Poly(2,6-dimethyl-1,4-phenylene oxide)s with Various Head Groups: Effect of Head Groups on the Properties of Anion Exchange Membranes

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ABSTRACT: Poly(2,6-dimethyl-1,4-phenylene oxide)s (PPOs)-based anion exchange membranes (AEMs) with four of the most widely investigated head groups were prepared. Through a combination of experimental and simulation approaches, the effects of the different types of head groups on the properties of the AEMs, including hydroxide conductivity, water content, physicochemical stability, and fuel cell device performance were fully explored. Unlike other studies, in which the conductivity was mostly investigated in liquid water, the conductivity of the PPO-based AEMs in 95% relative humidity (RH) conditions as well as in liquid water was investigated. The conductivity trend in 95% RH condition was different from that in liquid water but corresponded well with the actual cell performance trend observed, suggesting that the AEM fuel cell performance under in situ cell conditions (95% RH, 60 °C, H2/O2) is more closely related to the conductivity measured ex situ under 95% RH conditions (60 °C) than in liquid water. On the basis of the conductivity data and molecular simulation results, it was concluded that the predominant hydroxide ion-conducting mechanism in liquid water differs from that in the operating fuel cell environment, where the ionomers become hydrated only as a result of water vapor transported into the cells.

KEYWORDS: anion exchange membranes, head groups, Conducting mechanism, room humidity condition, molecular simulation

1. INTRODUCTION

Alkaline anion exchange membrane-based fuel cells (AEMFCs) have drawn much interest as an important class of clean and highly efficient energy devices for power station, vehicle, and portable electronic applications.1–3 It is the case that proton exchange membrane fuel cells (PEMFCs), in comparison to AEMFCs, are currently more developed and near commercially available. However, expectations for AEMFCs are very high, and thus, AAMFCs have become a preferred topic of various studies in recent years. This shift of focus from PEMFCs to AEMFCs has been mainly due to the high cost of platinum (Pt), which is used as the catalyst in PEMFCs. Utilizing AAMFCs can potentially reduce costs because operations in alkaline conditions allow nonprecious metals such as silver (Ag) or nickel (Ni) to be used as the electrocatalyst. Faster oxygen reduction at the cathode is another advantage of operating fuel cells under alkaline conditions.

Notwithstanding the aforementioned advantages, anion exchange membranes (AEMs), which are the key component of AAMFCs for the transport of hydroxide anions (OH−) through cationic functional groups (referred to below as “head groups”) from the cathode to the anode, have their own drawbacks. In particular, the ionic conductivity levels of AEMs are lower than those of proton exchange membranes (PEMs) because of the low intrinsic ion mobility of hydroxide ions compared to protons. Moreover, AEMs generally bear low chemical stability under the high pH (i.e., highly alkaline) conditions in which AAMFCs operate, mainly because of the...
degradation of the head groups in the membrane and electrode ionomer (ion-conducting polymer), especially at high temperatures, significantly decreasing the long-term durability of AEMs.

Numerous recent studies have sought to solve these problems. For example, introduction of spacers between the polymer backbone and head group; formation of polymer morphologies with block, graft, cluster-type, or comb-shaped architectures; and cross-linking of polymers with a high concentration of head groups have been proposed as ways to increase the ion conductivity in AEMs. These investigations have resulted in materials displaying a wide range of conductivity levels. Despite these studies, the molecular design rules for highly conductive AEMs that are useful in operating devices are not fully elucidated yet.

One way to increase the conductivity of an ionomer material is to add more head groups to the polymers, thereby increasing the ion-exchange capacity (IEC); however, while this approach generally yields a high ionic conductivity, it also inevitably adversely affects the physical and chemical properties of the corresponding AEMs. In fact, most AEMs are relatively unstable under the working conditions of AEMFCs (i.e., above 60 °C and high pH), and this chemical instability is aggravated for AEMs displaying high IECs. Therefore, significant efforts in recent years have focused on improving the chemical stability of AEMs, and these efforts have involved molecular engineering of polymer backbones and/or head groups.

Various types of polymer backbones, including poly-(phenylene)s, poly(styrene)s, poly(phenylene ether)s, imidazolium (IM), phosphonium, and host-guest molecular recognition-type cations, have been investigated. Among these, polymers including ary sulfone, ary ketone, and ary ether bonds with electron- withdrawing groups in their backbones activate attack by hydroxide ions, resulting in chain scission and hence a decrease in the alkaline stability of the corresponding AEMs.

Various head groups, including quaternary ammonium (QA), imidazolium (IM), guanidinium, sulfonium, phosphonium, and host-guest molecular recognition-type cations, have been incorporated into the abovementioned polymers as head groups. Among these cations, QA groups, particularly benzyltrimethyl QA and its derivatives, are predominant in the literature because of their easy preparation. Moreover, a variety of modifications of these cations, including side-chain-type architectures and multication-type structures, have been continuously developed to offer a wide range of conductivity and stability levels. IMs have also been widely used as head groups, but their stability levels are still under debate: the π-conjugated structure, which was originally indicated to endow IMs with good stability in alkaline conditions, has more recently been reported to lower their stability levels. Attachment of allyl groups to the reactive C2 position of the IM cation has been observed to enhance the stability of IM salts, with this improvement attributed to steric hindrance and σ-π hyperconjugation displayed by such C2-substituted groups.

Recently, heterocyclic aliphatic QA head groups, including piperidinium (PI) and pyrrolidinium groups, have been regarded to confer the greatest degree of stability because of their bulky cyclic structures which may hinder the approach of hydroxide ions to these head groups. These head groups have also shown the advantage of enhanced ion conductivity, which is attributed to their high levels of ion dissociation caused in turn by their bulky cyclic structures. The polymers functionalized with N-methyl PI and N-methyl pyrrolidinium groups have hence displayed high alkaline stability as well as high hydroxide conductivity. Also, in recent studies, AEMs incorporating morpholinium (MO) as a head group showed better phase separation and higher dimensional stability than the PI- and pyrrolidinium-functionalized AEMs, perhaps because of hydrogen bonding between MO and water. Trizole is also an example of a head group for which the hydrogen bond with water enhances the ion conductivity. It has yet to be determined, however, which specific polymer backbone and head group are best.

Some AEMs have been shown to be highly ion conductive and chemically stable ex situ in hydroxide ion conductivity and alkaline stability tests. These AEMs have therefore been hypothesized to also be durable and show superior performance in operating cells. Hence, the development of such highly conductive and chemically stable structures has been the focus of current research aimed at producing and using new AEMs. Recently, a few studies have sought to determine the relationship between the stability measured ex situ in alkaline conditions and the durability of the actual fuel cell; however, in regard to our understanding of the relationship between stability measured ex situ and fuel cell durability, these works did not go much beyond establishing that the ex situ stability was not directly proportional to the fuel cell durability because of the very complex environment in fuel cell devices.

The effect of head groups on AEM properties such as conductivity, water content, physicochemical stability, and most importantly fuel cell device performance has also been widely investigated. However, most of the studies have been limited to comparing the properties of individual head groups, such as conductivity, stability, and cell characteristics. To our knowledge, there have not been any systematic studies on the differences between these properties for the different types of head groups.

In the current study, we prepared poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)-based AEMs employing the four most widely studied head groups, that is, QA, IM, PI, and MO, to explore the effects of the head groups on the properties of their AEMs, particularly their ionic conductivity measured ex situ both in water and high (95%) relative humidity (RH) conditions, together with the in situ performance levels of their fuel cells. The purpose of this study was to determine the ion conduction mechanisms of the different head groups and the influence of the environment, that is, liquid water versus RH conditions, on these mechanisms, which were not explored extensively in previous reports. We also carried out a detailed investigation and comparison of the properties of the four different head group-functionalized PPO-based AEMs, including their thermostabilic properties, morphologies, ion conductivities, alkaline stabilities, and H2/O2 fuel cell performances and conducted molecular simulations.

2. EXPERIMENTAL SECTION

2.1. Materials. PPO was obtained from Asahi Kasei Co., Japan (Mn = 24,000 g mol−1, Mw = 58,000 g mol−1). 2,2′-Azobisisobutyronitrile (AIBN, 99%, Daejung), N-bromosuccinimide (NBS, 98%, TCI), N-methyl-2-pyrrolidone (NMP, 99%, Daejung), chlorobenzene (99.5%, Aldrich), N-methyl morpholine (99%, Aldrich), trimethylamine (TMA; 45 wt % aqueous solution, Aldrich), N-methyl piperidine (99%, Aldrich), and 1,2-dimethyl imidazole (99%, Aldrich).
were used as received. All other chemicals, unless otherwise mentioned, were obtained from commercial sources and used as received. Distilled water was used throughout this study.

2.2. Bromination of PPO To Give Br-PPO. A typical procedure for preparing the brominated PPO is as follows: in a 500 mL two-necked flask equipped with a magnetic stirrer, a nitrogen inlet, and a condenser, PPO (6.0 g, 50 mmol) was completely dissolved in chlorobenzene (100 mL), followed by the addition of NBS (4.0 g, 22.5 mmol) and AIBN (246 mg, 1.5 mmol) to this solution. The resulting mixture was heated at 65 °C for 3 h and then at 80 °C for 4 h. Each membrane was peeled off from the filter paper and washed three times. The polymer was collected and dried at 80 °C under vacuum for at least 24 h to produce the bromomethylated PPO (Br-PPO) as a yellow light powder (5.76 g, 96%) with the degree of bromination (DB) determined to be 30%: δ1 (400 MHz, CDCl3) 6.74–6.60 (6H, br signal, ArH2), 6.56–6.40 (14H, br signal, ArH3), 4.40–4.25 (6H, br signal, ArCH2Br), 2.20–1.94 (51H, br signal, ArCH3).

2.3. Synthesis of PPOs with Four Different Head Groups (QA-PPO, IM-PPO, PI-PPO, and MO-PPO). The procedure used to functionalize Br-PPO with different head groups is as follows.

2.3.1. QA-Functionalized PPO. Br-PPO (DB 30%) (1.44 g, 1 mmol) was dissolved in 25 mL of NMP. Subsequently, TMA (45 wt %) (1.97 g, 15 mmol) was added to this solution to form a homogeneous solution, which was then stirred at 40 °C for 45 h. The resulting mixture was poured into ethyl acetate (250 mL), and the obtained solid was filtered, washed with ethyl acetate three times, and then dried at 80 °C under vacuum for at least 24 h to give the QA-functionalized PPO (QA-PPO) 3a as a dark brown powder (1.28 g, 89%); δ1 (400 MHz, DMSO-d6): 7.10–6.82 (6H, br signal, ArH2), 6.64–6.38 (14H, br signal, ArH3), 4.63–4.15 (6H, br signal, ArCH2), 3.41–2.82 (27H, br signal, NCH3), 2.33–1.72 (51H, br signal, ArCH3).

2.3.2. IM-Functionalized PPO. Br-PPO was reacted with 1,2-dimethyl imidazole to give the IM-functionalized PPO (IM-PPO, 3b). Yield 97%; δ1 (400 MHz, DMSO-d6): 7.66–7.41 (6H, br signal, ArH2), 6.95–6.59 (6H, br signal, ArH3), 6.59–6.32 (14H, br signal, ArH3), 5.43–5.11 (6H, br signal, ArCH2), 3.78–3.50 (9H, br signal, NCH3), 2.58–2.37 (9H, br signal, CCH3), 2.27–1.70 (51H, br signal, ArCH3).

2.3.3. PI-Functionalized PPO. Br-PPO was reacted with piperidine to give the PI-functionalized PPO (PI-PPO, 3c). Yield 98%; δ1 (400 MHz, DMSO-d6): 7.30–6.82 (6H, br signal, ArH2), 6.66–6.38 (14H, br signal, ArH3), 4.63–4.19 (6H, br signal, ArCH2), 3.11–2.83 (9H, br signal, NCH3), 2.32–1.85 (51H, br signal, ArCH3), 1.85–1.64 (12H, br signal, NCH2CH3), 1.62–1.30 (9H, br signal, NCH2CH3).

2.3.4. MO-Functionalized PPO. Br-PPO was reacted with N-methyl monopiperidine to give the MO-functionalized PPO (MO-PPO, 3d). Yield 95%; δ1 (400 MHz, DMSO-d6): 7.15–6.82 (6H, br signal, ArH2), 6.68–6.36 (14H, br signal, ArH3), 4.78–4.36 (6H, br signal, ArCH2), 4.15–3.78 (12H, br signal, OCH2), 3.74–3.22 (12H, br signal, NCH3), 3.22–2.89 (9H, br signal, NCH3), 2.34–1.66 (51H, br signal, ArCH3).

2.4. Fabrication of PPO Membranes and Alkalization. Each membrane was prepared in an NMP solution of the corresponding PPO polymer using the solution-casting method, and the film thickness was controlled to be 40–50 μm using the doctor blade technique. All of the PPO polymers with different head groups, 3 (0.45 g), in their bromide forms were dissolved in NMP to a concentration of 5 wt%. Each solution was then filtered through a cotton plug and poured onto a clean glass plate with a diameter of 11 cm, and the film was cast and dried in a vacuum oven at 60 °C for 24 h and then at 80 °C for 4 h. Each membrane was peeled off by immersing it in deionized water, and the resultant membrane was then immersed in 1 M NaOH at rt for 48 h in a closed container to obtain the membrane in its OH− form. Finally, each membrane in its OH− form was washed with and immersed in deionized water for 24 h prior to taking further measurements.

2.5. Characterization and Measurements. 2.5.1. 1H NMR. 1H NMR spectra were obtained on an Agilent 400-MR (400 MHz) instrument using DMSO-d6 or CDCl3 as a reference or internal deuterium lock.

2.5.2. Fourier Transform Infrared Spectroscopy. Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on a PerkinElmer FT-IR Spectrum two spectrometer.

2.5.3. Molar Masses. Molar masses were determined by gel permeation chromatography using two PL Gel 30 cm × 5 μm mixed C columns at 30 °C running in dimethylformamide (DMF) and calibrated against polystyrene (Mw = 600–104 g mol−1) standards using a Knauer refractive index detector.

2.5.4. X-ray Diffraction. X-ray diffraction (XRD) patterns of the dry membranes were recorded using a Rigaku HR-XRD smartlab diffractometer by employing a scanning rate of 0.1° min−1 in a 2θ range from 0° to 40° with a Cu Kα X-ray (λ = 1.54 Å). The dried membranes were placed under vacuum at 80 °C for 12 h and were equilibrated with 50% RH at least 24 h prior to the measurement.

2.5.5. Glass-Transition Temperature. The glass-transition temperature (Tg) was measured by differential scanning calorimetry (DSC) on a PerkinElmer DSC 4000. Samples were prepared in aluminum pans and measured from 25 to 250 °C for 2 cycles. The heating and cooling rate was 10 °C per minute. The second heating plot was used to determine the Tg.

2.5.6. Tapping Mode Atomic Force Microscopy. Tapping mode atomic force microscopy (AFM) was performed using a Bruker multimode instrument. A silicon cantilever with an end radius <10 nm and a force constant of 40 N m−1 (NCHR, nanosensors, f = 300 kHz) was used to image the samples at ambient temperature. The samples were equilibrated with 50% RH at least 24 h prior to the imaging. The measurements were conducted under the same conditions for each sample to maintain consistency.

2.5.7. Tensile Properties. Tensile properties were measured on a Shimadzu EZ-TEST EZ-L instrument benchtop tensile tester using a crosshead speed of 1 mm min−1 at 25 °C under 50% RH. The membranes have a thickness between 40 and 50 μm. Engineering stress was calculated from the initial cross-sectional area of the sample, and Young’s modulus (E) was determined from the initial slope of the stress-strain curve. The membrane samples were cut into a rectangular shape with 40 mm × 10 mm (total) and 20 mm × 10 mm (test area).

2.5.8. Ion-Exchange Capacity. IEC of the membranes in the hydroxide form was measured by the back-titration method. Twenty milligrams of the hydroxide (OH−) form membrane samples were immersed in a 0.01 M HCl standard solution for 48 h in order to fully neutralize OH− ions in the membrane. The unreacted HCl was titrated by the 0.01 M NaOH standard solution with phenolphthalein as an indicator. The measured (or experimental) IEC value, IECw,exp, was calculated using the following equation:

\[ \text{IEC}_{w,\text{exp}} = \frac{V_{\text{NaOH}}C_{\text{NaOH}} - V_{\text{NaOH}}C_{\text{NaOH}}}{W_{\text{dry}}} \]

where \( V_{\text{NaOH}} \) and \( V_{\text{NaOH}} \) are the volume of NaOH consumed in the titration without and with membranes, respectively, \( C_{\text{NaOH}} \) is the molar concentration of NaOH, which is titrated by the standard oxalic acid solution, and \( W_{\text{dry}} \) is the weight of the dried membranes. The volumetric IEC values were calculated according to the following equation:

\[ \text{IEC}_{v,\text{dry}} = \frac{1}{\rho_{\text{polymer}}} \times \text{WU(wt %)} \]

where IECw,exp is the volumetric IEC of the dried membrane and IECv,dry is the volumetric IEC of the wet membrane and \( \rho_{\text{polymer}} \) is the density of the polymer.
density of the dried membrane and \( \rho_{\text{water}} \) is the density of the distilled water.

2.5.9. Total Water Uptake. Total water uptake (\( \% \)) was measured as follows: after soaking the membranes in distilled water for more than 24 h, they were wiped with a filter paper and weighed immediately (\( W_{\text{wet}} \)). The membranes were then dried under vacuum condition until a constant weight was obtained (\( W_{\text{dry}} \)). The water uptake (\( \% \)) by weight is the ratio of the hydrated membrane to the dried membrane. The value was calculated using the following equation:

\[
WU (\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100
\]

The number of water molecules per ionic group (\( \lambda \)) was determined using the following equation:

\[
\lambda = \frac{(W_{\text{wet}} - W_{\text{dry}})}{18 \times \text{IEC}}
\]

where \( W_{\text{wet}} \) and \( W_{\text{dry}} \) are the weight of wet and dry membranes, respectively.

2.5.10. Swelling Ratio. Swelling ratio (SR; \( \% \)) of the membranes was measured by immersing the round-shaped membranes into water at 20 and 80 °C, respectively, and the changes of through-plane (thickness direction) were calculated using the following equations:

\[
SR (\%) = \frac{t_{\text{wet}} - t_{\text{dry}}}{t_{\text{dry}}} \times 100
\]

where \( t_{\text{wet}} \) is the thickness of the immersed membranes in water for 24 h and \( t_{\text{dry}} \) refers to the thickness of the dried membranes. The dried membranes were prepared by placing membranes under vacuum at 40 °C for 24 h prior to the measurement. Three trials were conducted for each sample. The IEC, water uptake, and SRs were obtained by the average of three different measurements.

2.5.11. Conductivity. Hydroxide ion conductivity (\( \sigma \)) in plane direction of each membrane (size: 1 cm \( \times \) 4 cm in liquid water) was obtained using \( \sigma = 1/RA \) (\( R \): resistance between electrodes and \( A \): cross-sectional area of a membrane coupon), where the resistive term from KOH solution was subtracted.

Here, Ohmic resistance (\( R \)) was measured by two-point probe alternating current impedance spectroscopy using an electrode system connected with an impedance/gain-phase analyzer (SI-1260) and an electrochemical interface (SI-1287) over the frequency range from 10 to 200 kHz. The conductivity measurements in liquid water were performed at different temperature ranges from 20 to 80 °C. To minimize unwanted carbonate formation, the cell was completely immersed in degassed and deionized water, and the impedance spectrum was collected quickly. The conductivity value was obtained by the average of at least three trials with the same time intervals.

Hydroxide conductivity measurements in 95% RH at 60 °C were performed in a humidity temperature oven equipped with a conductivity cell, connected to the impedance/gain-phase analyzer. The membrane between the electrodes was exposed to RH of 95% for conductivity cell, connected to the impedance/gain-phase analyzer.

2.5.12. Alkaline Stability. The chemical stability of the membranes was evaluated by immersing the OH− form membranes into 1 M NaOH solution at 60 °C for up to 500 h to investigate the changes in ionic conductivity and IEC values. Before measurements, each membrane was washed with deionized water several times and soaked in deionized water for at least 24 h at room temperature to remove the free NaOH inside the membrane. The ionic conductivity of each membrane was measured in deionized water at 20 °C.

2.5.13. Simulation. In this study, the Material Studio (BIOVIA) was used for molecular dynamics (MD) simulation. As a force field, we chose Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies II (COMPASSII) and set force-field types and charges of all atoms to the default value in COMPASSII. First, QA-PPO, IM-PPO, PI-PPO, and MO-PPO chains with 106 of each membrane were measured in deionized water at 20 °C. 25 g mol\(^{-1}\), respectively, were built and geometrically optimized with the Forcite module with the smart algorithm, which is a combination of the steepest descent, adjusted basis set Newton–Raphson (ABNR), and quasi-Newton methods in a cascade.

Using the amorphous cell module, we constructed three-dimensional (3D) models of QA-PPO, IM-PPO, PI-PPO, and MO-PPO under 3D periodic boundary conditions. For the hydrated 3D amorphous models of PPO membranes, water molecules were added according to their water uptake values. After the models were geometrically optimized, we performed MD simulations to obtain the final model structures for analysis, for which specific procedures can be found in our previous study.58–60 The electrostatic and van der Waals (vdW) interactions were calculated by the Ewald summation method with an accuracy of 0.001 kcal mol\(^{-1}\). The Andersen temperature control method with a collision ratio of 1 and the Berendsen pressure control method with a decay constant of 0.1 ps were used. First, quenched dynamic calculations were performed at 293 K and 1 atm for 100 ps and at 593 K and 1 atm for 100 ps, respectively. The obtained PPO models were relaxed with the NPT (constant number of atoms, pressure, and temperature) MD simulation at 293 K and 1 atm for 100 ps. We then repeated the NPT simulation at 293 K and 1 atm for 100 ps, NVT (constant number of atoms, volume, and temperature) simulation at 593 K for 20 ps, NVT simulation at 293 K for 20 ps, and NPT simulation at 293 K and 1 atm for 100 ps until the 3D amorphous models were equilibrated. Additionally, the NPT simulation was carried out at 293 K for 5 ns for the mean square displacement (MSD) in order to calculate diffusion coefficients of the hydrated PPO models.

Diffusion coefficients were calculated from the slope of the MSDs of hydroxide molecules versus time using the Einstein equation:

\[
D = \frac{1}{6N_t \lim_{t \to \infty} \frac{d}{dt} \langle (r(t) - r(0))^2 \rangle}
\]

where \( N_t \) is the number of diffusing molecules of type \( \alpha \), \( r(t) \) and \( r(0) \) are the initial and final positions, respectively, of molecules (mass centers of particle \( i \)) over the time interval \( t \), and \( \langle (r(t) - r(0))^2 \rangle \) is the MSD averaged over the possible ensemble. The Einstein relationship assumes Brownian dynamics for the diffusing particles.

Fractional free volume (FFV) is the ratio of the free volume within a polymer and the specific volume of the polymeric material:

\[
\text{FFV} = \frac{V_f}{V_p}
\]

where \( V_f \) indicates the amount of free volume and the specific volume, \( V_p \) is defined as a reciprocal density. According to Bondi’s method, the amount of free volume can be estimated as

\[
V_f = V_p - 1.3V_{wD}
\]

where the vDW volume \( V_{wD} \) is calculated using the Visualizer module in the Material Studio. A universal “packing coefficient”, equal to 1.3, is used to convert the vDW volume of the repeat unit into the “occupied” volume.

For visualization of free volume distribution, we calculated the solvent surface inside #D models. Using the vDW surface, the solvent surface was defined as the surface that is the locus of the probe center as the probe rolls over the scaled vDW surface. This surface describes a space which could, in principle, be occupied by a probe of the given radius, where the volume on the side of the surface without atoms (the free volume) is used as the solvent free volume. The sorption simulation of water molecules was performed using a grand canonical Monte Carlo (GCMC) simulation. In this procedure, a Metropolis algorithm was used to accept or reject an insertion and deletion of a sorbate molecule.

The probabilities of addition and deletion of a sorbate molecule are given as
Scheme 1. Synthesis of QA-PPO (3a), IM-PPO (3b), PI-PPO (3c), and MO-PPO (3d)

$P_{dd} = \min \left\{ 1; \frac{1}{N_e + 1} \frac{pV}{kT} e^{-\Delta U/kT} \right\}$ and

$P_{ld} = \min \left\{ 1; \frac{N_e kT}{pV} e^{-\Delta U/kT} \right\}$

where $U$ is calculated from the sum of nonbond energies such as Coulombic and vdW interaction energies and $N_e$ is the number of water molecules. The addition is accepted if the energy change $\Delta U$ is negative or if the Boltzmann factor, $e^{-\Delta U/kT}$, is greater than a random number generated between 0 and 1.

2.5.14. Membrane Electrode Assembly Fabrication and Fuel Cell Testing. A well-dispersed catalyst ink was prepared by mixing 46.5 wt % Pt/C catalysts (Tanaka) with deionized water, 1-propanol, and ionomer solution (AS-4, Tokuyama, 5 wt %) using magnetic stirring and ultrasonication. To obtain catalyst-coated membranes (CCMs) for the electrodes, the as-prepared ink was coated onto the membrane using an air spray gun. The Pt loading and ionomer content in the catalyst layer were 0.50 mg cm$^{-2}$ and ~30 wt %, respectively. Subsequently, the assembly of carbon paper (HCP120, HESEN) and gaskets (Teflon, 15 wt %) were sandwiched between gas diffusion layers (10BC, Sigracet SGL carbon Inc.) and gaskets (Teflon). The $H_2/O_2$ fuel cell performance testing at 60 °C under partially hydrated humidification was carried out by a commercialized detecting system for fuel cells (CNL, Korea). The hydrogen and oxygen were supplied at 200 mL min$^{-1}$ to the anode and cathode, respectively. First, the MEA was activated under the potentialistic mode at 0.4 V about 6 h. Then, the polarization curve was obtained under the galvanostatic mode.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization of the PPOs with Various Head Groups. PPOs with four different head groups, namely, ammonium, IM, PI, and MO, 3, were prepared as outlined in Scheme 1. PPO, 1, was selected as the main polymer backbone because of its commercial availability and amenability for further modification. Furthermore, PPO contains only phenylene rings connected by ether linkages and, therefore, significantly more stable under alkaline condition than are other polymers having electronegative atoms in their backbones, such as photoelectron spectroscopy.

Br-PPO (2) with a DB of 30% at the benzylic position of PPO was first prepared by reacting PPO with NBS following the reported procedure. As shown in Scheme 1, each hydroxide-conducting group (or head group) was then introduced onto the benzylic position of the respective PPO sample by reacting Br-PPO with an excess of the corresponding precursor to the head group (TMA, 1,2-dimethylimidazole, N-methylpiperidine, and N-methylmorpholine) in NMP, following the Menshutkin reaction, to produce the corresponding QA-PPO, IM-PPO, PI-PPO, and MO-PPO, respectively. The conditions for these four reactions were kept the same to obtain similar IEC values for these four head group-PPO products.

The structures of Br-PPO and the PPOs having four different head groups, 3, were confirmed by carrying out $^1$H NMR spectroscopic analyses. First, the DB of Br-PPO was determined by comparing the relative integral ratio of the benzylic proton (H$_3$) in PPO 1 with that of the bromobenzylic proton (H$_3$) in Br-PPO 2 (Figure S1 in Supporting Information) and was found to be 30%.

The introduction of each functional group (or head group) was confirmed by observing that the $^1$H NMR peak corresponding to the bromobenzylic proton (H$_3$) at 4.3 ppm in Br-PPO disappeared and that corresponding to the new benzylic proton next to the head group (H$_3$) appeared at 4.3 ppm for QA, IM, PI, and MO, respectively appeared and did so quantitatively (Figure S2).

Further $^1$H NMR spectroscopic confirmation of the successful incorporation of each head group was also indicated by the appearance of new peaks—corresponding to the methyl group (H$_3$) of the QA at 3.1 ppm for QA-PPO (Figure S2a), the methyl IM group (H$_3$) at 2.5 ppm and H$_6b$ at 3.6 ppm and IM group (H$_3$) at 7.5 ppm for IM-PPO (Figure S2b), the methyl group and cyclic ring (H$_5$,H$_7$,H$_8$ at 1.6, 1.8, 3.0, and 3.3 ppm, respectively) of the IM group for PI-PPO (Figure S2c), and the methyl group (H$_5d$ at 3.1 ppm) and cyclic ring of the MO group (H$_5d$ and H$_7d$ at 3.5 and 4.0 ppm, respectively) for MO-PPO (Figure S2d); all other peaks of these head group-containing PPOs were identical to those of Br-PPO. For each of the four polymers, the theoretical IEC$_{\text{meq g}^{-1}}$ defined as the number of head groups per unit mass of polymer, was calculated from the corresponding $^1$H NMR spectrum and was found to be between 2.02 and 2.10 mequiv g$^{-1}$.

Four membranes were then prepared, using the four head group-containing PPOs, 3, in NMP solutions under the same conditions. All of the membranes were flexible with thicknesses...
of ca. 40–50 μm (Figure 1) and were readily soluble in organic solvents, including DMF, DMSO, dimethylacetamide, and NMP, and also soluble in MeOH and EtOH but were not soluble in isopropyl alcohol and water.

3.2. Water Uptake, Swelling Ratio, and $\lambda$ Value. Water uptake (WU) in most AEMs affects hydroxide conductivity, as the water is involved as a medium for conducting hydroxide ions. Excessive WU, however, has been observed to cause considerable swelling, rendering the membranes too mechanically weak to be used as AEMs. Therefore, achieving a high level of water uptake while keeping the SRs low (i.e., maintaining high-dimensional stability) is required for the development of AEMs. The water uptakes and SRs of the four PPO membranes having different head groups were measured at temperatures of 20 and 80°C, respectively (Table 1).

As mentioned above, the four membranes showed similar IEC$_w$ values, and hence, the influence of the number of head groups, that is, the IEC$_w$ value, on the water uptake and SR can be neglected.

We found that the PI-PPO membrane showed the highest water uptake and SR at both low (20°C) and high (80°C) temperatures. In order to understand the water uptake behavior of the PPO membranes, we performed MD simulations. In particular, because water molecules were absorbed and filled the free volume (or cavities) of the membranes at the first stage of hydration, we analyzed the free volumes inside the PPO models produced using the MD simulations (Figure 2) and performed a GCMC simulation to calculate the sorption of water molecules into PPO models (Table 1). As shown in Table 1, the free volume ratios of the QA-PPO and PI-PPO membranes were found to be higher than those of the IM-PPO and MO-PPO membranes, which were strongly correlated with the simulated amount of water sorption. This difference allowed the QA-PPO and PI-PPO membranes to absorb more water than could the other membranes, which corresponded well with the experimentally measured water uptake values. It should be noted that the relationship between the free volume and the water uptake is more complex than that of our simulation results. For example, at high hydrated condition, the water uptake of polymers is also affected by plasticization, distribution of functional groups, and many others. Because the simulation scheme used in this study could not consider all of these effects, our results limitedly suggest the underlying phenomena of the hydration behavior. However, considering that the AEM models in this study have the similar IEC and polymer backbone structure, we may conclude that their differences in the free volume distribution could be one of the factors determining their water uptake behavior.

To investigate the effect of each head group on its dimensional stability, we also calculated, for both low (20°C) and high (80°C) temperatures, the hydration number $\lambda$, defined as the number of water molecules absorbed per head group (QA, IM, PI, and MO group) (Table 1) as well as the SR divided by $\lambda$ (Figure 3). SR/$\lambda$ did not show a significant difference between 20 and 80°C for each of the QA-PPO, IM-PPO, and PI-PPO membranes but did so for the MO-PPO membrane. Moreover, the MO-PPO membrane showed considerably lower values of SR/$\lambda$ than did the other three membranes, especially at the low temperature.

Compared to PI groups in PI-PPO, the presence of an additional oxygen atom in MO groups in MO-PPO providing a site for hydrogen bonding with a water molecule or hydroxide ion was expected to increase the density as shown in Table S1 and hence to enhance the dimensional stability of the corresponding membrane. However, this hydrogen bond

![Figure 1. Photographs of PPO-based AEMs.](image)

![Figure 2. Models of the structures of the four head group-containing PPO membranes, showing their free volume distributions.](image)

<table>
<thead>
<tr>
<th>membrane code</th>
<th>WU (%)</th>
<th>SR (%)</th>
<th>$\lambda$ value (#)</th>
<th>simulated FFV</th>
<th>simulated sorption amount of water molecule (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>QA-PPO</td>
<td>55.6 ± 3.1</td>
<td>95.4 ± 4.0</td>
<td>18.2 ± 3.7</td>
<td>26.8 ± 3.0</td>
<td>16.6</td>
</tr>
<tr>
<td>IM-PPO</td>
<td>45.1 ± 1.9</td>
<td>73.8 ± 3.5</td>
<td>15.5 ± 2.8</td>
<td>23.7 ± 5.6</td>
<td>13.1</td>
</tr>
<tr>
<td>PI-PPO</td>
<td>59.7 ± 2.8</td>
<td>106.1 ± 3.8</td>
<td>19.6 ± 4.1</td>
<td>30.6 ± 6.4</td>
<td>17.0</td>
</tr>
<tr>
<td>MO-PPO</td>
<td>49.7 ± 4.0</td>
<td>75.8 ± 4.3</td>
<td>9.3 ± 3.6</td>
<td>20.5 ± 2.0</td>
<td>15.1</td>
</tr>
</tbody>
</table>
would be expected to begin to break upon increasing the temperature, lowering the original high-dimensional stability of the membrane to some extent. In fact, the MO-PPO membrane showed even less swelling than did the IM-PPO membrane, even though the IM-PPO membrane showed a lower water uptake value than did the other three membranes at both low (20 °C) and high (80 °C) temperatures (Table 1).

3.3. IEC and Conductivity. High hydroxide ion conductivity is one of the most important factors in developing AEMs, with higher IEC values generally contributing to the higher conductivity levels. To exclude the effect of IEC on the conductivity and to investigate only the effect of various types of head groups on the conductivity, the four membranes having different head groups (IM-PPO, QA-PPO, PI-PPO, and MO-PPO) were designed to have similar IEC values, within the 2.03–2.10 mequiv g⁻¹ range. Both the theoretical IEC, calculated from the degree of functionalization based on the comparative ¹H NMR spectroscopic methods, and the experimental IEC measured using the back-titration method, showed similar values for all four membranes—although the observed experimental IEC values were slightly lower than the corresponding theoretical IEC values for all four membranes, possibly because of the strong electrostatic attraction between hydroxide ions and head groups and the steric hindrance of the polymer having caused an incomplete neutralization between H⁺ and OH⁻ ions during titration. It was, moreover, noteworthy that the PI-PPO membrane showed the highest measured IEC of 1.95 mequiv g⁻¹, whereas the lowest value was obtained for the MO-PPO membrane (1.83 mequiv g⁻¹). Because the same experimental conditions were used for the functionalization of head groups using the same Br-PPO (and accordingly nearly the same theoretical IEC values were calculated), this difference in the measured IEC values was ascribed to the different structures of the head groups. The high ion dissociation tendency of the PI group, due to its bulky ring structure, was thought to have resulted in PI-PPO having the highest IEC value. The relatively low IEC value for MO-PPO may have been due in part to the oxygen atom of the ring structure of the MO group having hydrogen-bonded hydroxide ions and hence impeding the dissociation of these ions, an assessment corresponding to the MD simulation results listed in Table S2.

To further understand the water absorption behavior of the four PPO membranes, that is, those having the different head groups, the IEC, an index representing the number of head groups per unit volume in the hydrated state, was further calculated. Both IEC in the hydrated state, denoted as IECw, and the IEC in the dry state, IECdry, were calculated from the IEC density, and water uptake values of each membrane (Table 2). Of these two values, IECw was of greater significance because it was determined from the conditions used to actually measure the conductivity levels of the AEMs. The IM-PPO membrane displayed an IECw greater than those of the other three membranes. This result was attributable to this membrane having also displayed a water uptake lower than those of the other three because water uptake is inversely proportional to IECw. The low water uptake of the IM-PPO membrane was caused by the relatively high density of this membrane, which in turn resulted from the π–π interactions between IM groups.

Interestingly, the MO-PPO membrane showed an experimental IEC (1.83 mequiv g⁻¹) lower than those of the other three membranes, yet an IECw (1.38 mequiv cm⁻³) higher than those of the others except for the IM-PPO membrane. This result for the MO-PPO membrane may have resulted from its relatively low water uptake, which in turn was attributed to its relatively high density in its hydrated state resulting from hydrogen bonding of the MO groups with hydroxide ions causing an increase in the hydroxide ion concentration. The IECw values of the PI-PPO and QA-PPO membranes also reflected their water uptake values: the PI-PPO membrane, having the highest water uptake value, showed the lowest IECw value, and the results for the QA-PPO membrane followed the same trend.

The hydroxide ion conductivities of all four membranes were measured in water at temperatures ranging from 20 to 80 °C (Figures 4a and S3 and Table 2). At the low temperature (20 °C), the conductivities were between 27 and 29 mS cm⁻¹ for the QA-PPO, IM-PPO, and PI-PPO membranes but significantly higher, specifically 35.3 mS cm⁻¹, for the MO-PPO membrane. In fact, the conductivity per IEC (both IEC and IECw) value at the low temperature (20 °C) was higher for MO-PPO than for the PPOs containing any of the other three head groups analyzed (Figure 4b), suggesting the MO group to conduct the hydroxide ion most effectively, especially at low temperature.

### Table 2. IEC and OH⁻ Conductivity Values of the Four PPO-Based AEMs with the Different Head Groups

<table>
<thead>
<tr>
<th>membrane code</th>
<th>IECa (mequiv g⁻¹)</th>
<th>IECb (mequiv g⁻¹)</th>
<th>IECdry (mequiv cm⁻³)</th>
<th>IECw (mequiv cm⁻³)</th>
<th>OH⁻ conductivity (mS cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20 °C</td>
</tr>
<tr>
<td>QA-PPO</td>
<td>2.10</td>
<td>1.86 ± 0.05</td>
<td>2.14</td>
<td>1.30</td>
<td>27.9 ± 0.5</td>
</tr>
<tr>
<td>IM-PPO</td>
<td>2.03</td>
<td>1.91 ± 0.11</td>
<td>2.63</td>
<td>1.63</td>
<td>27.6 ± 1.7</td>
</tr>
<tr>
<td>PI-PPO</td>
<td>2.04</td>
<td>1.95 ± 0.07</td>
<td>2.30</td>
<td>1.35</td>
<td>28.6 ± 0.2</td>
</tr>
<tr>
<td>MO-PPO</td>
<td>2.03</td>
<td>1.83 ± 0.03</td>
<td>2.21</td>
<td>1.38</td>
<td>35.3 ± 0.7</td>
</tr>
</tbody>
</table>

aCalculated from ¹H NMR spectra. bTitrated values.
have been shown to feature high water uptake and hence having bulky structures, such as PI and pyrrolidinium groups, rates of hydroxide ions and hence diffusion by the Grotthuss mechanism (to conduct OH\(^-\)). MO group was therefore apparently more effective than the PI and MO-PPO membrane. The ion conduction in the case of the membranes, apparently because of its weaker hydrogen bonding (so does the ion conduction by the Grotthuss mechanism) at increased temperatures.

In contrast, IM-PPO, that is, that having IM as a head group, showed the lowest conductivity per IEC (both IEC\(_w\) and IEC\(_v\)) values at both the low (20 °C) (Figure 4b) and high (80 °C) (Figure 4c) temperatures tested, suggesting the ion conduction efficiency of the IM group to be lower than those of the other tested head groups. The relatively poor ion conduction resulting from the IM groups may have been due to the \(\pi-\pi\) interactions between them.\(^{66}\) In contrast, the hydrogen bonding between the MO oxygen atom and water and/or hydroxide ions apparently promoted the ion conduction for MO-PPO, particularly at the low temperature (20 °C) (vide infra).

It should also be noted that for MO-PPO, the conductivity increased modestly as the temperature was increased. PI-PPO, that is, that having the PI group, on the other hand, yielded a sharp increase in conductivity as the temperature was increased and yielded the highest conductivity at 80 °C, with a value of 77.3 mS cm\(^{-1}\), among the four head groups. The large difference in the conductivity increase upon temperature increase between MO and PI, despite their very similar structures, may have been related to the different diffusion rates of hydroxide ions and hence different hydroxide ion conduction mechanisms for these two head groups. Ionomers having bulky structures, such as PI and pyrrolidinium groups, have been shown to feature high water uptake\(^{69,70}\) and hence facilitate the ion dissociation from head groups accordingly. Therefore, the activity of the dissociated hydroxide ions in our experiments increased with increasing temperature, which led to the more significant increase of conductivity with the increase of temperature for PI-PPO.

The ability of the MO group, despite its structural similarity with PI, to form hydrogen bonds with water and/or hydroxide ions\(^{69,70}\) (Table S2) apparently inhibited the ion diffusion of the MO-PPO membrane. The ion conduction in the case of the MO group was therefore apparently more effective through the Grothuss mechanism (to conduct OH\(^-\) by combining with water through the formation of H\(_3\)O\(_2^+\)),\(^{64,66}\) rather than by surface diffusion (one of the vehicular mechanisms and to conduct OH\(^-\) through direct interaction with the head groups by charge transport),\(^{67}\) leading to the high conductivity especially at the low temperature tested (20 °C). The increase in conductivity with increasing temperature was, however, less dramatic for the MO-PPO membrane than for the other membranes, apparently because of its weaker hydrogen bonding (so does the ion conduction by the Grothuss mechanism) at increased temperatures.

The results of MD simulations were consistent with these peculiar behaviors of the ion conductivities of PI-PPO and MO-PPO. Table S3 shows the diffusion coefficients of hydroxide ions through the water channels inside the PPO models. Because diffusion coefficients of ions are calculated solely based on the vehicular mechanism (to conduct OH\(^-\) by overlapping first hydration shells of the head group through charge transport),\(^{68}\) we compared these results with the experimentally measured ion conductivity values based on the Grothuss mechanism. Also, we estimated the effect of the Grothuss mechanism on the ion conductivities of the PPOs having different head groups. As expected, the diffusion coefficient of the PI-PPO membrane was found to be greater than those of the PPOs functionalized with the other head groups (Table S3). The observation of more rapid diffusion in the PI-PPO membrane can be attributed to the high water uptake of this membrane because of its large water channels as well as the facile dissociation of hydroxide ions in this membrane caused by the bulky PI, which in combination would be expected to give rise to a rapid increase in conductivity as the temperature is increased.

The MO-PPO membrane, on the other hand, showed a very low hydroxide ion diffusion coefficient, despite the MO group having a structure similar to that of PI, because of its much lower water uptake compared to PI-PPO. Nevertheless, the MO-PPO membrane displayed the highest ionic conductivity at the low temperature tested (20 °C), which indicated the hydrogen bond-induced Grothuss mechanism to be more dominant than the vehicular mechanism at low temperatures, that is, temperatures amenable to stable hydrogen bonds.

Last, for the IM-PPO membrane, the \(\pi-\pi\) interactions between its IM groups apparently led to this membrane, despite its high IEC\(_v\) displaying a water uptake lower than those of the other three membranes, which in turn displayed the lowest conductivity levels throughout the entire temperature range measured as well as the lowest ion diffusion coefficient.

3.4. Conductivity under a Partially Hydrated RH Condition. Designing AEMs that display high ion conductivity levels at hydrated RH conditions is important because such conditions approximate the actual driving conditions for the fuel cells. However, there have not been many investigations of the ion conduction characteristics of ionomers with various head groups at hydrated RH conditions.

The hydroxide ion conductivities of the four PPO membranes studied here were measured at 60 °C in 95% RH conditions for the fuel cells. However, there have not been many investigations of the ion conduction characteristics of ionomers with various head groups at hydrated RH conditions.

The hydroxide ion conductivities of the four PPO membranes studied here were measured at 60 °C in 95% RH conditions for the fuel cells. However, there have not been many investigations of the ion conduction characteristics of ionomers with various head groups at hydrated RH conditions.

![Figure 4. Hydroxide ion conductivities in water as a function of temperature (a) and values of OH\(^-\) conductivity divided by IEC at 20 °C (b) and at 80 °C (c) for the four PPO-based AEMs, each containing a different head group.](image-url)
RH, conditions similar to those of the actual cell operation (Table S4), and the results were compared with the conductivities measured in liquid water at 60 °C (Figure 5).

As expected, a much lower conductivity was observed for all four membranes at the 95% RH condition. Interestingly, the conductivity trends differed for these two conditions: at 95% RH, the highest conductivity was observed for QA-PPO, followed by MO-PPO, PI-PPO, and then IM-PPO, whereas PI-PPO showed the highest conductivity, followed by MO-PPO, QA-PPO, and then IM-PPO in water (Figure 5 and Table S4). These results indicated the hydroxide ion-conducting mechanism to be different in water than at 95% RH.

The Grotthuss, vehicular, and surface diffusion mechanisms have been shown to be the main ion conduction mechanisms operating in AEMs, and these mechanisms have been shown to determine the hydroxide conductivity. Disassociation of a bound hydroxide ion will be less favorable at 95% RH than in liquid water, as the disassociation of a hydroxide ion from a head group proceeds more easily in an environment with more water. Therefore, most head groups experience a relatively high rate of increase in conductivity per unit increase of temperature when the diffusion-induced vehicular mechanism is operating. This observation is generally attributed to the disassociation of the ion from the head groups being facilitated at elevated temperatures and also in liquid water. Moreover, high ion conductivity at elevated temperatures is most apparent for bulky head groups, such as PI, because ions most readily dissociate from such head groups because of the steric hindrance these head groups show.

In contrast to the liquid water state where ion conductivity predominantly occurs via the ion diffusion-induced vehicular mechanism, the fewer water molecules in a wet but only 95% RH state reduces the rate of disassociation of ions from head groups, and thus, ion transport would be expected to become more reliant on the hydrogen bond-induced Grotthuss mechanism and/or the surface diffusion mechanism, where ions are transported directly between head groups. Accordingly, because of the steric hindrance caused by the large PI moiety, PI-PPO showed a high ion dissociation rate but at the same time inhibited surface diffusion (i.e., the path of direct ion transfer), leading to a relatively low conductivity (3.8 mS cm⁻¹) at 60 °C in 95% RH. Despite the similar structures of the PI and MO head groups, the MO-PPO membrane in 95% RH showed a conductivity level (4.1 mS cm⁻¹) higher than that of PI-PPO, attributable to the MO hydrogen bonds overcoming the relative scarcity of water molecules and efficiently transporting ions.

QA-PPO showed lower ionic conductivity in water than did PI-PPO and MO-PPO, corresponding to the observed diffusivity trend and attributed to the ammonium group of QA-PPO, creating less steric hindrance than the PI and MO groups and hence QA-PPO releasing bound ions more slowly compared to PI-PPO and MO-PPO. However, at 95% RH, QA-PPO is expected to have the highest surface diffusion efficiency because of its smallest size of the head group, which results in a higher conductivity at RH 95% compared to PI-PPO and MO-PPO even though this system exhibits a lower conductivity in water than the other two membranes.

Last, the IM-PPO membrane showed the lowest conductivity in both water and at 95% RH (Figure 5 and Table S4). This result was attributed to this membrane having the lowest water uptake because of π−π interactions between IM groups.

3.5. Morphological Analysis. Morphological analyses of the four membranes were carried out using small-angle X-ray scattering (SAXS) and AFM to investigate the size and dispersion of ion clusters of the ionomers having different head groups. In the SAXS graphs (Figure 6a), the ionomer peaks were observed at 0.02 Å for all four polymer membranes, and the d-spacing calculated using the equation $d = 2\pi/q$ was approximately 30 nm. Unlike other ionomers, however, additional peaks at about 0.2 Å were observed for the MO-PPO and IM-PPO membranes, which were attributed to the π−π interactions between the IM groups for IM-PPO and
the hydrogen bonding between MO and water and/or hydroxide for MO-PPO. These interactions between molecules apparently contributed to the formation of ionic clusters.

Phase separation between dark hydrophobic and bright hydrophilic areas was observed in the AFM images of all four polymer membranes (Figure 6b). The morphologies of the four polymer membranes did, however, vary significantly: relatively small clusters were observed to be regularly dispersed throughout the QA-PPO membrane, that is, that having the QA groups, the smallest of the head groups tested. The PI-PPO membrane, on the other hand, showed the least distinct cluster formation, perhaps because of its bulky PI group having inhibited ion cluster formation. Relatively well-aligned conducting channels, however, were still observed for the PI-PPO membrane. The domains of the IM-PPO and MO-PPO membranes were observed to be larger than those of the QA-PPO and PI-PPO membranes, possibly because of the presence of additional \( \pi-\pi \) interactions between IM groups in IM-PPO and to the hydrogen bonding between the MO and water molecules/OH\(^-\) ions in MO-PPO, as also indicated by the SAXS analyses.

Further evidence for the presence of \( \pi-\pi \) interactions for IM-PPO and hydrogen bonds for MO-PPO was provided by measuring the densities of the four PPO membranes. As shown in Table S1, the densities of the IM-PPO and MO-PPO membranes in both dry and wet states were observed to be significantly greater than those of the other two membranes, indicative again of the additional interactions made in these membranes.

3.6. Thermal and Mechanical Properties. The \( T_g \) of each polymer was determined using DSC to characterize the thermal properties of the four PPOs with different head groups in their hydroxide forms (Figure 7 and Table S5). An endothermic peak was not observed for the QA-PPO membrane at any temperature up to 250 °C, unlike the cases for the other polymeric membranes. This result was due to the enhanced molecular interactions between QA-PPO polymer backbones resulting from the relatively little steric hindrance caused by the QA groups, compared to other head groups, on the side chain of the polymers. The \( T_g \) of IM-PPO was determined to be lower than that of QA-PPO. This low \( T_g \) of IM-PPO presumably resulted from the strong \( \pi-\pi \) interactions between its IM groups interfering with the attraction between the polymer backbones.

Endothermic peaks were observed at temperatures below 235 °C for the MO-PPO and PI-PPO membranes. This observation was attributed to the interactions between their polymer backbones being relatively weak, for example, weaker than that of QA-PPO, which in turn is due to the presence of their sterically bulky side chains. In addition, the \( T_g \) of PI-PPO, at 220 °C, was found to be significantly different from that of MO-PPO, at 233 °C. This difference occurred despite the MO and PI groups both including a similar head group in their structures and was attributed, as mentioned above, to the extra oxygen atoms of MO-PPO having formed hydrogen bonds with water molecules and/or hydroxide ions and hence having provided additional interactions.

The mechanical properties of the four PPO membranes incorporating different head groups were further measured in their hydroxide forms (Figure S4 and Table S5) because the AEMs need to be mechanically strong enough to withstand the cell operating conditions. All four membranes showed relatively high tensile strengths above 30 MPa. Yet, despite employing the same polymer backbone, their tensile strengths differed, as did their elongations. In particular, the PI-PPO and MO-PPO membranes, both employing the head groups with bulky cyclic structures, showed the highest tensile strength values, and the MO-PPO membrane showed a much higher elongation at break than did the PI-PPO membrane. The IM-PPO membrane, on the other hand, showed the lowest elongation and slight brittleness, attributable to the crystalline structure caused by the \( \pi-\pi \) interactions.

3.7. Alkaline Stability. Developing an AEM displaying alkaline stability is important for producing AAEMFCs displaying long-term stability. The conductive ion, that is, OH\(^-\), can attack not only the polymer backbone but also the head groups of the AEM, especially at high temperatures, rapidly worsening the physical properties and decreasing the conductivity of the AEM over time. Numerous studies have yet reported that the degradation of the head groups is more dominant than that of polymer backbones and this is mostly caused by the SN2 reaction and Hofmann elimination.\(^{24,25}\) To eliminate the influence of the polymer backbone, we employed in the current study polymer membranes incorporating different head groups but the same polymer backbone (PPO) and investigated their alkaline stability levels by measuring the conductivity and IEC reduction levels of the membranes over time in 1 M KOH at 60 °C for up to 500 h (Figure 8). The four membranes (QA-PPO, IM-PPO, PI-PPO, and MO-PPO) all showed significant decreases in both conductivity and IEC within 200 h.

Unlike the results of other studies, where high alkaline stability of IM was observed and attributed to its resonance structure, IM-PPO in the current study showed the lowest alkaline stability, despite the introduction of an alkyl group on the reactive C2 position of IM, with only about 20% of the original conductivity and 37% of the original IEC retained even after 500 h. This result was ascribed to the resonance structure of the IM, which increases the stability of the OH\(^-\)-bound intermediates and hence causes the lowest unoccupied molecular orbital (LUMO) energy of IM-PPO to be lower than those of other head groups. Moreover, unlike other head groups that only have \( \sigma \)-LUMO orbitals that are prone to OH\(^-\) ion attack, IM-PPO also has \( \pi \)-LUMO orbitals,\(^{69}\) which causes this membrane to have the lowest stability against OH\(^-\) ions and hence to have the lowest stability under alkaline conditions.
The PI-PPO and QA-PPO membranes showed much higher alkaline stabilities than did the IM-PPO membrane. In particular, the PI-PPO membrane, that is, that employing the bulky cyclic PI group, showed a slightly higher stability than did the QA-PPO membrane, with almost 80% of the conductivity and 79% of IEC retained even after 500 h. This enhanced alkaline stability for PI-PPO was attributed to this bulky cyclic structure creating steric hindrance that suppressed the approach of OH$^{-}$ ions, as also reported in other studies.46 The MO-PPO membrane, despite employing a similar cyclic structure, displayed a lower alkaline stability than did PI-PPO and retained only 57% of its initial conductivity and 67% of its initial IEC after 500 h. This result was mainly caused by the presence of the electronegative oxygen atom of MO destabilizing the MO by reinforcing its positive charge as well as by the hydrogen bonds of the same oxygen atom increasing the membrane density, which allowed OH$^{-}$ ions to more easily approach the head group.

The differences between the stability levels of the membranes with different head groups can also be explained in terms of their water absorption properties, as recent studies suggested that sufficient water molecules are required to generate a microsolvation sphere around the OH$^{-}$ ion, which can shield the OH$^{-}$ sterically as well as electronically, decreasing the nucleophilicity of the OH$^{-}$ ion and hence increasing the stability of the head group in alkaline solutions.16,70 Therefore, PI-PPO, having the highest water uptake value, showed the highest alkaline stability, followed by QA-PPO, MO-PPO, and then IM-PPO, which corresponded to the order of their water uptake values (Table 1).

3.8. Fuel Cell Performance. A key goal when designing AEMs is to develop AAEMFCs that are effective in alkaline conditions and that do not contain any precious metal catalysts at all. However, during the early stages of such research, it is necessary to carry out benchmarking with Pt-based AAEMFCs to be able to compare the results of different laboratories because quality-controlled commercial Pt-based fuel cell catalysts are still in common use. Hence, in the current work, we conducted Pt/C cathode and Pt/C anode H$_2$/O$_2$ AEMFC tests to provide a comparison between our QA-PPO, IM-PPO, PI-PPO, and MO-PPO AEMs and those of other laboratories. We kept all other test conditions the same (including the ionomer used in the CCM) and acquired the I–V curves of these four AEMs under the 95% RH condition at 60 °C (Figure 9). Their peak power densities are summarized in Table S6. Because all electrolyte membranes show relatively high open-circuit voltage, there is no problem in cell performance measurement. It is also expected that the performance degradation due to lack of fuel and oxidant will not occur because of excessive hydrogen and oxygen supply.

Ionic conductivity has been generally considered to be the most important factor in determining the cell performance. As described above, in liquid water at 60 °C, PI-PPO showed the highest conductivity (65.8 mS cm$^{-1}$), followed by MO-PPO, QA-PPO, and then IM-PPO (Table 2), whereas under 95% RH at this temperature, QA-PPO showed the highest conductivity (4.3 mS cm$^{-1}$), followed by MO-PPO, PI-PPO, and then IM-PPO (Table S4). This latter trend was also observed for the cell performance: the power density and current density were also observed to be greatest for QA-PPO, followed by MO-PPO, PI-PPO, and then IM-PPO (Table S6). The difference between the conductivity trend in liquid water and the actual fuel cell performance under 95% RH cannot be wholly accounted for by the conductivity behaviors under different hydration states, but this result still strongly supported our hypothesis that the predominant hydroxide ion-conducting mechanism in the liquid water environment differs from that in the operating fuel cell environment, where the ionomers become hydrated only as a result of water vapor transported into the cell such as in gas-fed fuel cells.

As discussed above, the hydroxide ions were expected to dissociate from the polymer more easily in liquid water than under 95% RH, and such impeded dissociation was expected...
to interfere with conduction driven by surface diffusion. Therefore, unlike PI-PPO, where hydroxide ion conduction was indicated to be mainly dominated by surface diffusion, the hydrogen bond-induced Grotthuss mechanism was indicated to prevail over surface diffusion for the MO group, thus allowing MO-PPO to conduct ions more effectively than PI-PPO under environments with less water and resulting in the observed considerably higher conductivity and better cell performance.

The surface diffusion of ions, with hydroxide ions transported from one head group to another as induced by the voltage difference, was as discussed above expected to be more facile for the QA-PPO membrane than for the polymer membranes having other head groups because of the relatively small size of the QA group of QA-PPO. Therefore, under the tested 95% RH conditions, where the water content was relatively low, hopping of hydroxide ions from one head group to another likely occurred more easily in the QA-PPO membrane than in the PI-PPO or MO-PPO membranes composed of sterically bulky head groups and apparently helped result in QA-PPO showing the highest conductivity and best cell performance under the actual cell operating conditions (60 °C, 95% RH, H₂/O₂). Overall, the AEM fuel cell performance under in situ cell conditions corresponded well with the conductivity trend measured ex situ under the 95% RH conditions.

4. CONCLUSIONS

The present study constitutes the first systematic investigation of head groups on AEM properties by combining both experimental and simulation approaches. For the first time, varied mechanisms are proposed for different head groups and under different conditions (95% RH and water). PPOs incorporating the four most widely studied head groups, that is, QA, IM, PI, and MO, were prepared with similar IEC values, and the effects of the different types of head groups on the properties of PPO-based AEMs were examined, including conductivity, water content, and physicochemical stability. Unlike other studies, in which conductivity has been mostly investigated only in liquid water, we also measured the conductivities of the PPO-based AEMs under 95% RH. We confirmed the AEM fuel cell performance under in situ cell conditions (95% RH, 60 °C, H₂/O₂) to more closely resemble the conductivity measured ex situ under 95% RH conditions at 60 °C than that in liquid water.

Moreover, molecular simulation results indicated the predominant hydroxide ion conduction mechanism in liquid water to differ from that in operating fuel cell environments, where the ion-conducting polymers become hydrated only as a result of water vapor transported into the cell. In general, the hydroxide ions were expected to dissociate from head groups more easily in liquid water than under the wet tested conditions of 95% RH where the amount of water was limited.

Although it is very difficult to generalize the dominant mechanism for each head group because the ion (especially OH⁻) conduction mechanism is very complex and is heavily dependent on many factors such as types of head groups, humidity, or temperature conditions and hence further studies are necessary for determining the dominant mechanism, it can still be concluded, from our findings, that the mechanism of hydroxide ion conduction can vary not only based on the head groups but also on different environments, that is, in water or under RH condition.

In water, both Grotthuss and vehicular mechanisms are generally dominated for the ammonium- and IM-based head groups (QA-PPO and IM-PPO, respectively). In contrast, the PI head group, having a bulky cyclic structure, causes hydroxide ions to dissociate from the head groups relatively easily especially at high temperatures, suggesting a diffusion-induced vehicular mechanism to be predominant for PI-PPO. In the case of MO as a head group (MO-PPO), the hydrogen bond-induced Grotthuss mechanism is predominant in water because MO can form hydrogen bonds with water molecules and hydroxide ions, especially at low temperatures.

Meanwhile, under the RH 95% or actual cell operating (60 °C, 95% RH, H₂/O₂) conditions, where the water content was relatively low, the QA-PPO yielded the highest conductivity and best cell performance. We attributed these observations to the small size of the QA head group, facilitating the surface diffusion of hydroxide ions by hopping of ions from one head group to another. The IM head group is also thought to be facilitated by surface diffusion, but the lowest conductivity and cell performance were obtained for the IM-PPO under RH conditions, possibly because of its low uptake of water, which in turn is due to the strong π−π interactions between IM head groups. We found that the MO conducted ions more effectively than PI under the RH environments with less water, and similarly, MO-PPO exhibited better cell performance than PI-PPO and attributed these observations to the MO head group forming hydrogen bonds with water and hydroxide ions. These observations again indicated that the hydrogen bond-induced Grotthuss mechanism prevails over surface diffusion for MO under environments with less water. In the case of PI as a head group, hydroxide ion conduction is thought to be still driven by surface diffusion even under RH 95% conditions.

This investigation provides very important insights and directions for the development of AEMs with superior cell performance.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b13016.

Details of additional characterization, membrane properties, and simulation data (PDF)

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Notes
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