTIR spectra for PFT6-TMA-Br and PFT6-Pip-Br thin films. The absorbance of -O-H stretching vibration and H₂O bending vibration increased along with RH, indicating that the prepared anion exchange thin films were absorbing more water.

Vico and co-authors investigated the hydration properties of polysulfone-based AEM by ATR-FTIR at different water content. With increasing water content, the absorbance of the -C-H stretching vibration band in $[-N(CH_3)_3^+]$ reduced. Vandiver and co-authors collected the ATR-FTIR of polyethylene-b-poly(vinylbenzyl trimethylammonium) anion conductive polymer under various RH to get the polymerwater interaction. Position shift was found for -C-H stretching vibration band.³⁶ Based on these results, the -C-H stretch vibration band in $[-N(CH_3)_3^+]$ was analyzed to understand the hydration and dissociation of cation-anion pairs with the increase of RH.

The expanded region for -C-H stretching vibrations of PFT6-TMA-Br thin film is shown in Figure 3-11b. The band at 3006 cm⁻¹ is assigned to the -C-H stretch vibration in $[-N(CH_3)_3^+]$ at dry condition. With the increasing of RH, the absorbance of -C-H stretch vibration in $[-N(CH_3)_3^+]$ decreased, while the position of -C-H stretch vibration band in $[-N(CH_3)_3^+]$ shifted to high wavenumber. Higher wavenumber of -C-H stretch vibration band means the stronger force constant of -C-H bond. The strong interaction caused the presence of cation-anion pairs under 0% RH. Due to the bound state between cation and Br⁻, Br⁻ can share lone pair electrons with H of -C-H in $[-N(CH_3)_3^+]$, causing the less positive charge of H.^{33,37} With the increase of RH, the water content of anion exchange thin films enhanced and the dissociation of Br⁻ occurred. The more positive charge of H resulting the increase of force constant and reduced absorbance of -C-H. This is the first time that RH-controlled in situ FTIR with a transparent mode has been used to examine ion-pairs dissociation in the anion exchange thin films. The expanded region for -C-H stretching vibrations of PFT6-Pip-Br thin film is shown in Figure 3-11d. There is no clear -C-H stretch vibration band due to the less -CH₃ group of Pip.



Figure 3-11. In situ FTIR spectra of (a, b) PFT6-TMA-Br and (c, d) PFT6-Pip-Br thin films as a function of RH. (a) Wavenumber range between 1250 and 4000 cm⁻¹ of PFT6-TMA-Br thin film, (b) Wavenumber range between 2600 and 3200 cm⁻¹ of PFT6-TMA-Br thin film, (c) Wavenumber range between 1250 and 4000 cm⁻¹ of PFT6-Pip-Br thin film, (d) Wavenumber range between 1250 and 4000 cm⁻¹ of PFT6-Pip-Br thin film.

3.3.4 Morphology of Thin Films

The morphology of PFT6-TMA-Br and PFT6-Pip-Br thin films was studied using RH-controlled GI-SAXS. Figure 3-12 displays the 1D GI-SAXS profiles of PFT6-TMA-Br and PFT6-Pip-Br thin films at 0% RH and 95% RH. For PFT6-TMA-Br thin film, the absence of a recognizable scattering peak suggests that it has an amorphous structure. For

PFT6-Pip thin film, a very faint scattering peak $q_z = 3.84 \text{ nm}^{-1}$ (d = 1.6 nm) in the out-ofplane direction was observed, regardless of RH. PFT6-Pip-Br thin film had very few ordered structures. However, the majority of the PFT6-Pip-Br thin film remains amorphous.



Figure 3-12. 1D GI-SAXS profiles in the out-of-plane and in-plane directions at 0% and 95% RH of (a and b) PFT6-TMA-Br and (c and d) PFT6-Pip-Br thin films. Those scattering peaks at q_y=10.8 and 12.0 nm⁻¹ were originated from the Lumirror window of the humidity-controlled cell.

IR pMAIRS was carried out to confirm the amorphous of prepared anion exchange thin films. The pMAIRS spectra of PFT6-TMA-Br and PFT6-Pip-Br thin films are shown in Figure 3-13. The stretching vibration of the aromatic rings was observed at 1498 cm⁻¹, as seen in Figure 3-13. The aromatic ring stretching vibration absorbance in the IP direction is the same as in the OP direction for the prepared anion exchange thin films, implying an amorphous structure of the anion exchange thin films. Anion exchange thin films with amorphous structure have been reported.^{1,3,4} The literature reported amorphous structure in a variety of hydrocarbon-based anion exchange thin films.⁴ Anion exchange thin films have a significantly weaker nanophase separation than proton exchange thin films. The fact that quaternary ammonium groups are less hydrophilic than sulfonic acid groups is one of the possible explanations for the poor nanophase separation observed in anion exchange thin films. Furthermore, it may be caused by an insufficient electron density contrast.



Figure 3-13. pMAIRS spectra of (a) PFT6-TMA-Br and (b) PFT6-Pip-Br thin films.

The surface morphology of PFT6-TMA-Br and PFT6-Pip-Br thin film was investigated by SEM. Figure 3-14 shows the SEM images of PFT6-TMA-Br and PFT6-Pip-Br thin films. As shown in Figure 3-14, the surface of PFT6-TMA-Br and PFT6-Pip-Br thin films was homogeneous are smooth, no pores or cracks were visible.



Figure 3-14. SEM images of prepared anion exchange thin films (a) PFT6-TMA-Br and (b) PFT6-Pip-Br.

3.3.5 Anion Conductivity

The anion conductivity of PFT6-TMA and PFT6-Pip thin films spin-coated on quartz substrates was obtained by RH-controlled impedance spectroscopy. Figure 3-15 shows the RH dependence anion conductivity of PFT6-TMA and PFT6-Pip thin films. As shown in Figure 3-15, the anion conductivity of prepared anion exchange thin films increased with the increasing of RH. With the increasing of RH, the dissociation degree of anions increased, which indicates that mobile anion increased. Hence, the increased anion conductivity or prepared mobile anion and water content. The Br⁻ conductivity of PFT6-TMA and PFT6-Pip thin films are 4.3×10⁻³ S cm⁻¹ and 1.5×10⁻³ S cm⁻¹, respectively, at 25 °C under 95% RH. The OH⁻ ion conductivity of PFT6-TMA and PFT6-Pip thin films are 1.8×10⁻² S cm⁻¹ and 6.8×10⁻³ S cm⁻¹, respectively, at 25 °C under 95% RH.



Figure 3-15. RH dependence of anion conductivity of PFT6-TMA and PFT6-Pip thin

films at 25 °C.

The OH^- is easily converted to carbonate and bicarbonate in the air, leading to the reduction of OH^- conductivity. To avoid this situation, the OH^- conductivity measurement process was conducted under N₂ atmosphere. To confirm the OH^- conductivity, the HCO_3^- conductivity of PFT6-TMA and PFT6-Pip thin films was measured under various RH. As shown in Figure 3-16, much higher OH^- conductivity than HCO_3^- conductivity under various RH, suggesting the successful measurement of OH^- conductivity.



Figure 3-16. RH dependence of anion conductivity of PFT6-TMA and PFT6-Pip thin

To further get the relationship between anion conductivity and water content, the anion conductivity as a function of number of water molecule is plotted as Figure 3-17. The much lower water uptake of Br⁻ form anion exchange thin films than their OH⁻ form limited the comparison at high hydration level. As shown in Figure 3-16, similar curves were observed for PFT6-TMA and PFT6-Pip thin films. Comparing the result of OH⁻

films at 25 °C.

conductivity and Br⁻ conductivity under low number of water molecules, it is obvious that OH⁻ conductivity is lower than Br⁻ conductivity, which is different with the RH dependence anion conductivity. Higher halide conductivity than OH⁻ conductivity was reported under low hydration conditions in another literature.³² Due to the strong interaction with water, Peng and co-authors demonstrated that the OH⁻ mobility in Tokuyama A201 membrane is lower than Cl⁻ under low number of water molecules.³⁸ Because the OH⁻ requires more water to dissociate than the Br⁻, the dissociation of OH⁻ from counter cation is greatly reduced under low hydration conditions. Effective ion mobility and mobile anion concentration are used to determine the anion conductivity as follow³⁹,

$\sigma = n\mu e$ (5)

where n signifies the concentration of mobile anion carriers, μ stands for the effective mobility of anion carriers, and e is the elementary charge. Under low number of water molecules, reduced mobile OH⁻ concentration and decreased mobility are the main reason for the lower OH⁻ conductivity. Under high number of water molecules, the OH⁻ can expect a high amount of dissociation form cation and a rise in mobile OH⁻ concentration, corresponding to the superior OH⁻ conductivity. In the case of same anion form, PFT6-TMA thin film showed higher conductivity than PFT6-Pip thin films at similar number of water molecules. The possible reasons will discuss in the next section.



Figure 3-17. Anion conductivity of PFT6-TMA and PFT6-Pip thin films as a function of number of water molecules at 25 °C. The line was used to guide the eyes.

To investigate the anion conduction activation energy, in situ temperature dependence of OH⁻ conductivity measurement technique was constructed utilizing inhouse made equipment. Anion conductivity was measured under 90% RH at different temperatures. The Br⁻ and OH⁻ conductivity of the PFT6-TMA and PFT6-Pip thin films as a function of temperature is shown in Figure 3-18. PFT6-TMA-OH, PFT6-TMA-Br, PFT6-Pip-OH, and PFT6-Pip-Br thin films showed Arrhenius-type temperature dependency of anion conductivity from 20 to 50 °C. The activation energies (E_a) of PFT6-TMA-OH, PFT6-TMA-Br, PFT6-Pip-OH and PFT6-Pip-Br thin films were calculated to be 33.2 kJ mol⁻¹, 44.6 kJ mol⁻¹, 35.7 kJ mol⁻¹ and 49.8 kJ mol⁻¹, respectively. The activation energy of OH⁻ conduction in both PFT6-TMA and PFT6-Pip thin films were lower than that of Br⁻ conduction, indicating that the energy barrier required to be

overcome for Br⁻ transport is higher than OH⁻ transport. The possible reason is that OH⁻ can be transported through Grotthuss and vehicle mechanism, while halide can only be transported by vehicle mechanism.^{34,40-42}



Figure 3-18. Arrhenius plots of the anion conductivity for the PFT6-TMA and PFT6-Pip thin films under 90% RH.

The anion conduction activation energy of PFT6-TMA thin films was comparable to PFT6-Pip thin films. As shown in Figure 3-17, the OH⁻ and Br⁻ forms of PFT6-TMA thin films exhibited much higher conductivity than each identical form of PFT6-Pip thin films at similar λ . The anion conductivity of anion exchange thin films depends on IEC, water uptake, dissociation degree of ion-pairs, morphology, conduction mechanism, hydrophobicity and size of cationic group. The IEC values of PFT6-TMA-OH and PFT6-Pip-OH were 2.34 and 2.11 meq g⁻¹. As shown in the water uptake part, each identical form of PFT6-TMA and PFT6-Pip thin films exhibited the similar dissociation degree

and water uptake results. Besides, both PFT6-TMA-Br and PFT6-Pip-Br thin films showed amorphous structure. The comparable activation energy of anion conduction between PFT6-TMA and PFT6-Pip thin films suggests a similar ion conduction mechanism in the PFT6-TMA and PFT6-Pip thin films. The hydrophobicity and size of the cationic group are more hydrophobic and bulkier in Pip, respectively. According to the above analysis, we can propose that higher IEC, less hydrophobicity and smaller size of TMA is attributed to the higher anion conductivity of PFT6-TMA thin films than each identical form of PFT6-Pip thin films at similar λ . The higher anion conductivity in TMA-based anion conductive polymers than that of Pip-based anion conductive polymers can be seen with other reported anion conductive polymers.^{43–45}

The anion conductivity of PFB-TMA and PFT6-TMA thin film as a function of number of water molecules was compared as shown in Figure 3-19. Under the same number of water molecules, higher anion conductivity was found in PFB-TMA thin films than that of PFT6-TMA thin films due to the much higher IEC of PFB-TMA thin films. Similar Br⁻ conductivity and OH⁻ conductivity were observed in PFB-TMA-Br and PFB-TMA-OH thin films under the low number of water molecules in chapter 2. As discussed above, reduced mobile OH⁻ concentration and decreased mobility are the main reason for the lower OH⁻ conductivity under the low number of water molecules in PFT6-TMA thin films. Under the same number of water molecules, the mobile OH⁻ concentration is governed by the OH⁻ dissociation degree and IEC. Under low hydration conditions, the OH⁻ dissociation degree is reduced, but the IEC of OH⁻ form anion conductive polymer

is higher than that of Br⁻ form. The IEC of PFB-TMA-Br and PFB-TMA-OH are 2.93 and 3.58. The IEC difference between PFB-TMA-OH and PFB-TMA-Br is 0.65. The IEC of PFT6-TMA-Br and PFT6-TMA-OH are 2.03 and 2.34. The IEC difference between PFT6-TMA-OH and PFB-TMA-Br is 0.31. The much larger IEC difference between PFB-TMA-OH and PFB-TMA-Br can attenuate the effect on OH⁻ conductivity due to the low dissociation degree and low mobility of OH⁻ under the low number of water molecules. Hence, similar Br⁻ conductivity and OH⁻ conductivity was found in PFB-TMA thin films under a low number of water molecules.



Figure 3-19. Anion conductivity of PFB-TMA and PFT6-TMA thin films as a

function of number of water molecules.

3.4. Conclusions

In this chapter, high-performance fluorene-thiophene-based anion conduction thin films were newly synthesized. The hydration properties, anion conduction properties, and molecular structure of poly(fluorene-thiophene)-based thin films with different cationic groups were investigated. OH⁻ form PFT6-TMA and PFT6-Pip thin films exhibited higher water uptake than their Br⁻ form thin films at the same RH. Water uptake results imply that the anions, rather than cations, dominate the hydration properties of anion exchange thin film. Anion conduction properties of anion exchange thin films depend on the number of water molecules. Superior OH⁻ conductivity was observed under high hydration conditions with enhanced ion mobility and full dissociation. While Br⁻ conductivity was higher than OH⁻ conductivity under the low number of water molecules. Despite the presence of a very weak ordered structure in the PFT6-Pip-Br thin film, there is no strong contribution to the anion conduction. Under 90% RH, PFT6-TMA and PFT6-Pip thin films exhibit similar activation energy for anion conduction in each anionic form. Higher IEC, less hydrophobicity and smaller size of TMA are contributed to the higher conductivity of PFT6-TMA thin films. This result provides detailed information of anion exchange thin films in OH⁻ form which can benefit the development of efficient anion exchange thin film.

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Chapter 4

Anion Conductive and Hydration Properties of Fluorene-thiophene-Based Anion Exchange Thin Films with Different Side Chains Lengths

Abstract

Poly[(9,9-bis(3'-(N,N,N-trimethylammonium)propyl)fluorene)-alt-(3,3'-dihexyl-2,2'-bithiophene)] (PFT3-TMA) was newly synthesized in this chapter. Compared with PFT6-TMA in Chapter 3, a shorter n-propyl alkyl spacer existed between backbone and cationic group in PFT3-TMA. The hydration and anion conductive properties of PFT3-TMA thin films were investigated. The OH⁻ conductivity of PFT3-TMA-OH and PFT6-TMA-OH thin films at 25 °C under 95% relative humidity (RH) were 2.0×10⁻² and 1.8×10^{-2} S cm⁻¹, respectively. The ion exchange capacity (IEC) of PFT3-TMA-OH and PFT6-TMA-OH were 2.57 and 2.34 meq g⁻¹. The higher IEC of PFT3-TMA-OH is contributed to the slightly higher OH⁻ conductivity of PFT3-TMA-OH thin film. The hydration number λ (number of water molecules per functional group) of PFT3-TMA-OH and PFT6-TMA-OH thin films at 25 °C under 95% RH were 11.2 and 11.4, respectively. Results suggest that the water uptake of fluorene-thiophene-based thin films was not dependent on side chain length. Under high hydration conditions, similar OHconductivity was observed for PFT3-TMA-OH and PFT6-TMA-OH thin films. While higher OH⁻ conductivity was found in PFT3-TMA-OH thin film than PFT6-TMA-OH thin film under low number of water molecules. The activation energies of OH- conduction in PFT3-TMA-OH and PFT6-TMA-OH thin films were 22.3 and 34.1 kJ mol⁻¹, suggesting that the energy barrier to be overcome for OH⁻ transport in PFT3-TMA-OH thin film is lower than that of PFT6-TMA-OH thin film.

4.1 Introduction

As mentioned in chapter 2 and chapter 3, the properties of anion exchange thin films, especially the OH⁻ form thin film need to be extensively investigated. In the second chapter, the anion conductivity of 273-nm-thick poly[(9,9-bis(6'-(N,N,Ntrimethylammonium)-hexyl)fluorene)-alt-(1,4-benzene)] (PFB-TMA) films were observed. Higher OH⁻ conductivity than Br⁻ conductivity was observed at 25 °C under 95% RH. In the third chapter, the effect of the cationic group on the hydration and OH⁻ conductive properties of fluorene-thiophene-based thin film has been investigated systematically. The water uptake and ion conduction activation energy (E_a) of anion exchange thin films are strongly dependent on the anion rather than the cationic group. Meanwhile, the cationic group and water content affected the OH⁻ conductive of fluorenethiophene-based thin films. However, there are still unclear points in understanding the properties of anion exchange thin films in OH⁻ form.

In addition to the cationic groups, how the side chain length of an anion conductive polymer governs its properties, especially in the thin film form, is another unexplored point. The effect of side chain length on the properties of anion exchange membrane has been investigated widely.^{1–6} Lin and co-authors investigated how the length of the alkyl spacer affected the OH⁻ conductivity of quaternized poly(ether sulfone)-based anion conductive polymers. With the increase of alkyl spacer length, the OH⁻ conductivity of synthesized anion conductive polymers increased first and then decreased.³ Koronka and co-authors studied the effect of side chain length on the OH⁻ conductivity of Pip
functionalized fluorene-based copolymers. The OH⁻ conductivity of prepared anion conductive polymer with n-propyl alkyl spacer was 5.7×10^{-2} S cm⁻¹ at 30 °C in water which is higher than that of anion conductive polymers with longer alkyl spacers.⁶ Accordingly, the side chain length can affect the properties of anion conductive polymers. However, the literature about the side chain length influence on the water uptake and anion conduction of thin films is limited. Under high relative humidity (RH), similar hydration number was found in Br⁻ form quaternized poly(p-phenylene oxide) thin films with various side chain lengths. The water uptake and OH⁻ conductive properties of thin films in OH⁻ form with different side chain length are still unexplored.⁷ To this end, this chapter will focus on the properties of anion exchange thin film with different side chain lengths.

The design of anion conductive polymer is based on Chapter 3. The same fluorenethiophene-based-polymer was also chosen as the polymer backbone.^{8–15} Compared with Chapter 3, a shorter n-propyl alkyl spacer between the backbone and cationic group was designed in this chapter. The hydration properties of anion exchange thin films were investigated by in situ quartz crystal microbalance (QCM) and in situ Fourier transform infrared spectroscopy (FTIR) under different RH. The anion conductive properties of anion exchange thin films were measured by in situ impedance spectroscopy measurements under controlled RH. Grazing-incidence small-angle X-ray scattering (GI-SAXS) was used to analyze the morphology of anion exchange thin films under different hydration conditions.

4.2 Experimental Section

4.2.1. Materials

1,3-Dibromopropane, 2,7-dibromofluorene, bis(pinacolato)diboron, tetrabutylammonium bromide (TBAB), [1,1-bis(diphenylphosphino)ferrocene] dichloro palladium (II) (PdCl₂) (dppf), 5, 5'-dibromo-3, 3'-dihexyl-2, 2'-bithiophene and tetrakis(triphenylphosphine) palladium (0) (Pd (PPh₃)₄) were obtained from Tokyo Chemical Industry Co. Ltd., Japan. NaOH, CH₂Cl₂, NaCl, NaHCO₃, magnesium sulfate anhydrous, dioxane, hexane, methanol, CHCl₃, tetrahydrofuran (THF), toluene, K₂CO₃, 30% trimethylamine solution, and diethyl ether were used as received from Fujifilm Wako Pure Chemical Corp., Japan.

4.2.2 Synthesis of monomer and polymer

Scheme 4-1 shows the synthetic route of 2,7-dibromo-9,9-bis(3'bromopropyl)fluorene (DBF3) and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis(3'-bromopropyl)fluorene (TDBF3) by following the reported literature.^{16,17}



Scheme 4-1. Synthetic route of DBF3 and TDBF3.

DBF3

The synthesis of compound A was set up by mixing 65 mmol of 1,3-dibromopropane, 2 mmol of tetrabutylammonium bromide (TBAB), 30 mL of 50 wt% NaOH solution, and 10 mmol of 2,7-dibromofluorene into a 100 mL three-necked flask. The mixture reacted at 60 °C for 8 h under the protection of argon. The organic layer was obtained after extracting the reaction mixture with dichloromethane. After washing with water and brine, the organic layer was dried with MgSO₄. Subsequently, the surplus 1,3-dibromopropane was evaporated by vacuum distillation. Finally, the product was produced with a 60% yield by column chromatography using hexane.

TDBF3

A 100 mL three-neck flask was filled with 5 mmol of compound A, 12 mmol of bis(pinacolato)diboron, 35 mmol of potassium acetate, and 50 mL of dioxane. The mixture was degassed using a freeze–pump–thaw cycle, which was repeated three times. Then, 0.1 mmol of PdCl₂(dppf) was added to the reaction mixture. The reaction took place at 85 °C for 12 h under the protection of argon. After the reaction, the solvent was removed from the reaction mixture using a rotary evaporator. After that, the mixture was extracted with dichloromethane, washed with water and brine, and dried with magnesium sulfate to remove any remaining water. Finally, the product was obtained by column chromatography using hexane and ethyl acetate (20:1) with a 77% yield.

Poly[(9,9-bis(3-bromopropyl)fluorene)-alt-(3,3'-dihexyl-2,2'-bithiophene)] (PFT3)

Scheme 4-2 shows the synthetic route of PFT3 and PFT3-TMA-Br. PFT3 was synthesized by Pd-catalyzed Suzuki cross-coupling reaction.¹⁸ A mixture of 0.5 mmol of compound B, 15 mL of toluene, and 4 mL of 2 M potassium carbonate aqueous solution were added into a 50 mL three-neck flask. 0.5 mmol of 5, 5'-dibromo-3, 3'-dihexyl-2, 2'-bithiophene was added to the degassed mixture through two freeze–pump–thaw cycles.

After another three time degas, 0.05 mmol of Pd (PPh₃)₄ was added into the reaction mixture under argon atmosphere. The reaction was performed at 95 °C for 48 h under the protection of argon. After the reaction, the polymer was precipitated from the mixture of methanol and deionized water. Soxhlet extraction using a mixture of methanol, hexane, and acetone (1:1:1 v/v/v) was used to purify the crude polymer. After dried the polymer under vacuum, the solid polymer was obtained with a 78% yield.

Poly[(9,9-bis(3'-(N,N,N-trimethylammonium)propyl)fluorene)-alt-(3,3'-dihexyl-

2,2'-bithiophene)] (PFT3-TMA-Br)

PFT3 solution was prepared by dissolving 200 mg of PFT3 in 5 mL THF. Next, 1 mL of 30% trimethylamine solution was added to the solution. After the precipitation appeared, 2 mL of DI water was added into the reaction mixture. The quaternization reaction was conducted at room temperature for 48 h with stirring. After the reaction, the concentrate was dissolved in MeOH and precipitated in diethyl ether. After dried under vacuum, PFT3-TMA-Br was obtained with an 86% yield.



Scheme 4-2. Synthetic route of PFT3 and PFT3-TMA-Br.

4.2.3 Characterization

¹H NMR spectra of monomer and polymers were recorded on (400 MHz) Bruker Avance III spectrometer (Bruker Analytik GmbH). CDCl₃ or MeOD-*d4* was used as a solvent. ATR-FTIR spectra were obtained by an FTIR spectrometer (Nicolet 6700; Thermo Fisher Scientific Inc.) with a wavenumber ranging of 400-4000 cm⁻¹. The weight average molecular weight (M_w), number average molecular weight (M_n), and polydispersity index (PDI, M_w/M_n) of PFT3 were estimated using gel permeation chromatography (GPC) (GPC, LC-2000plus; Jasco Inc.) equipped with Shodex GPC KF-805L column, using THF as mobile phase and polystyrene as standards. The polymer solution was filtered before injection into the column. On a thermogravimetric analyzer, the thermal decomposition of PFT3-TMA-Br was measured in the temperature range 40-600 °C with a heating rate of 10 °C min⁻¹ under N₂ atmosphere. The polymer was dried overnight at 40 °C under a vacuum before being measured. TM3030Plus miniscope (Hitachi) was used to perform scanning Electron Microscope and Energy Dispersive Xray Spectroscopy (SEM-EDX). 15 kV was used as the accelerating voltage.

4.2.4 Ion Exchange Process

To get OH⁻ form PFT3-TMA, PFT3-TMA-Br was immersed in 1 M NaOH solution under the protection of argon at room temperature for 2 days. Replaced with fresh 1 M NaOH solution every 16 h. After that, degassed ultra-pure water was used to wash PFT3-TMA (in OH⁻ form) until the pH was neutral. The ion exchange process was characterized by SEM-EDX. To obtain HCO3⁻ form of PFT3-TMA, PFT3-TMA-Br was immersed in 1M NaHCO₃ solution at room temperature for 2 days. Replaced with fresh 1 M NaHCO₃ solution every 16 h. After that, ultra-pure water was used to wash PFT3-TMA (in HCO₃⁻ form) until the pH was neutral. All the washing and transfer processes for OH⁻ form anion conductive polymers were carried out under the protection of N₂. PFT3-TMA-based anion conductive polymers in OH⁻ or HCO₃⁻ forms were denoted as PFT3-TMA-OH and PFT3-TMA-HCO₃.

4.2.5 Preparation of Anion Exchange Thin Films

PFT3-TMA-Br, PFT3-TMA-OH, and PFT3-TMA-HCO₃ were dissolved in methanol to prepare the dispersion. The spin-coating (ACT-200; Active Co. Ltd.) of thin films was done on SiO₂ substrates, Si substrate, and Au-coated quartz crystal microbalance (QCM) substrates (Seiko EG&G Co. Ltd.). The substrates were cleaned using 2-propanol and vacuum plasma (Cute-MP; Femto Science Inc., Korea) before spin-coating. For the preparation of PFT3-TMA-OH thin films, the dispersion preparation and spin-coating process were performed under the N₂ atmosphere.

4.2.6 White Light Interferometric Microscopy

The white light interferometric microscope (BWsingle bondS506; Nikon Corp.) was used to measure the thickness of thin film. 480 nm-thick films were used for the in situ FTIR, pMAIRS, water uptake and conductivity measurements. In addition, 510 nm-thick film was used for the RH-controlled in situ grazing-incidence small-angle X-ray scattering (GI-SAXS) measurements.

4.2.7 RH-controlled In Situ FTIR Spectroscopy

Si substrate with thin film was placed in a small home-made chamber. Transmission IR spectra were recorded using an FTIR spectrometer (Nicolet 6700; Thermo Fisher Scientific Inc.) with a deuterium triglycine sulfate (DTGS) detector. Precise dew point generator (me-40DP-2PW; Micro equipment) was used to generate various RH conditions. Smoothing process was applied to improve visibility.

4.2.8 RH-controlled In Situ Grazing-Incidence Small-Angle X-ray Scattering Measurements (GI-SAXS)

RH-controlled GI-SAXS was conducted on an X-ray diffractometer (FR-E; Rigaku Corp.) with an R-AXIS IV two-dimensional detector. Cu-K α X-ray source (wavelength = 1.54 Å, beam size approximately was 300 µm × 300 µm). Humidity-controlled cell on the goniometer and vertical stage (ATS-C316-EM/ALV-3005-HM; Chuo Precision Industrial Co. Ltd.) was used to hold the thin film. Nitrogen gas and water vapor were used to control the RH. The humidified cell holds Lumirror windows. The camera length was 300 mm, and the incidence angle was set in the range of 0.20°–0.22°.

4.2.9 Water Uptake Measurement of Anion Exchange Thin Films

Under controlled 0-95% RH conditions, the water uptake of PFT3-TMA-Br and PFT3-TMA-OH thin films was obtained using an in situ quartz crystal microbalance (QCM) system. Figure 4-1 shows the schematic diagram of in situ QCM system. QCM substrates were coupled to a frequency counter and a DC power source in an oscillation circuit (53131 A; Agilent Technologies, Inc.). QCM substrates with or without thin film

were held in a small home-made chamber with a high-resolution RH sensor to monitor the temperature and RH. Humidity controller (BEL Flow; Mirrorable Corp.) was utilized to create 0-95% RH conditions through modulating the N₂ and water vapor. The frequencies of substrates with or without thin film were measured under 0% RH. The mass of dry thin film mass can be obtained by the following Sauerbrey equation,

$$\Delta m = \frac{S \times \sqrt{\rho \mu}}{2 \times F^2} \times (-\Delta F) \quad (1)$$

Where S is the surface area of the electrode; ρ is quartz density; μ is the quartz shear modulus respectively and F is the fundamental frequency of QCM substrate.

Water uptake λ was calculated by the following equation:

$$\lambda = \left(\frac{m}{m_0} - 1\right) \times \frac{EW}{M_{H_2O}} \quad (2)$$

Where *m* is the mass of the film under each humidity, m_0 represents the mass of film at the dry condition, M_{H_20} is the molecular weight of water molecules, and *EW* is equivalent weight of PFT3-TMA.



Figure 4-1. Schematic illustration of QCM system.

4.2.10 Impedance Spectroscopy at Various Relative Humidity (RH)

The conductivity of PFT3-TMA-Br, PFT3-TMA-OH, and PFT3-TMA-HCO₃ thin films spin-coated on quartz substrates was measured by impedance spectroscopy using a frequency response analyzer (SI1260; Solartron Analytical) equipped with a highfrequency dielectric interface (SI1296; Solartron Analytical). Figure 4-2 shows the schematic diagram of in situ OH⁻ conductivity measurement system. Humiditytemperature chamber (SH-222; Espec Corp.) was used to generate the 40-95% RH, which was the condition for the conductivity measurement of thin films in Br⁻ and HCO₃⁻ forms. For conductivity measurement of PFT3-TMA-OH thin films, the thin film electrodes were placed in a sealed box with a high-resolution RH sensor. The temperature was controlled by humidity-temperature chamber (SH-222; Espec Corp.). Precise dew point generator (me-40DP-2PW; Micro equipment) was used to generate the 40-95% RH under the N₂ atmosphere which was the condition for the conductivity measurement of PFT3-TMA-OH thin films. Anion conductivity (σ) was calculated as follows,

$$\sigma = \frac{d}{Rlt} \qquad (3)$$

where d denotes the distance between the Au electrodes, R represents the resistance value from impedance, l, and t stand for the length of the contact electrodes and thickness of the film, respectively.

The temperature dependence anion conductivity of PFT3-TMA thin films was measured from 20 °C to 50 °C under fixed RH=90%. The estimated activation energy of anion conduction was estimated according to the Arrhenius equation.

$$\sigma T = \sigma_0 ex \, p\left(\frac{-E_a}{RT}\right) \ (4)$$

where R denotes the gas constant, T represents the temperature, and σ_0 represent preexponential factor.



Figure 4-2. Schematic illustration of anion conductivity measurement system.

4.2.11 p-Polarized Multiple Angle Incidence Resolution Spectrometry (pMAIRS)

pMAIRS was used to investigate the molecular orientation of PFT3-TMA-Br thin film. Then the measurement was conducted on a Fourier-transform infrared (FTIR) spectrometer (Nicolet 6700; Thermo Fisher Scientific Inc.) equipped with a mercury cadmium telluride (MCT). Single-beam spectra were recorded at angles of incidence ranging from 38° to 8° in 6° steps.

4.3 Results and Discussion

4.3.1 Characterization of Monomers and Polymers

The chemical structure of DBF3 was confirmed by ¹H NMR. Figure 4-3 shows the ¹H NMR spectrum of DBF3. As shown in Figure 4-3, the proton signals that appeared at 7.40-7.80 ppm are assigned to the aromatic protons of the fluorene ring. The observed proton signals at 1.00-3.40 ppm suggest the introduction of alkyl side chains. The proton signal of terminal methylene groups appeared at 3.20 ppm. The result of ¹H NMR suggests that compound A was synthesized successfully.



Figure 4-3. ¹H NMR spectrum of DBF3.

The chemical structure of TDBF3 was characterized by ¹H NMR. Figure 4-4 shows the ¹H NMR spectrum of monomer. As shown in Figure 4-4, the proton signals that appeared at 7.40-7.80 ppm are assigned to the aromatic protons of the fluorene ring. The protons of side chain appeared at 1.00-3.40 ppm. The new peak that arises at 1.39 ppm corresponds to the proton signals of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane. The result of ¹H NMR suggests that compound B was synthesized successfully.



Figure 4-4. ¹H NMR spectrum of TDBF3.

The chemical structure of PFT3 was confirmed by ¹H NMR. Figure 4-5 shows the ¹H NMR spectrum of PFT3. The proton signals of the fluorene ring were found at 7.40-7.80 ppm. The proton signal, which was detected at 7.24 ppm, belongs to the thiophene ring. The peaks at 0.40-3.40 ppm are assigned to alkyl side chains. ¹H NMR result proves that PFT3 was successfully synthesized. The weight-average molecular weight (M_w) and PDI of PFT3 obtained from gel permeation chromatography (GPC) using THF eluent were found to be 26 kg mol⁻¹ and 2.2.



Figure 4-5. ¹H NMR spectrum of PFT3.

PFT3-TMA-Br were obtained by quaternization of PFT3. The chemical structure of PFT3-TMA-Br was characterized by ¹H NMR. Figure 4-6 shows the ¹H NMR spectrum of PFT3-TMA-Br. Compared to PFT3, a new peak appeared at 2.90 ppm which was ascribed to the protons of TMA.



Figure 4-6. ¹H NMR spectrum of PFT3-TMA-Br.

Furthermore, the synthesized PFT3 and PFT3-TMA-Br were characterized by ATR-FTIR. Figure 4-7 shows the ATR-FTIR spectra of PFT3 and PFT3-TMA-Br. As shown in Figure 4-7, the stretching vibrations of -CH₂ of the side chains were found at 2925 cm⁻¹ and 2854 cm⁻¹. The absorption band at around 1465 cm⁻¹ belongs to the stretching vibration of thiophene and benzene rings. The absorption band at around 1600 cm⁻¹ belongs to the bending vibration of H₂O. Moreover, the broadband that appeared at 3400 cm⁻¹ in PFT3-TMA-Br belongs to the stretching vibrations of ν (O-H) of water molecules. After the introduction of the cationic group, PFT3-TMA-Br exhibited enhanced hydrophilicity than PFT3.



Figure 4-7. ATR-FTIR spectra of PFT3 and PFT3-TMA-Br.

TGA was performed to investigate the thermal stability of prepared anion conductive polymers under the N₂ atmosphere. Figure 4-8 shows the TGA curve of PFT3-TMA-Br. Three distinct weight loss steps were observed in Figure 4-8. The first weight loss step was observed below 100 °C, which can be ascribed to the removal of residual water. The second weight loss step was obtained between 150 and 250 °C, which can be attributed to the decomposition of TMA of PFT3-TMA-Br. The decomposition of cationic group in PFT6-TMA-Br started from 200 °C. The long alkyl spacer of PFT6-TMA-Br hindered movement of molecular segments which is the possible reason for increased thermal stability of PFT6-TMA-Br.¹⁰ The third weight loss step, the degradation of polymer backbone occurred above 350 °C. The thermal stability results clearly implied that the degradation temperature of prepared anion conductive polymers was above the normal operating temperature of AEMFC.



Figure 4-8. TGA curve of PFT3-TMA-Br.

Figure 4-9 exhibits the EDX spectra before and after ion exchange of PFT3-TMA-Br and PFT3-TMA-OH were shown in Figure 4-9. The EDX spectra indicated that Br⁻ ions decreased sharply after immersed in degassed 1 M NaOH solution for 48 h. For



both PFT3-TMA and PFT6-TMA, more than 91% Br⁻ ions changed to OH⁻ ions.

Figure 4-9. SEM-EDX spectra of PFT3-TMA-Br and PFT3-TMA-OH.

4.3.2 Water Uptake

The OH⁻ conductivity of anion exchange thin films is directly affected by the water uptake. The water uptake observation of anion exchange thin films can provide deeper understanding of the properties of anion exchange thin films. Figure 4-10 exhibits the water uptake of PFT3-TMA-OH and PFT3-TMA-Br thin films. As can be seen from 4-10, as the RH increases, the water uptake of PFT3-TMA-OH and PFT3-TMA-Br thin films continuously increases. As discussed in Chapter 3, the water uptake of PFT3-TMA-OH thin film is much higher than PFT3-TMA-Br thin film. The higher hydration number and more negative hydration energy of OH⁻ suggest the higher water affinity than Br⁻, consequently the higher water uptake of PFT3-TMA-OH under low RH range.^{19,20} Under high RH, OH⁻ from cation dissociates much higher than Br⁻, causing much higher osmotic pressure and water uptake of PFT3-TMA-OH thin film.²¹⁻²³



Figure 4-10. Water uptake of PFT3-TMA-OH and PFT3-TMA-Br thin films under various RH at 25 °C.

The water uptake was compared between PFT3-TMA and PFT6-TMA thin films in Figure 4-11 to understand the effect of side chain length on the water uptake of anion exchange thin films. PFT3-TMA-Br thin film shows similar water uptake with PFT6-TMA-Br thin film. PFT3-TMA-OH thin film exhibits similar water uptake with PFT6-TMA-OH thin film. The results suggest that the water uptake remains unchanged by decreasing the alkyl spacer length from n-hexyl to n-propyl. With the increase of side chain length, free volume in the thin film increases, resulting in enhanced water uptake. On the other hand, the increased side-chain length caused enhanced hydrophobicity, decreasing the water uptake. Hence, the water uptake of thin films is governed by these two factors.⁶ Similar result was observed in the literature. Kushner and co-authors demonstrated that quaternized poly(2,6-dimethyl-1,4-phenylene oxide) (QA-PPO) thin films with different side chain length exhibit similar water hydration number λ .⁷



Figure 4-11. Water uptake of PFT3-TMA and PFT6-TMA thin films under various RH at 25 °C.

4.3.3 Hydration Properties of Thin Film

IR can provide helpful information for the water adsorption and ion dissociation properties of ion conductive polymers.^{24–26} In situ FTIR measurement was conducted to explore the hydration characteristics and proton dissociation of acidic ionomers to understand the detailed hydration properties in previous research.^{27,28} In situ FTIR measurement was carried out in this chapter to investigate the hydration and anion dissociation of PFT3-TMA-Br thin film under various RH. Figure 4-12 shows the in situ FTIR spectra of PFT3-TMA-Br thin film under various RH. The -O-H stretching vibration modes and H₂O bending vibration modes can be seen at around 3400 cm⁻¹ and 1640 cm⁻¹. In conjunction with increasing RH, the intensity of -O-H stretching vibration

modes and H₂O bending vibration modes increased, revealing the increased water uptake of PFT3-TMA-Br thin film.

Vico and co-authors used ATR-FTIR to examine the hydration properties of polysulfone-based anion exchange membrane.²⁴ The absorbance of the [-N(CH₃₎₃⁺] stretching vibration band decreased with water content. Vandiver and co-authors measured the polymer-water interaction using ATR-FTIR under controlled RH. The -C-H stretching vibration band shifted position with the increase of RH.²⁶ Based on these findings, the -C-H stretch vibration band in [-N(CH₃₎₃⁺] was investigated in order to understand the hydration and dissociation of ion pairs as a function of RH. Figure 4-11b depicts the extended region for -C-H stretching vibrations in PFT3-TMA-Br thin film. The -C-H stretching vibrations in $[-N(CH_{3)3}^+]$ is attributed to the band at 3006 cm⁻¹ when the thin film is in the dry state. With the increase of RH, the absorption of the C-H stretch vibration in $[-N(CH_{3)3}^+]$ reduced, but its position shifted to a high wavenumber, as shown in Figure 4-11b. For the -C-H stretching vibration band, a higher wavenumber equals a stronger force constant. When the thin film is in dry state, strong interaction creates cation-anion pairs. Br⁻ can share lone pair electrons with H of -C-H in $[-N(CH_{3})^{+}]$ due to the bound state between TMA and Br^{-.29} The water uptake of PFT3-TMA-Br thin film increased as the RH increased, and the dissociation of Br⁻ happened as a result. When H has a higher positive charge, the force constant of the -C-H increases, and the absorbance of the -C-H decreases. Because of the more [-N(CH₃)₃⁺] groups in PFT3-TMA-Br, -C-H stretching vibration band was more obvious in PFT3-TMA-Br thin film.



Figure 4-12. In situ FTIR spectra of PFT3-TMA-Br thin film as a function of RH. (a) Wavenumber range between 1250 and 4000 cm⁻¹, (b) Wavenumber range between 2600 and 3200 cm⁻¹.

4.3.4 Morphology of Thin Films

GI-SAXS was used to investigate the morphology of PFT3-TMA-Br thin film under controlled RH. Figure 4-13 displays the 1D GI-SAXS profiles of PFT3-TMA-Br thin film under dry state and 95% RH. A very weak scattering peak $q_z = 3.84$ nm⁻¹ (d = 1.6 nm) in the out-of-plane direction was seen for the PFT3-TMA-Br thin film at 0% RH. The PFT3-TMA-Br thin film had a few organized structures. The majority region of the PFT3-TMA-Br thin film, on the other hand, remains amorphous.



Figure 4-13 1D GI-SAXS profiles of PFT3-TMA-Br thin film at 0% RH and 95% RH. Those scattering peaks at $q_y=10.8$ and 12.0 nm⁻¹ originated from the Lumirror window of the humidity-controlled cell.

pMAIRS was carried out to confirm the amorphous of PFT3-TMA-Br thin film. The pMAIRS spectra of PFT3-TMA-Br thin film are shown in Figure 4-14. The stretching vibration of the aromatic rings was observed at 1471 cm⁻¹, as seen in Figure 4-14. The aromatic ring stretching vibration absorbance in the IP direction is the same as in the OP direction for the prepared PFT3-TMA-Br thin film, implying an amorphous structure of the PFT3-TMA-Br thin film.



Figure 4-14. pMAIRS spectra of PFT3-TMA-Br thin film.

It has been reported that anion exchange thin films with an amorphous structure and weak nanophase separation exist.^{7,30,31} Amorphous structure and weak nanophase separation have been reported in a variety of hydrocarbon-based anion exchange thin films, according to the literature. Analogous to proton exchange thin films, anion exchange thin films have a significantly weak nanophase separation. The weak nanophase separation of anion exchange thin film is due to the less hydrophilic of quaternary ammonium.³²

The surface morphology of PFT3-TMA-Br thin film was investigated by scanning SEM. Figure 4-15 shows the SEM images of PFT3-TMA-Br thin film. As shown in Figure 4-15, the surface of PFT3-TMA-Br thin film was homogeneous are smooth, no pores or cracks were visible.



Figure 4-15. SEM image of PFT3-TMA-Br thin film.

4.3.5 Anion Conductivity

Anion conductivity is an important property of anion exchange thin films. Increased OH⁻ conductivity is, as a result, proportional to the increase in the performance of AEMFC. It is a critical factor in the overall efficiency of AEMFC. The anion conductivity of PFT3-TMA-Br and PFT3-TMA-OH thin films spin-coated on quartz substrates was obtained by in situ impedance spectroscopy under a controlled RH environment. Figure 4-16 depicts the anion conductivity of PFT3-TMA-Br and PFT3-TMA-OH thin films under various RH. The anion conductivity of PFT3-TMA-Br and PFT3-TMA-OH thin films increased along with RH. As discussed in water uptake and hydration properties of anion exchange thin films, the water uptake and mobile anion increased with the increase of RH. Therefore, the increased anion conductivity with RH results from an increase in mobile anion as well as an increase in water uptake. The Br⁻ conductivity and OH⁻ conductivity of PFT3-TMA-Br and PFT3-TMA-OH thin films were 5.3×10⁻³ S cm⁻¹ and 2.0×10⁻² S cm⁻¹ at 25 °C under 95% RH. The OH⁻ conductivity of PFT6-TMA-OH thin film was 1.8×10⁻² S cm⁻¹ at 25 °C under 95% RH. The ion exchange capacity (IEC) of PFT6-TMA-OH and PFT3TMA-OH were 2.34 and 2.57 meg g⁻¹. The higher IEC is contributed to the slightly higher OH⁻ conductivity of PFT3-TMA-OH thin film.



Figure 4-16. Anion conductivity of PFT3-TMA-Br and PFT3-TMA-OH thin films as a function of RH at 25 °C.

The OH⁻ is quickly changed to $CO_3^{2^-}$ and HCO_3^{-} in the air, resulting in a decreased OH⁻ conductivity of anion exchange thin films. To avoid this issue, OH⁻ conductivity measurements were performed under an N₂ atmosphere. In addition, the HCO_3^{-} conductivity of PFT3-TMA-HCO₃ thin film was measured to confirm the accuracy of OH⁻ conductivity measurement. Figure 4-17 shows the anion conductivity of PFT3-TMA-HCO₃ thin films as a function of RH at 25 °C. As shown in Figure 4-17, much higher OH⁻ conductivity than HCO_3^{-} conductivity was observed within the whole RH measurement region. The HCO_3^{-} conductivity of PFT3-TMA-HCO₃ thin film was 4.0×10^{-3} S cm⁻¹ at 25 °C under 95% RH, which is much lower than OH⁻ conductivity of PFT3-TMA-OH thin film. The above analysis suggests the successful measurement of OH⁻ conductivity.



Figure 4-17. Anion conductivity of PFT3-TMA-OH and PFT3-TMA-HCO₃ thin films as a function of RH at 25 °C.

To further get the relationship between water uptake and anion conductivity. The number of water molecules dependent anion conductivity of PFT3-TMA-OH and PFT3-TMA-Br was plotted in Figure 4-18. The Br⁻ conductivity and the OH⁻ conductivity both increased when the RH increased. As illustrated in Figure 4-18, Less water uptake of PFT3-TMA-Br thin film limited the comparison with PFT3-TMA-OH thin film under high hydration level. Interestingly, it is obvious that OH⁻ conductivity is lower than Br⁻ conductivity under the low number of water molecules. It has been observed that the halide conductivity is greater than the OH⁻ conductivity when the number of water molecules is low. This is because the dissociation degree of the OH⁻ from cation is severely reduced when the number of water molecules is low.²³ Peng and co-authors demonstrated that the OH⁻ mobility of the Tokuyama A201 membrane is lower than the

Cl⁻ mobility under a low number of water molecules conditions, which they attribute to the strong interaction with water.³³ According to these analyses, both reduced OH⁻ mobility and mobile OH⁻ are responsible for the significantly lower OH⁻ conductivity observed under the condition of the low number of water molecules.

To understand the effect of side chain length on the anion conductivity of fluorenethiophene-based thin films, the anion conductivity comparison of PFT6-TMA and PFT3-TMA thin films under the same number of water molecules was also plotted in Figure 4-18. As shown in Figure 4-18, the anion conductivity in PFT3-TMA and PFT6-TMA thin films was dependent on the number of water molecules. With the increase of the number of water molecules, the anion conductivity increased. It is worth noting that slightly higher OH⁻ conductivity was found in PFT3-TMA-OH thin film than PFT6-TMA-OH thin film under low number of water molecules. Almost the same Br⁻ conductivity was observed in PFT3-TMA-Br and PFT6-TMA-Br thin films. Results suggest that OHconductivity was more sensitive to the increased IEC than Br conductivity under a low number of water molecules. Similar OH⁻ conductivity was observed in PFT3-TMA-OH and PFT6-TMA-OH thin films under the region of high number of water molecules. Akiyama and co-authors compared the OH⁻ conductivity of quaternized aromatic semiblock copolymer with different side chain lengths under high hydration conditions. Their results revealed that the OH⁻ conductivity was not dependent on the side chain length under fully hydration conditions.³⁴ This study provided new insight into the OH⁻ conduction properties of anion conductive polymers with different side chain lengths under low number of water molecules.



Figure 4-18. Anion conductivity comparison of PFT3-TMA and PFT6-TMA thin films as a function of number of water molecules at 25 °C. The line was used to guide the

eyes.

The activation energy of anion conduction in the thin film can provide useful information to understand the anion conductive properties. Temperature dependence anion conductivity was measured at 20-50 °C under 90% RH. The temperature dependence anion conductivity of PFT3-TMA thin films is shown in Figure 4-19. The calculated activation energies of PFT6-TMA-OH and PFT3-TMA-Br are 22.3 and 34.1 kJ mol⁻¹. The activation energy of OH⁻ conduction in PFT3-TMA-OH thin film is lower than that of Br⁻ conduction in PFT3-TMA-Br thin film, revealing that lower energy barrier for OH⁻ transport in PFT3-TMA-OH thin film. According to the literature, this may be due to the fact that OH⁻ can be conducted through both Grotthuss and vehicle mechanism,

but that halide can only be conducted through vehicle mechanism.^{25,35} In chapter 3, we demonstrated that the calculated activation energies (E_a) of PFT6-TMA-OH and PFT6-TMA-Br thin films were 33.2 kJ mol⁻¹ and 44.6 kJ mol⁻¹, respectively. Lower energy barrier for anion conduction was confirmed in PFT3-TMA thin films under high hydration conditions.



Figure 4-19. Arrhenius plots of the anion conductivity for the PFT3-TMA and PFT6-TMA thin films under 90% RH.

Kushner and co-authors investigated the swelling-strain of quaternized poly(2,6dimethyl-1,4-phenylene oxide) (QA-PPO) thin films with different lengths of side chain. QA-PPO thin film with a short side chain exhibited increased swelling-strain even under a similar number of water molecules.⁷ In this case, the film thickness of PFT3-TMA thin films may be higher than that of PFT6-TMA thin films under high hydration conditions, which can reduce the mobile ion concentration. The combined impact of reduced mobile ion concentration and low OH⁻ conduction activation energy of PFT3-TMA-OH thin film is one of the possible reasons for the slightly higher OH⁻ conductivity of PFT3-TMA-OH thin film than that of PFT6-TMA-OH thin film. Under the same number of water molecules, in the case of similar mobile ion concentrations, the tortuosity (τ) relating to the connectivity of hydrophilic domains may be different between PFT3-TMA-OH and PFT6-TMA-OH thin films.^{31,32} Therefore, the combine impact of tortuosity (τ) and OH⁻ conduction E_a is another possible reason for the slightly for the slightly higher OH⁻ conductivity of PFT3-TMA-OH thin film than that of PFT6-TMA-OH thin film.

Figure 4-20 shows the OH⁻ conductivity comparison of PFB-TMA-OH, PFB-TMA-OH, PFT6-Pip-OH, and PFT3-TMA-OH thin films at 25 °C under 95% RH. As shown in Figure 4-19, the OH⁻ conductivity increased along ion exchange capacity (IEC). PFB-TMA-OH thin film shows superior OH⁻ conductivity due to its much higher ion exchange capacity (IEC). TMA-based anion exchange thin film exhibited superior OH⁻ conductivity than that Pip-based anion exchange thin film because of high ion exchange capacity (IEC), less hydrophobicity, and smaller size of TMA.



Figure 4-20. OH⁻ conductivity comparison and chemical structure of PFB-TMA-OH, PFB-TMA-OH, PFT6-Pip-OH, and PFT3-TMA-OH thin films at 25 °C under 95% RH.

4.4 Conclusions

PFT3-TMA with a n-propyl alkyl spacer between the backbone and cationic group was newly synthesized in this chapter. The hydration and anion conductive properties of PFT3-TMA and PFT6-TMA thin films were compared. At 25 °C under 95% RH, PFT3-TMA-OH thin film has an OH⁻ conductivity of 2.0×10^{-2} S cm⁻¹, which is slightly higher than that of PFT6-TMA-OH thin film due to its higher IEC. The hydration number λ (number of water molecules per functional group) of PFT3-TMA-OH and PFT6-TMA-OH thin films at 25 °C under 95% RH were 11.2 and 11.4, respectively. Water uptake results suggest that side chain length does not affect the water content of prepared fluorene-thiophene-based anion exchange thin films. Under high hydration conditions, similar OH⁻ conductivity was observed for PFT3-TMA-OH and PFT6-TMA-OH thin film than PFT6-TMA-OH thin film under low number of water molecules. Lower OH⁻ conduction activation energy was observed in PFT3-TMA-OH thin films than PFT6-TMA-OH thin film under 90% RH.

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Chapter 5

General Conclusions

5.1 Conclusions

Anion exchange thin film is a critical part in triple-phase interface of anion exchange membrane fuel cell (AEMFC). The limited available literature focused on the anion exchange thin film in halide and HCO_3^- forms due to the requirement of a CO_2 -free atmosphere during the measurement process of OH^- form thin films. In this case, there is still a large gap to systematically understand the OH^- form thin films.

The three chapters focused on the systematically understanding of hydration and OH⁻ conductive properties of thin films. The effect of film thickness, cationic groups, and side chain length on the water uptake and OH⁻ conductivity of anion exchange thin films were systematically revealed in three chapters.

In Chapter 2, the in situ OH⁻ conductivity and water uptake measurements under the N₂ atmosphere were established. The water uptake and OH⁻ conductivity of reported poly[(9,9-bis(6'-(N,N,N-trimethylammonium)-hexyl)fluorene)-alt-(1,4-benzene)] (PFB-TMA) thin films were investigated. At 25 °C under 95% relative humidity (RH), the OH⁻ conductivity of PFB-TMA-OH (273-nm-thick) thin film is 5.3×10^{-2} S cm⁻¹, which is similar to that of the membrane in the literature. In addition, the film thickness dependence of water uptake and OH⁻ conductivity of PFB-TMA-OH was also investigated. The decreased water uptake of a thinner film is contributed to the reduced

OH⁻ conductivity. Under the same number of water molecules, only slightly decreased OH⁻ conductivity was found in the thinner film.

In chapter 3, fluorene-thiophene-based anion exchange thin films were newly prepared. In situ temperature dependence of OH⁻ conductivity measurement process was established by home-made equipment. The effect of cationic group and counter-anion on the hydration and anion conductive properties of fluorene-thiophene-based anion exchange thin films were systematically investigated. The activation energy of anion conduction in thin films is determined by the counter-anion rather than the cation. TMA-based anion exchange thin film exhibited superior OH⁻ conductivity than that Pip-based anion exchange thin film, 1.8×10^{-2} S cm⁻¹ at 25 °C under 95% relative humidity (RH), because of high ion exchange capacity (IEC), less hydrophobicity and smaller size of TMA. The number of water molecules strongly affects the anion conductive properties of thin films.

In chapter 4, fluorene-thiophene-based anion conductive polymer with a shorter npropyl alkyl spacer was synthesized. The water uptake and anion conductive properties of fluorene-thiophene-based anion exchange thin films with different side chain lengths were compared. Similar water uptake results were observed in fluorene-thiophene-based anion exchange thin films with different side chain lengths in the identical anion form. Under high hydration conditions, similar OH⁻ conductivity was observed in fluorenethiophene-based thin films with different side chain lengths. While higher OH⁻ conductivity was found in fluorene-thiophene-based thin films with shorter n-propyl alkyl spacer under the low number of water molecules. This study provided new insight into the OH⁻ conduction properties of anion conductive polymers with different side chain lengths under the low number of water molecules.

5.2 Future Scope

This thesis has revealed the effect of the cation, side chain length, and film thickness on the hydration properties and OH⁻ conductive properties of anion exchange thin films. According to the current studies, the future prospects of this research are shown as follows:

- 1. In the AEMFC, two H2O molecules were used at cathode, while four H₂O molecules were produced at the anode. In this case, it is important to keep the water balance between ionomer hydration and catalyst layer flooding or dry out. To improve the electrochemical performance of AEMFC, many operation conditions have been adjusted, such as low RH condition and enhanced gas flow rate. However, the alkaline stability of ionomer under low RH conditions is unknown. The available alkaline stability properties of anion conductive polymers are focused on the fully hydration conditions. Hence, the establishment of in situ OH⁻ conductivity measurement process is useful for the development of AEMFC. The operation of AEMFC under low RH conditions. However, the alkaline stability of ionomer under low RH differs from that under high RH conditions. The in situ OH⁻ conductivity measurement method which was established in this study can be used to investigate the alkaline stability of thin film under different RH.
- 2. How the polymer backbone of an anion conduction polymer governs its properties, especially in the thin-film form, is another important question. The effect of backbones on the properties of anion exchange membrane has been investigated widely. In the previous work, Maurya and co-authors demonstrated that the AEMFC

performance increased when the backbone of the anion exchange ionomer contained less phenyl groups.¹ Chen and co-authors synthesized a series of 1,2-diphenylethane (DP)-containing poly(aryl piperidinium)s (PAP) anion conduction polymers for AEMFC applications.² Results suggested that poly(diphenylethane-co-terphenyl piperidinium) with low phenyl content exhibited high water uptake and excellent peak power density when used as ionomer in the cathode of fuel cell. The effect of backbones on the properties of anion exchange thin films remains unexplored. The effect of backbone architecture on the properties of anion exchange thin films such as anion conductivity, water uptake, anion conduction activation energy, and morphology will be investigated to get insight into the polymer design for anion exchange thin film. In addition to cationic groups and side chains, how the polymer backbone of an anion conduction polymer governs its properties, especially in the thin film form, is another important question. Hence, anion conductive polymers with different polymer backbones can be synthesized and investigated as thin films.

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Achievements

Research Publications:

- Fangfang Wang, Shusaku Nagano, Mitsuo Hara, and Yuki Nagao*, Hydration and OH⁻/Br⁻ Conduction Properties of Fluorene-Thiophene-Based Anion Exchange Thin Films Tethered with Different Cations, ACS Applied Polymer Materials 4 (2022) 5965–5974.
- Fangfang Wang, Dongjin Wang, and Yuki Nagao*, OH⁻ Conductive Properties and Water Uptake of Anion Exchange Thin Films, ChemSusChem, 14 (2021) 2694–2697. (Selected as cover art)

Conferences:

- Fangfang Wang, Dongjin Wang, and Yuki Nagao "Relations of OH⁻ Conductivity and Water Uptake of Anion Exchange Membrane in Thin Film Form" 3rd Symposium on Industrial Science and Technology, 2021/8. (Oral Presentation)
- Fangfang Wang, Dongjin Wang, and Yuki Nagao "OH⁻ Conduction and Hydration Properties of Anion Exchange Ionomer" 70th Symposium on Macromolecules, 2021/8. (Oral Presentation)
- Fangfang Wang, Dongjin Wang, and Yuki Nagao "Relations of OH⁻ Conductivity and Water Uptake of Anion Exchange Ionomer" Solid State Proton Conductors (SSPC-20), 2021/9. (Oral Presentation)
- 4. Fangfang Wang, Dongjin Wang, and Yuki Nagao "OH⁻ Conductivity and Water Uptake of Anion Exchange Ionomer" 34th International Microprocesses and

Nanotechnology Conference (MNC 2021), 2021/10. (Poster)

 Fangfang Wang, Dongjin Wang, and Yuki Nagao "Anion conduction and Hydration Properties of Anion Exchange Thin Films" Excellent Core Student Symposium in 2021, 2021/11. (Poster)

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Professor's Selection Award at the Excellent Core Student Symposium 2021 of JAIST International Research Center for Silent Voice Sensing

Abstract of Minor Research

In this study, poly (ethylene oxide)/poly (vinylidene fluoride) (PEO/PVDF) in the weight ratio of 1:1 as a composite binder was investigated for graphite anode in lithiumion batteries (LIBs). The electrochemical properties of PEO/PVDF-based anodic half-cell were investigated. Compared to PVDF-based anodic half-cells, the PEO/PVDF-based anodic half-cell exhibited slightly higher lithium-ion diffusion. According to electrochemical impedance spectroscopy (EIS) results, PEO/PVDF-based anodic halfcell had lower interfacial resistance after cyclic voltammetry (CV) than PVDF-based anodic half-cell. PEO/PVDF-based anodic half-cell showed higher discharge capacity at all current rates than PVDF-based anodic half-cell. The highest discharge capacity of PEO/PVDF-based anodic half-cell was 265 mAh/g at 1C rate (372 mA/g as 1C of graphite) which is higher than that obtained from PVDF-based anodic half-cell. Further, 93% capacity retention with 95% coulombic efficiency after 321 cycles was observed for PEO/PVDF-based anodic half-cell. Compared to PVDF-based anodic half-cell, the superior performance of PEO/PVDF-based anodic half-cell can be attributed to the lower interfacial resistance of solid electrolyte interface (SEI) and well-developed ion channels for Li⁺ conduction.

Keywords: PEO/PVDF composite binder, discharge capacity, capacity retention, interfacial resistance, solid electrolyte interface (SEI)