An effective strategy to increase hydroxide-ion conductivity through microphase separation induced by hydrophobic-side chains

L. Zeng, T.S. Zhao*

Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong Special Administrative Region

HIGHLIGHTS
• An effective strategy to increase hydroxide-ion conductivity was introduced.
• The microstructure of ionomers was manipulated by grafting hydrophobic side chain.
• Well nano-phase separated domains with connected ionic channels were established.
• An ionic conductivity of 65 mS cm\(^{-1}\) was achieved in the self-aggregated ionomers.

ABSTRACT
A highly conductive and durable anion exchange membrane (AEM) is an essential component for alkaline electrochemical conversion and storage systems. Contrary to the conventional wisdom that the ionic conductivity can be improved by increasing the ion exchange capacity (IEC) through a cross-linking process, in this work, a new approach to improve the ionic conductivity by enhancing the ionic mobility is adopted. The microstructure of quaternary ammonia poly (2, 6-dimethyl-1, 4-phenylene oxide) (QAPPO) is manipulated through grafting with hydrophobic side chains, which will drive the well-established hydrophilic/hydrophobic domains and nano-phase separated, well-connected ionic channels. As a result, the local hydroxide concentration is enhanced by the novel microstructure, thereby improving the ionic conductivity of the as-prepared ionomers. The as-prepared ionomers, denoted as self-aggregated QAPPO-CF, with an intermediate IEC value achieved an ionic conductivity of 65 mS cm\(^{-1}\) at 80 \(^{\circ}\)C, outperforming the QAPPO with an even higher IEC value. This result suggests that the microphase separation is an effective approach to enhance the ionic conductivity.

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1. Introduction
As one of the most promising low-temperature energy-conversion devices, anion exchange membrane fuel cells (AEMFCs) have recently been revitalized by the promising progress in anion exchange membranes (AEMs) in the latest past decades [1–4]. Though attractive, the performance of AEMFCs, currently using non-precious metal (oxide) catalysts or even platinum-based catalysts, is still much lower than that of the acid counterpart, proton exchange membrane fuel cells (PEMFCs). For example, the state-of-the-art performance of AEMFCs (1.0 A cm\(^{-2}\) @ 0.6 V) [5] is much lower than that of PEMFCs (2.3 A cm\(^{-2}\) @ 0.6 V) [6] in the open literature. The practical cell performance of AEMFCs is largely
restricted by the low ionic conductivity of AEMs. To address this issue, intensive researches on AEMs have been performed and some promising results have been achieved.

Borrowed from the theoretical calculation equation \( \sigma_{\text{OH}} = \mu \text{FC}_{\text{OH}} \) in liquid solutions, the ionic conductivity (\( \sigma \)) is determined by the ionic mobility (\( \mu \)) and the local ionic concentration (\( C \)), i.e., ion exchange capacity (IEC) in solid polymer electrolytes (SPEs). Hence, there are two approaches to increase the ionic conductivity. The first approach is to increase the IEC, responding to the number of the conductive groups tethered in the polymer backbones or side chains. While intuitive, this strategy is not as straightforward as it seems. Due to the hydrophilic properties of the functional groups (typically quaternary ammonium groups (QAs)), AEMs with a high IEC will cause a high water uptake, and in turn causes swelling in the AEMs or dissolution into the solvents, especially at elevated temperatures [7]. To address this issue, a cross-linking process is indispensable. The cross-linking process significantly suppresses the water uptake, stabilizing the AEMs with high IEC values even at elevated temperatures. To improve conductivity even further, several approaches have been reported recently such as by (self-)cross-linking the AEMs with high IEC values [7], modifying the functional groups to other cationic groups [11], fabricating two phase morphology. The second approach is to increase the IEC even further, several approaches have been reported recently such as by (self-)cross-linking the AEMs with high IEC values [7], modifying the functional groups to other cationic groups [11], fabricating two phase morphology. The second approach is to increase the IEC even further, several approaches have been reported recently such as by (self-)cross-linking the AEMs with high IEC values [7], modifying the functional groups to other cationic groups [11], fabricating two phase morphology.

The second approach is to manipulate the microstructure of AEMs with a moderate IEC, so that the hydroxide ions are readily conducted with an improved effective mobility. Perfluorosulfonic acid (PSFA, typically Nafion) is known as a highly efficient proton conductor due to the broad and well-connected hydrophobic/hydrophilic phase separation [11]. The hydrophobic phase consisting of PTFE main chains contributes to the mechanical properties of the solid polymer electrolyte while the well-connected hydrophilic phase consisting of sulfonic acid groups contributes to the high proton conduction. However, in the development of AEMs, the wisdom in building nano-phase separated, and well-connected hydrated channels for hydroxide conduction has not been well recognized until recently.

Zhong et al. [7,12] introduced long alkyl side-chains to quaternary ammonium polysulphone (QAPSF) with a moderate IEC. It was demonstrated that the introduction of hydrophobic side chains could drive the aggregation of the hydrophilic domains, thus increasing the local hydroxide concentration and enhancing the hydroxide hopping conduction. This microphase-separation structure in QAPSF promoted the hydroxide ion conduction efficiently. It was demonstrated that the conductivity reached 0.11 S cm\(^{-1} \) at 80 °C, which was even higher than that of Nafion at the same temperature. Watanabe et al. [13] synthesized the quaternized aromatic multiblock copolymers with a well-developed hydrophobic/hydrophilic phase separation and interconnected ion transporting pathway for hydroxide conduction. The as-prepared AEMs exhibited a hydroxide ion conductivity of 0.144 S cm\(^{-1} \) at 80 °C, which represented the highest hydroxide conductivity so far. Li and Hickner [14–16] fabricated a series of quaternary ammonium poly(2, G-dimethyl-1, 4-phenylene oxide) (QAPPO) containing long alkyl side chains pendant to the nitrogen-centered cation. The comb-shaped AEMs showed a well-defined microstructure, which was demonstrated to a dramatic enhancement in hydroxide conductivity and water uptake resistance. The highest ionic conductivity of 0.043 S cm\(^{-1} \) was achieved at 20 °C for these comb-shaped AEMs. Although promising progress has been made, research on this microstructure separation to enhance the ionic conductivity is still in its initial stages, and the nanoscale morphology in the AEMs is difficult to be precisely controlled.

In this work, the QAPPO was selected to tune the microstructure through a self-aggregating design, in which the hydrophobic long alkyl side-chains were selected to be grafted on the bromomethylated PPO (BrPPO) backbone. The two different types of hydrophobic side chains and the amount of hydrophobic side chains were meticulously tuned during the synthesis process. The synthesis route is presented in Scheme 1. The microphase-separated structures were detected by atomic force microscopy (AFM) and small angle X-ray scattering (SAXS). The ionic conductivities of these novel AEMs were determined by the two-probe AC impedance method. The alkaline stability test was performed in an accelerated test protocol. Finally, these AEMs were used to alkaline polymer electrolyte water electrolysis, demonstrating that these QAPPO-based AEMs with a high ionic conductivity and enhanced durability were a promising candidate for alkaline electrochemical conversion and storage systems.

2. Experimental

2.1. Materials

Butylamine (99.5%), 2,2,3,3,4,4,4-heptfluorobutylamine (7FBUA, 96%), N-nitrosourea (NBS), 2,2’-Azobis-isobutyronitrile (AIBN), trimethylamine (TMA) and potassium hydroxide (KOH) were purchased from Sigma–Aldrich. Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with a molecular weight of 350,000 g mol\(^{-1} \) was obtained from SABIC Innovative Plastics (PP06130). AIBN was twice recrystallized from methanol. The PGM-free Acta 3030 OER power catalyst and PGM-free Acta 4030 HER power catalyst were obtained from Acta S.p.A. The anode and cathode gas diffusion layers, nickel foam and carbon paper were purchased from Hohsen and E-TEK, respectively. All other chemical agents were used as-received unless otherwise noted.

2.2. Synthesis of bromomethylated PPO

The preparation process of the bromomethylated PPO (BrPPO) with different degrees of bromomethylation (DOB, \( x \)) was achieved by controlling the ratio between the PPO and NBS, as reported elsewhere [17]. Generally, PPO (40 mmol) was dissolved in 200 mL chlorobenzene at 50 °C to obtain a clear solution. The solution was then added into a three-neck flask equipped with a water-cooling condenser and heated in an oil bath at 145 °C while magnetically stirred. The reaction was held at this temperature for 24 h after a desired mole of NBS and 4 mmol AIBN were successively added. Once the reaction was complete, the mixture was cooled to room temperature. The resulting deep red solution was poured slowly into 1000 mL methanol to precipitate the brown polymer. The polymer was then filtrated, carefully rinsed with methanol several times, and subsequently dissolved in chloroform and re-precipitated in the hot methanol solution. The polymer was then dried overnight in a vacuum oven at 80 °C.

2.3. Synthesis of QAPPO, QAPPO-CH and QAPPO-CF

The dried BrPPO (2.0 g) was dissolved into DMF to form a 5 wt.% solution. Subsequently, butylamine with the desired mole ratio (\( y \)) was added dropwise with stirring at 40 °C for 5 h. After that, TMA with the mole ratio of \( x(100–y) \) was then added. The solution was stirred at 40 °C for an additional 5 h, precipitated in methanol and dried under vacuum at 60 °C to obtain QAPPO-CH. BrPPO was then grafted with 7FBUA and aminated by TMA with the same process to obtain QAPPO-CF. For the purpose of comparison, the ionomer solely aminated by TMA with a mole ratio of \( x \) was also prepared,
denoted by QAPPO.

2.4. Physical characterization

$^1$H NMR spectra were recorded on a high resolution NMR spectrometer (Varian Mercury 300 MHz) at room temperature, using CDCl$_3$ or DMSO-d$_6$ as the solvent. Fourier Transform infrared spectroscopy (FTIR) measurements were recorded using Vertex 70 Hyperion 1000 (Bruker) with the assistance of attenuated total reflectance (ATR) accessories. The absorption spectra were recorded from 4000 cm$^{-1}$ to 400 cm$^{-1}$ with a resolution of 4 cm$^{-1}$.

Small angle X-ray scattering (SAXS) measurements were performed on a multi-purpose XRD (PAN analytical, Empyrean) with the generator voltage and current of 40 kV and 40 mA, respectively. All the data were recorded at room temperature. The thin-film membranes were prepared by the solution cast method. Typical exposure time was in the range from 20 min to 40 min, depending on the thickness of the membrane sample. The accessible range of scattering vectors was calculated by:

$$q = \frac{4 \pi \sin \theta}{\lambda}$$  \hspace{1cm} (1)

where $\lambda$ is the X-ray wavelength (0.154 nm) and 20 is the Bragg scattering angle. The Bragg distance $d$ was obtained by:

$$d = \frac{2 \pi}{q}$$  \hspace{1cm} (2)

To measure the AFM phase images of the ionomers, the as-prepared ionomers (Br$^-$ forms) were diluted with DMF to 1 wt.%. The solutions were sprayed onto a pristine mica substrate (TED Pella Inc.) to form a thin film after the solvent completely evaporated in a vacuum oven at 40 °C. AFM tapping-mode height profiles were performed with a NanoScope-MultiMode/Dimension (Digital Instruments). The instrument was equipped with a NanoWizard scanner. A commercial Si cantilever (TESP tip) of about 320 kHz resonant frequency from JPK was used for tapping-mode AFM. The set-point used for imaging varied between 0.8 V and 1.3 V. All AFM phase images were shown as recorded without any additional image processing.

2.5. Water uptake and swelling degree

Water uptake (WU) and swelling degree (SD) were determined as reported elsewhere [18,19]. The ionomers were cast into a membrane in Br$^-$ form. A determined weight ($m_{dry}$) and volume ($V_{dry}$) of the membrane was immersed into 1.0 M KOH for 48 h. The membrane was washed with DI water several times. The wet weight ($m_{wet}$) and volume ($V_{wet}$) of the membrane were then measured after quickly wiping the excess water from the surface with tissue paper. Accordingly, the WU and SD were calculated by:

$$WU = \frac{m_{wet} - m_{dry}}{m_{dry}} \times 100\%$$  \hspace{1cm} (3)

$$SD = \frac{V_{wet} - V_{dry}}{V_{dry}} \times 100\%$$  \hspace{1cm} (4)

2.6. Ionic exchange capacity and ionic conductivity measurement

The membranes cast from the ionomer solution in Br$^-$ form were immersed into 1.0 M KOH for 48 h for ionic exchange. This process was repeated twice to ensure a complete ion-exchange. The ionic exchange capacity (IEC) of the membrane was determined by the back titration method. Membranes with a predetermined weight were immersed in 20 ml of 0.1 M HCl for 48 h. The solution was titrated with a 0.1 M KOH to pH 7. The membranes were washed and immersed in DI water for 24 h to remove any remaining acid and then dried overnight in a vacuum at 60 °C, and weighed to determine the dry mass. The IEC of the membrane is determined by:

$$IEC (\text{meq g}^{-1}) = \frac{M_1 - M_2}{m_d}$$  \hspace{1cm} (5)

where $M_1$ and $M_2$ are the equivalents of hydrochloric acid before and after membrane neutralization (mmol), respectively. $m_d$ is the mass of the dried membrane in Cl$^-$ form.

The ionic conductivity of the as-prepared membrane was determined with a potentiostat (EG&G Princeton, model M2273) through a two electrode conductivity clamp using an AC impedance method. The membrane samples were sandwiched by a pair of Au-coated stainless steel electrodes. The electrodes were subsequently sandwiched between two PTFE plates and placed in a home-made container filled with N$_2$-saturated DI water to prevent possible interference from CO$_2$. A frequency range from 100 kHz to 1 Hz with a wave amplitude of 10 mV was applied to the conductivity
clamp to obtain the AC impedance spectra. The membrane resistance ($R_0$) was obtained by calculating the intercept of the high frequency region. The ionic conductivity $\sigma$ was determined from:

$$\sigma = \frac{L}{R_0 \times A} \quad (6)$$

where $L$ represents the thickness of the membrane (cm) and $A$ is the surface area of the membrane coated with gold (cm²).

2.7. AEM water electrolysis test

A home-made water electrolysis setup was employed to evaluate the performance of QAPPO-series ionomers. The membrane with a thickness of 60 μm was cast with QAPPO-series ionomer solution (5 wt.%). The catalyst ink was prepared by mixing Acta 3030 OER powder catalyst, QAPPO-series ionomer, ethanol and water. The catalyst ink was ultrasonicated for 30 min at room temperature and manually spread onto the nickel foam. The OER catalyst loading in the as-prepared electrode was 10 mg cat cm⁻². The cathode electrode was fabricated with the same procedure. A catalyst ink consisting of Acta 4030 HER powder catalyst and QAPPO-CF ionomer was manually spread onto the carbon paper. The HER catalyst loading in the as-prepared electrode was 4 mg cat cm⁻². To reduce the contact resistance, the membrane sandwiched by the anode electrode and cathode electrode was hot-pressed at 60 °C at a pressure of 1 MPa for 5 min. The fabricated MEAs were placed in the home-made electrolysis setup, which included two Au-coated titanium end plates, on which a serpentine channel with an area of 5 cm² was machined. The polarization curves of MEAs were pumped into the electrode channels by a peristaltic pump at a flow rate of 2 ml min⁻¹. The cell temperature (60 °C) was maintained by an electric heating rod and measured by a thermocouple placed near the anode and cathode current collectors.

3. Results and discussion

3.1. Synthesis of QAPPO, QAPPO-CH and QAPPO-CF

The QAPPO-based ionomers grafted with different types of hydrophobic side chains were synthesized. The degree of bromomethylation (DOB, x) and the ratio of the hydrophobic side chains (y) were readily controlled to investigate the influence of the self-aggregation process on the hydroxide ionic conductivity. The DOB was controlled by different NBS stoichiometries and measured by aggregation process on the hydroxide ionic conductivity. The DOB were readily controlled to investigate the in situ fluorination (DOB, x). The BrPPO was then respectively grafted with BuA and 7FBuA and aminated with TMA. To confirm the grafting reaction, FTIR was performed and the resulting spectra for QAPPO-series ionomers with DOBs equaling 50 and y equaling 40 are shown in Fig. 2. As exhibited in Fig. 2a, the spectrum of BrPPO shows a broad band ranging from 3600 cm⁻¹ to 3200 cm⁻¹, which is ascribed to the stretching vibration of C–H, and maybe a certain degree of water absorption. The characteristic absorption bands of BrPPO located at ~1710 cm⁻¹, ~1649 cm⁻¹ are assigned to the stretching vibration of the aromatic rings and the bending vibration of methylene, respectively. The bands located at ~1066 cm⁻¹, ~736 cm⁻¹ are ascribed to the bending vibration of CH₂–Br and the stretching vibration of CH–Br, respectively. After the amination process, the peak at ~2963 cm⁻¹, ~1605 cm⁻¹ and a sharp peak at ~1461 cm⁻¹ emerge in the FTIR spectra of QAPPO-series ionomers, indicating that QA groups were successfully grafted on the BrPPO backbones due to these characteristic peaks being attributed to the stretching vibration of QA groups [20]. Comparing the spectrum of QAPPO-CH with QAPPO, some new characteristic peaks at ~2936 cm⁻¹, ~2876 cm⁻¹, ~736 cm⁻¹ and ~667 cm⁻¹ are observed, which are attributed to the stretching vibration and bending vibration of methylene groups (~CH₂~), demonstrating that the hydrophobic side chains were grafted on the BrPPO backbones. Meanwhile, the characteristic peaks at ~1221 cm⁻¹, ~1118 cm⁻¹, and 787 cm⁻¹ emerge in the QAPPO-CF spectrum, which belong to the stretching vibration of C–F.

X-ray photoelectron spectroscopy (XPS) was also performed to ascertain the chemical structure of QAPPO-series ionomers. The XPS survey spectra of QAPPO-series ionomers with x equaling 50 and y equaling 40 are presented in Fig. 3. As revealed in Fig. 3a, the wide scan spectrum of QAPPO-CF is similar to that of QAPPO and QAPPO-CH, while new peaks located at 688.2 eV and 834.2 eV emerge, which are assigned to the F 1s core level spectrum and F Auger spectrum, respectively. The presence of fluorine in the QAPPO-CF sample was also confirmed by the high resolution F 1s spectra (Fig. 3b), unambiguously testifying that the hydrophobic side chains were grafted on the BrPPO backbones. The high resolution N 1s spectra are illustrated in Fig. 3c for distinguishing the chemical state of nitrogen in the QAPPO-series ionomers. A sole peak located at 402.6 eV emerges in the QAPPO ionomer, while in
QAPPO-CH and QAPPO-CF ionomers, there are two peaks located at 399.4 eV and 402.6 eV, corresponding to the secondary amines in the side chains and the quaternary ammonium groups at the PPO backbones, respectively [7,12]. It can be understood that the binding energy of quaternary ammonium groups is higher than that of secondary amines due to their electron-withdrawing property [7]. Meanwhile, the binding energy of N 1s belonging to secondary amines was slightly shifted to a lower energy (0.18 eV), as a result of the electron-donor effect from the \( \text{CF}_2 \) segment. Therefore, these analyses demonstrate that the PPO backbones were grafted by bromomethyl groups, which were partly grafted with the hydrophobic side chains through the secondary amine and partly converted to the quaternary ammonium groups during the course of amination.

### Table 1

<table>
<thead>
<tr>
<th>Samples</th>
<th>Theoretical x (%)</th>
<th>Mole NBS/mole PPO</th>
<th>Experimental x (%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BrPPO-1</td>
<td>30</td>
<td>1.15</td>
<td>40</td>
<td>85</td>
</tr>
<tr>
<td>BrPPO-2</td>
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<td>50</td>
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<td>BrPPO-3</td>
<td>60</td>
<td>1.95</td>
<td>66</td>
<td>83</td>
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<tr>
<td>BrPPO-4</td>
<td>80</td>
<td>2.33</td>
<td>80</td>
<td>79</td>
</tr>
</tbody>
</table>

AFM technology has been widely utilized to analyze the phase separation in homogenous membranes [14,21–23]. Here, the phase images of the QAPPO-series ionomers using tapping mode AFM under ambient atmosphere (room temperature, relative humidity: 60%) are illustrated in Fig. 4. The dark regions correspond to the hydrophilic ionic clusters and the bright domains correspond to the hydrophobic aromatic polymer backbones in AFM tapping phase images [22]. In the AFM image of the QAPPO sample (Fig. 4a), there is no obvious microphase separation pattern, indicating that the hydrophilic domains, that is, the functional groups, are randomly distributed. While, in the QAPPO-CH and QAPPO-CF samples, these grafted hydrophobic groups effectively drive the microscopic phase separation of hydrophilic/hydrophobic domains and create the nano-phase separated, well-connected ionic channels, as presented in Fig. 4b–c and illustrated in Fig. 5. The sizes of small hydrophilic ionic domains range from 5 nm to 10 nm, which are similar to the results reported in the literature [12,14]. It should be noted that there is no significant difference in AFM phase images between QAPPO-CH and QAPPO-CF when the same amount (20 mol%) of hydrophobic side chains were grafted on the BrPPO backbones. However, when the number of hydrophobic side chains is further...
increased to 30 mol% (Fig. 4d), the hydrophilic domains are separated by over-aggregating hydrophobic domains, particularly in the QAPPO-CF sample. These separated hydrophilic domains adversely affected the ionic conductivity. Hence, the hydrophobic content...
was fixed at 20 mol.% in this work.

The microphase separation structure in QAPPO-CH, QAPPO-CF was also quantitatively confirmed by SAXS (Fig. 6). There is no pattern in the SAXS signal of dry QAPPO; while for QAPPO-CH and QAPPO-CF, a SAXS peak emerges at 1.64 nm\(^{-1}\). This result is indicative of a microphase separation established between the hydrophilic functional groups and the hydrophobic aliphatic side chains. The Bragg spacing is determined to be about 3.8 nm for QAPPO-CH and QAPPO-CF. The calculated hydrophilic domain size is smaller than AFM observation, likely resulting from the dry state of samples during the course of SAXS measurement. It should be noted that the SAXS pattern of QAPPO-CF is similar to that of QAPPO-CH, indicating that there is no significant difference in microstructure between QAPPO-CH and QAPPO-CF, as shown by AFM phase images.

### 3.3. IEC, ionic conductivity analyses

As previously mentioned, the BrPPO with DOBs equaling 0.4, 0.5, 0.66 and 0.8 was synthesized. However, the QAPPO with a high DOB (0.8) was dissolved into the hot water at elevated temperatures. Hence, the BrPPO with DOBs equaling 0.4, 0.5 and 0.66 was applied to prepare QAPPO-series ionomers. IEC values calculated from the DOB, \(^1\)H NMR and titration method are listed in Table 2. It can be seen that the IEC values calculated from the NMR and titration method range from 1.31 to 2.40 mmol g\(^{-1}\), which are consistent with the calculated values from the DOB. Due to the grafted hydrophobic side chains, the IEC values of the QAPPO-CH series and QAPPO-CF series are lower than those of QAPPO series with the same DOB.

The water uptakes and swelling ratios of these ionomers measured at room temperature are also listed in Table 2. The swelling ratios exhibit the same trend with the water uptake, i.e., high swelling degree accompanying high water uptake. As expected, ionomers with higher IEC values absorb more water due to the increased hydrophilic content. However, the water uptake of the QAPPO-CH series and QAPPO-CF series are much lower than that of the QAPPO series under the same level of DOB. For instance, with the same DOB of 50%, the QAPPO, QAPPO-CH and QAPPO-CF exhibit a water uptake of 187 wt.%, 34 wt.% and 25 wt.%, respectively. Meanwhile, the swelling ratio for QAPPO-CH (28%) and QAPPO-CF (21%) are also much lower than that of QAPPO (165%).

These results demonstrate that the water uptake and swelling ratio in the QAPPO-CH series and QAPPO-CF series are restricted, resulting from the self-aggregating structure [12].

The hydroxide conductivities of these ionomers were then measured and presented in Fig. 7. The conductivity retention was calculated to assess the durability of these ionomers. The inset shows the weight loss percentage of different ionomers after the durability test.
measured in N₂-saturated DI water by varying the temperatures; the results are presented in Fig. 7a. Theoretically, with the same DOB, the QAPPO has a higher IEC value than QAPPO-CH and QAPPO-CF, therefore the conductivity of the QAPPO series should be higher than that of the QAPPO-CH series and QAPPO-CF series. However, it is demonstrated that the QAPPO-CH series and QAPPO-CF series outperform the QAPPO series in terms of the ionic conductivity. For instance, with the same DOB (50 mol.%), the ionic conductivity of QAPPO-CH is 43.5 mS cm⁻¹ at 80 °C, in comparison to 28.9 mS cm⁻¹ for QAPPO. The increased ionic conductivity is ascribed to the aggregation of the microphase-separated structures, which affects the ionic conductivity in the two following aspects. First, the local hydroxide ion concentration could be improved due to the establishment of the hydrophilic and hydrophobic microphase separation, which has been proven by AFM phase images and SAXS analysis. On the other hand, the microphase separation will effectively drive the hydroxide ion transfer in the established hydrophilic channels. More interestingly, the ionic conductivity of QAPPO-CF is superior to that of QAPPO-CH with the same hydrophobic content, particularly at elevated temperatures. For example, the QAPPO-CF has a hydroxide conductivity of 50.8 mS cm⁻¹, which is higher than that of QAPPO-CH (43.5 mS cm⁻¹). Due to the QAPPO-CH and QAPPO-CF having the similar microphase structures, the enhanced ionic conductivity is attributed to an enhancement of hydrophobic property of 7FBuA when compared with BuA. Among all the QAPPO-series ionomers, the QAPPO-CF with an intermediate IEC value exhibits the highest ionic conductivity of 65 mS cm⁻¹ at 80 °C, which is comparable to or better than that of ionic conductivities reported in the literature (Table 3). This comparison demonstrates that the microphase separation is an effective approach to improve the ionic conductivity. The enhancement in ionic conductivity can be further proven by the reduction of the activation energy. Based on the Arrhenius equation, the activation energies for QAPPO, QAPPO-CH and QAPPO-CF are 13.93 kJ mol⁻¹, 12.22 kJ mol⁻¹ and 11.65 kJ mol⁻¹, respectively. The reduced activation energies in QAPP-CH and QAPPO-CF suggest that the conduction of hydroxide ions is less dependent on temperature, proving that the QAPPO-CH and QAPPO-CF are able to effectively conduct the hydroxide ions.

3.4. Chemical stability test

The conductivity stability of these ionomers was continuously monitored in N₂-saturated DI water at 80 °C for 500 h. As demonstrated in Fig. 7b, the ionic conductivity of QAPPO is reduced from the initial 28.5 mS cm⁻¹ to 23.5 mS cm⁻¹, with a degradation rate of 17.7%. This severe conductivity degradation should be caused by the degradation pathways for tetraalkylammonium ions, including β-H Hofman elimination, direct nucleophilic substitution at α-C, and/or nitrogen-containing ylide formation [15]. However, QAPPO-CH and QAPPO-CF with the same DOB exhibit a superior chemical stability. The ionic conductivities of QAPPO-CH and QAPPO-CF exhibit a slight decrease after a small initial conductivity drop (from 43.2 mS cm⁻¹ to 40.8 mS cm⁻¹ for QAPPO-CH, from 50.7 mS cm⁻¹ to 47.5 mS cm⁻¹ for QAPPO-CF). This behavior was also observed reports elsewhere [12], in which the initial conductivity loss was ascribed to a leaching of low-molecular-weight components. The weight loss of the ionomers before and after the chemical stability test was also measured. As shown in inset of Fig. 7b, the weight losses of QAPPO-CH and QAPPO-CF are much lower than that of QAPPO after the durability test. The enhanced chemical stability for QAPPO-CH and QAPPO-CF may derive from the microphase separation structure, which confines the hydroxide ions. Hence the polymer backbones are well-protected as a result of the reduced attack by the hydroxide ions which were demonstrated as strong nucleophilic reagents.

3.5. AEM water electrolysis

Finally, we fabricated MEAs with a commercial platinum group metal (PGM)-free catalyst and the QAPPO-based AEMs for AEM water electrolysis. The QAPPO-series suspension (5 wt.% in DMF) was also applied as the ionomer in the catalyst layer with a mass loading of 25 wt.%. Fig. 8 shows the polarization curves of MEAs employing QAPPO and QAPPO-CF as AEMs, respectively. For the MEA with QAPPO as the AEM, a current density of 575 mA cm⁻² at 2.10 V was achieved. While the current density was boosted to 925 mA cm⁻² at 2.10 V when the MEA was used with QAPPO-CF as the AEM. Due to the performance of water electrolysis being performed with different AEMs under other identical MEA fabrication and test conditions, the performance improvement is clearly

### Table 3

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Ionic conductivity (mS cm⁻¹)</th>
<th>IEC (mmol g⁻¹)</th>
<th>Temperature (°C)</th>
<th>Ref.</th>
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<td>QAPPO-CF</td>
<td>65</td>
<td>1.80</td>
<td>80</td>
<td>This work</td>
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</table>
ascribed to the enhanced ionic conductivity of QAPPO-CF, which largely reduces the ohm resistance. To obtain a better analysis of the influence of membrane resistance on the electrolysis performance, polarization curves with current densities ranging from 200 mA cm\(^{-2}\) to 800 mA cm\(^{-2}\) were linearly fitted and the ohm resistance was obtained from the fitted slope. The ohm resistance for the MEA with QAPPO-CF as the AEM is 0.60 Ω cm\(^2\), which is significantly lower than that of the MEA with QAPPO as the AEM (0.81 Ω cm\(^2\)). This analysis further demonstrates that QAPPO-CF AEMs outperform QAPPO AEMs. However, the performance of the AEM water electrolysis reported here was lower than that of the performance reported in the literature [24] since the platinum-group catalysts (IrO\(_2\) as the anode and Pt black as the cathode) were adopted. The performance of the AEM water electrolysis reported here was also lower than that of the performance reported in the literature [25] due to the weak alkaline solutions (pH = 10–14) were adopted. Our electrolysis performance is comparable with the performance reported in the ref. [26], in which the non-PGM catalysts were employed as the OER and HER catalyst while pure water was supplied as the electrolyte. It should be noted that the ohm resistances derived from the AEMs were relatively low (0.26 Ω cm\(^2\) for QAPPO vs. 0.15 Ω cm\(^2\) for QAPPO-CF). Apparently, the contact resistance between the electrode and membrane, and the thick electrode contributed to a high ohm resistance; improvement can be expected when the MEA structure is further optimized.

4. Conclusions

In summary, hydrophobic side chains were grafted on the BrPPO backbone to increase the ionic conductivity of QAPPO ionomers due to the microphase separation. The well-established hydrophilic/hydrophobic domains and the nano-phase separated, well-connected ionic channels were formed and proved by AFM and SAXS measurements. As a result, the local hydroxide concentration connected ionic channels were formed and proved by AFM and hydrophobic domains and the nano-phase separated, well-to the microphase separation. The well-established hydrophilic/hydrophobic backbone to increase the ionic conductivity of QAPPO ionomers due to the microphase separation. The chemical stabilities for the self-aggregated ionomers were also improved since the polymer backbones (hydrophilic domains) were well-protected from the attack of hydroxide ions, which were considered to be confined in the hydrophilic domains. The superior performance of self-aggregated ionomers was verified in the AEM water electrolysis system, in which the QAPPO-CF AEMs outperformed the QAPPO AEMs. Hence, the microphase separation approach is demonstrated as an effective way to increase the ionic conductivity.

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References