ABSTRACT: Novel anion-conductive polymers containing perfluoroalkyl and ammonium-functionalized fluorene groups were synthesized and characterized. The quaternized polymers synthesized using a dimethylaminated fluorene monomer had a well-defined chemical structure in which each fluorenyl group was substituted with two ammonium groups at specific positions. The resulting polymers had a high molecular weight ($M_n = 8.9 - 13.8$ kDa, $M_w = 13.7 - 24.5$ kDa) to provide bendable thin membranes with the ion-exchange capacity (IEC) ranging from 0.7 to 1.9 mequiv g$^{-1}$ by solution casting. Both transmission electron microscopy images and small-angle X-ray scattering patterns suggested that the polymer membranes possessed a nanoscale phase-separated morphology based on the hydrophilic/hydrophobic differences in the polymer components. Unlike typical anion-exchange membranes found in the literature, hydroxide ion conductivity of the membranes did not increase with increasing IEC because of their high swelling capability in water. The membrane with IEC = 1.2 mequiv g$^{-1}$ showed balanced properties of high hydroxide ion conductivity (81 mS cm$^{-1}$ at 80 °C in water) and mechanical strength ($>100\%$ elongation and 14 M Pa maximum stress at 80 °C, 60\% relative humidity). The polymer main chains were stable in 4 M KOH for 1000 h, whereas the trimethylbenzyl-type ammonium groups degraded under the conditions to cause loss in the hydroxide ion conductivity. An H$_2$/O$_2$ fuel cell with the membrane with IEC = 1.2 mequiv g$^{-1}$ exhibited a maximum power density of 242 mW cm$^{-2}$ at 580 mA cm$^{-2}$ current density.

INTRODUCTION

Polymer electrolyte fuel cell is one of the most attractive electrochemical systems for energy conversion. In particular, proton-exchange membrane fuel cells (PEMFCs) have been commercialized for applications in stationary cogeneration systems and electric vehicles. However, the highly acidic PEMCs require the use of precious metals such as Pt as electrocatalysts, which makes the PEMFCs less cost-effective. In contrast, anion-exchange membrane fuel cells (AEMFCs) have gained growing attention because of their possible use of abundant non-platinum group metals as electrocatalysts. However, the chemical instability and low anion conductivity of the existing AEMs have been major concerns for practical use. Addressing these issues, a wide variety of aromatic polymers such as poly(arylene ether),$^9,10$ polystyrenes,$^{11,12}$ and poly(phenylene oxide)$^{13,14}$ functionalized with quaternary ammonium groups have been studied. Among them, cardo structures such as fluorene and phenolphthalein derivatives seem attractive as the scaffold for the ammonium groups because multiple functionalization with ammonium groups is easily achievable. Furthermore, the bulky structures enable the formation of a large free volume in the membrane, which could serve as an ion-conducting pathway.

Previously, we have synthesized anion-conductive polymers containing ammonium-functionalized fluorenyl groups via a chloromethylation reaction.$^{15-17}$ The effect of the substitution number and position of ammonium groups on membrane properties was investigated in detail, which showed that a membrane having approximately two ammonium groups per fluorenyl group exhibited optimum membrane properties such as a well-developed phase-separated morphology, high hydroxide ion conductivity, and chemical stability. However, since the harmful chloromethylation reaction often accompanies unfavorable side reactions including the cross-linking reaction, the detailed molecular structure for the optimum membrane properties remain unclear. The objective of the present study was to synthesize a series of partially fluorinated polymers containing ammonium-functionalized fluorenyl groups with a well-defined structure. A preaminated monomer was designed such that each fluorenyl group was substituted with two ammonium groups at specific positions. The effect of the copolymer composition or ion-exchange capacity (IEC) on...
the membrane properties such as morphology, anion conductivity, mechanical strength, alkaline stability, and fuel cell performance was investigated. The properties were compared with those of our previously reported membranes prepared via the chloromethylation method.

**RESULTS AND DISCUSSION**

**Synthesis of Monomer 1 and Polymers 2 and 3.** Bis(dimethylaminomethyl)fluorenyl monomer 1 was synthesized according to Scheme 1. First, p-BCF was chloromethylated with chloromethyl methyl ether (CMME) via Friedel–Crafts reaction using TiCl₄ as the Lewis acid catalyst. Under optimized conditions, the reaction proceeded quantitatively and regioselectively at the 2 and 7 positions (or 4 in p-BCF in Scheme 1) of fluorene groups as suggested by the ¹H NMR spectrum (Figure 1). The chloromethylated compound (p-

![Scheme 1. Synthesis of Hydrophilic Monomer (1)](image)

BCF-cm) was aminated with dimethylamine in tetrahydrofuran (THF) solution. Complete amination reaction was confirmed by the ¹H NMR spectrum, where the methylene proton (6) appeared at a higher magnetic field (3.4 ppm) compared with that of p-BCF-cm (4.6 ppm). Methyl protons (7) appeared at 2.2 ppm.

**Synthesis of Quaternized Polymer 4.** The synthetic procedure for the title quaternized polymer 4 is shown in Scheme 2. The precursor copolymer (3) was synthesized by Ni-promoted polycondensation reaction of the monomers 1 and 2. The reaction proceeded successfully as confirmed by ¹H and ¹⁹F NMR spectra. In the ¹H NMR spectrum (Figure 2a), all peaks were well-assigned to the supposed chemical structure. The copolymer composition estimated from the integral peak ratios were in good accordance with those of the feed comonomer ratios (Table 1). In the ¹⁹F NMR spectrum (Figure S1a), three fluorine peaks were observed to confirm no side reactions in the hydrophobic component. A series of copolymers (3) with different compositions (m:n) were obtained with high molecular weight ($M_n = 8.9$–$13.8$ kDa, $M_w = 13.7$–$24.5$ kDa) and reasonable polydispersity (1.5–2.1). The quaternization reaction of 3 was carried out using dimethyl sulfate in N,N-dimethylacetamide (DMAc) solution. The progress of the reaction was confirmed by the shift of the methylene and methyl protons to the lower magnetic field in the ¹H NMR spectra (Figure 2b). The ¹⁹F NMR spectrum (Figure S1b) did not show evidences of any side reactions. The resulting quaternized copolymer 4 was soluble in polar organic solvents such as dimethyl sulfoxide (DMSO) and DMAc, and provided brown and transparent membranes by casting from DMAc solution (thickness: 40–45 μm for 4-1, 50–70 μm for 4-2, 30–40 μm for 4-3, 30–40 μm for 4-4). The solvent solubility and membrane-forming capability of the copolymers were better than those of our previous copolymer membranes with a similar chemical structure prepared via the chlor-
omethylation method. Molecular weight measurements of 4 were unavailable because of the strong interaction with our gel permeation chromatography (GPC) columns. The IEC values of 4 membranes determined by titration ranged from 0.7 to 1.9 mequiv g\(^{-1}\), which were in fair agreement with those (0.7–1.7 mequiv g\(^{-1}\)) calculated from the copolymer compositions obtained from the \(^1\)H NMR spectra of 3.

**Water Uptake and Hydroxide Ion Conductivity.** Water uptake and hydroxide ion conductivity of 4 membranes are shown in Figure 3. The water uptake increased nearly proportional to IEC. The highest IEC membrane (4-4) exhibited 152 wt % water uptake. The dimensional changes of the 4-3 membrane were 24% (through-plane) and negligibly small (in-plane), respectively. The conductivity also increased with IEC up to IEC = 1.2 mequiv g\(^{-1}\) (47 mS cm\(^{-1}\)), and then decreased to 41 mS cm\(^{-1}\) with further increase in IEC. Taking the absorbed water into account, practical IEC values in water were 0.57 mequiv g\(^{-1}\) for 4-1, 0.79 mequiv g\(^{-1}\) for 4-2, 0.87 mequiv g\(^{-1}\) for 4-3, and 0.65 mequiv g\(^{-1}\) for 4-4 membranes, respectively, which explains the dependence of the conductivity on IEC. The 4-3 membrane with IEC = 1.2 mequiv g\(^{-1}\) showed the best balanced properties with the highest conductivity (47 mS cm\(^{-1}\)) and a reasonably low water uptake (59%).

Temperature dependence of the OH\(^-\) conductivity in water is shown in Figure 4. All samples showed an approximate Arrhenius-type temperature dependence of the conductivity up to 80 °C. The apparent activation energies for the ion conduction calculated from the slopes were 7.1 kJ mol\(^{-1}\) for 4-1, 9.9 kJ mol\(^{-1}\) for 4-2, 10 kJ mol\(^{-1}\) for 4-3, and 8.2 kJ mol\(^{-1}\) for 4-4. These values were similar and comparable to those of our previous anion-conductive membranes and typical for the conduction of hydrated hydroxide ions.

**Morphology.** The morphology of 4 membranes was analyzed by transmission electron microscopy (TEM) images (Figure 5). The membranes showed a phase-separated morphology with small hydrophobic (bright areas) and hydrophilic (dark areas) domains. The domain sizes were both ca. 4–5 nm in all membranes. Compared with our previous membrane (5–8 nm) prepared via the chloromethylation method followed by quaternization, the domain sizes and their distribution were slightly smaller. The results suggest that casting from quaternized polymers could provide membranes with more homogeneous morphologies than those of the membranes that were quaternized afterward.

Then, effect of the humidity on the morphology of 4 membranes was investigated by small-angle X-ray scattering (SAXS) analyses (Figure 6). At 30% relative humidity (RH), the membranes showed a clear scattering peak at q = 0.54

| Table 1. Composition and Molecular Weight of 3 and Ion-Exchange Capacity (IEC) and Water Uptake of 4 |
| --- |
| **Composition (m:n)** | Molecular weight\(^a\) (kDa) | IEC (mequiv g\(^{-1}\)) | NMR\(^b\) titration water uptake\(^c\) (%) |
| 3-1 | 1.00:0.20 | 1.00:0.19 | 8.9 | 13.7 | 1.5 | 0.7 | 0.7 | 22 |
| 3-2 | 1.00:0.35 | 1.00:0.35 | 13.0 | 20.1 | 1.6 | 1.0 | 1.0 | 42 |
| 3-3 | 1.00:0.45 | 1.00:0.47 | 13.8 | 23.8 | 1.7 | 1.4 | 1.2 | 59 |
| 3-4 | 1.00:0.65 | 1.00:0.62 | 11.6 | 24.5 | 2.1 | 1.7 | 1.9 | 152 |

\(^a\) Measured for 3. \(^b\) Calculated from the \(^1\)H NMR spectra of 3. \(^c\) Measured at room temperature (soaked in water for 24 h).
nm$^{-1}$ or $d = 11.6$ nm for 4-1, $q = 0.66$ nm$^{-1}$ or $d = 9.5$ nm for 4-2, $q = 0.69$ nm$^{-1}$ or $d = 9.1$ nm for 4-3, and $q = 0.75$ nm$^{-1}$ or $d = 8.4$ nm for 4-4. The peak became larger in intensity and the $d$ spacing also became larger with increasing humidity; $q = 0.53$ nm$^{-1}$ or $d = 11.9$ nm for 4-1, $q = 0.64$ nm$^{-1}$ or $d = 9.8$ nm for 4-2, $q = 0.63$ nm$^{-1}$ or $d = 10.0$ nm for 4-3, and $q = 0.72$ nm$^{-1}$ or $d = 8.7$ nm for 4-4 at 90% RH, respectively. Development of the peak on increasing the water uptake suggests that it is associated with periodic hydrophilic domains. The $d$-spacings observed in SAXS curves were larger than the cluster sizes in the TEM images because of the swelling with the absorbed water. The well-ordered periodic structure of the hydrophilic domains could be responsible for the high hydroxide ion conductivity of the membranes in water. The $d$-spacing decreased (Figure S2) and the peak became prominent with increasing IEC at both humidities. In the higher IEC membranes, smaller hydrophilic domains with homogeneous size were more likely to form.

**Mechanical Properties.** Mechanical properties of the membranes were evaluated by tensile strength (Figure 7) and dynamic mechanical analyses (Figure 8). The 4-1 membrane with a lower molecular weight was not available because of the insufficient strength for the analyses. Other membranes (4-2, 4-3, and 4-4) showed high elongation ($>100\%$) at 80 °C and 60% RH. The 4-2 and 4-3 membranes showed reasonably high maximum stress (15 and 14 MPa, respectively); however, the 4-4 membrane with the highest IEC showed the lowest maximum stress (8 MPa) because of its highest water absorbability. In DMA analyses, three 4 membranes showed similar curves. The storage modulus $E'$ decreased with increasing temperature, and a broad peak was observed in the loss modulus $E''$ at ca. 70 °C. The peak would be associated with the glass transition of the polymers. Since the transition temperature was similar among the membranes with different IEC values (and thus, different water contents), it is presumably related to the hydrophobic components. The DMA properties of 4 membranes were similar to those of our previously reported membranes prepared via the chloromethylation method.\textsuperscript{18}

**Thermal and Alkaline Stability.** The thermal stability of the 4-3 membrane (in Cl$^-$ form) was measured by thermogravimetric analysis (Figure S3). Two-step weight loss was observed. The initial weight loss from 150 °C was ca. 10% corresponding to the amount of NMe$_2$Cl groups (decomposition of the ammonium groups), whereas the second weight loss above ca. 400 °C would be due to the main chain degradation. The alkaline stability of the 4-3 membrane (in OH$^-$ form) was evaluated in 1 and 4 M KOH at 80 °C (Figure 9). The hydroxide ion conductivity of the membrane decreased with testing time and the decrease was faster in 4 M KOH than in 1 M KOH. After 1000 h, the conductivity was 15 mS cm$^{-1}$.

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**Figure 6.** SAXS profiles of (a) 4-1 (b) 4-2 (c) 4-3 (d) 4-4 membranes in Cl$^-$ forms at 40 °C, 30–90% RH.

**Figure 7.** Stress–strain curves of 4 membranes at 80 °C and 60% RH.

**Figure 8.** Temperature dependence of the dynamic mechanical properties of 4 membranes at 60% RH.
(1 M KOH) and 13 mS cm\(^{-1}\) (4 M KOH) (the remaining percentage was 28 and 25%), respectively. The IEC of the postmortem membrane determined by titration also decreased to 0.7 mequiv g\(^{-1}\) under both conditions. Although the postmortem membrane retained bendability, it was insoluble in organic solvents. In the IR spectrum of the postmortem membrane (Figure 10), the peak around 1600 cm\(^{-1}\) assigned to the C–H stretching vibration of methyl groups and the peak around 900 cm\(^{-1}\) assigned to the C–N\(^+\) stretching vibration were smaller. The changes suggest the chemical degradation of the ammonium groups and are not contradictory to the losses in hydroxide ion conductivity and IEC. Since the large peaks at 1100–1200 cm\(^{-1}\) assignable to C–F symmetric and asymmetric stretching vibration did not change, the polymer main chain seemed intact. The postmortem membrane was subjected to morphological analyses via SAXS (Figure 11), in which humidity dependence of the scattering peaks was not observed. The results suggest that the decomposition of the ammonium groups (loss of IEC) eventually hampered morphological development in the quaternized membranes, and both of these caused decreased hydroxide ion conductivity.

**Fuel Cell Performance.** A catalyst-coated membrane was prepared with the 4-3 membrane (37 \(\mu\)m thick), our homemade QPAF-4 ionomer,\(^{20}\) and the Pt/CB catalyst for the anode and cathode. The fuel cell was operated at 60 °C by supplying fully humidified pure H\(_2\) and O\(_2\) gases at a flow rate of 100 mL min\(^{-1}\) to the anode and the cathode, respectively. The current density/voltage (\(I/V\)) and current density/power density (\(I/W\)) curves, and ohmic resistance of the fuel cell are shown in Figure 12. The fuel cell showed a relatively high open circuit voltage (OCV, 0.96 V) typical for an H\(_2\)/O\(_2\) alkaline fuel cell. The ohmic resistance was ca. 0.15 \(\Omega\) cm\(^2\), which was approximately three times higher than the area-specific resistance of the membrane (0.05 \(\Omega\) cm\(^2\)) calculated from the hydroxide ion conductivity (67 mS cm\(^{-1}\) in water at 60 °C, Figure 4) and the thickness. The difference in the resistance could be due to the lower hydroxide ion conductivity of the membrane under humidified conditions than in water. The contact resistance between the membrane and the catalyst layers could also be responsible to some extent. The fuel cell achieved high maximum power densities of 242 mW cm\(^{-2}\) at a current density of 580 mA cm\(^{-2}\).

**Conclusions**

A series of copolymers containing perfluoroalkyl and ammonium-functionalized fluorenyl groups were synthesized and characterized. Compared with our recent anion-exchange membranes with a similar chemical structure prepared via chloromethylation (which often accompanied unfavorable side reactions), the present copolymer membranes had better solubility in organic solvents and membrane-forming capability. Because of the well-defined hydrophilic structure where each fluorenyl group was substituted with two ammonium groups, the resulting polymer membranes exhibited a well-ordered phase-separated morphology as suggested by TEM images and SAXS analyses. The copolymer membranes exhibited a hydroxide ion conductivity that was less dependent on the gravimetric ion-exchange capacity (IEC) of the dry membranes, which was well-understood taking absorbed water into account. The optimum IEC value of the copolymer membranes was found to be 1.2 mequiv g\(^{-1}\) considering water uptake, hydroxide ion conductivity, and mechanical properties. In the accelerated alkaline stability test, the polymer main...
chain with no heteroatom linkages was stable; however, the trimethyl benzylammonium groups degraded to cause some losses in the ion conductivity. The hydrogen/oxygen fuel cell was operable under fully humidified conditions to obtain a high OCV and low ohmic resistance, as expected from the membrane properties. Using better-performing catalysts in alkaline media would further enhance the fuel cell’s performance.

### EXPERIMENTAL SECTION

**Materials.** Titanium(IV) chloride (16–17% as Ti in dil. hydrochloric acid, Wako Chemical), chloromethyl methyl ether (CMME) (>95%, TCI), 40 wt % dimethylyamine aqueous solution (Kanto Chemical), tetrahydrofuran (>99.5% Kanto Chemical), hydrochloric acid (35–37%, Kanto Chemical), 2,2′-bipyridine (>99%, TCI), bis(1,5-cyclooctadiene)nickel(0) (Ni(cod)₂) (>95%, Kanto Chemical), and dimethyl sulfate (>99%, Kanto Chemical) were used as received. 

N,N-dimethylacetamide (DMAc) (>99%, Kanto Chemical) was dehydrated over molecular sieve 4A prior to use.

18 1,6-Diiodoperfluorohexane (2) were synthesized according to the literature.

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was partly supported by CREST (JPMJCR12C3), Japan Science and Technology Agency (JST), and the Ministry of Education, Culture, Sports, Science and Technology (MEXT) Japan through a Grant-in-Aid for Scientific Research (18H02030, 18K19111). K.M. acknowledges the Ogasawara Research Foundation for the Promotion of Science and Engineering for financial support.

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02742.

**Notes**

The authors declare no competing financial interest.
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