Low-cost anion exchange membrane fuel cells have been investigated as a promising alternative to proton exchange membrane fuel cells for the last decade. The major barriers to the viability of anion exchange membrane fuel cells are their unsatisfactory key components—anion exchange ionomers and membranes. Here, we present a series of durable poly(fluorenyl aryl piperidinium) ionomers and membranes where the membranes possess high OH− conductivity of 208 mS cm−1 at 80 °C, low H2 permeability, excellent mechanical properties (84.5 MPa TS), and 2000 h ex-situ durability in 1 M NaOH at 80 °C, while the ionomers have high water vapor permeability and low phenyl adsorption. Based on our rational design of poly (fluorenyl aryl piperidinium) membranes and ionomers, we demonstrate alkaline fuel cell performances of 2.34 W cm−2 in H2-O2 and 1.25 W cm−2 in H2-air (CO2-free) at 80 °C. The present cells can be operated stably under a 0.2 A cm−2 current density for ~200 h.
A

nion exchange membrane fuel cells (AEMFCs) have made significant advances, especially in power density, that represents a parallel track to proton exchange membrane fuel cells (PEMFCs)13. Operating in alkaline environments, AEMFCs possess evident cost advantages due to the possibility of using non-platinum group metal (non-PGM) catalysts. AEMFCs intend to address high-cost issues associated with PEMFCs and to raise the economic competitiveness of low-temperature fuel cells with other power generation technologies in many burgeoning areas, particularly in light-duty transportation4. However, the major barriers to the viability of AEMFCs are their key but unsatisfactory materials including anion exchange polyelectrolytes (AEPs), which can be used both as anion exchange ionomers (AEIs) and membranes (AEMs)9–12. AEPs consist of polymer backbones and the pendant cationic groups that act as ion transporting species to conduct OH− and to transport water molecules13–16. Although numerous cationic groups (ammonium17, imidazolium15,16, phosphonium18, sulfonium19, and organometallic cation20,21) and polymer backbones22–28 have been employed in AEPs so far, only a few AEPs display satisfactory performance at high pH and temperature (>80 °C)17,29. Few AEPs exhibit preferable alkaline stability (stable in 1 M NaOH at 80 °C for 720 h) compared to BTMA-type AEPs, while the PPD of these AEMFCs was limited to below 1.6 W cm−2. Wang et al.15 also reported stable poly(biphenyl piperidinium) (PFBP-0) ionomers and copoly(aryl piperidinium) (c-PAP) AEMs. Their H2−O2 AEMFCs reached a PPD of 1.89 W cm−2 with a 0.7 mg cm−2 Pt–Ru/C anode. However, biphenyl or terphenyl groups in PAP AEIs have been documented to possess high phenyl adsorption on catalysts34,37–39. Currently, AEI research has been highlighted as a crucial issue by the latest US Department of Energy (DOE) protocol for the next decade. However, we lack sufficient insight from ionomer research, which has not revealed the effects of water vapor transport behavior and molecular dimensions of AEIs on the cell performance.

Here, we present poly(fluorenyl aryl piperidinium) (PFAP) copolymers for AEIs and AEMs. The fluorene (FLN) segment in the copolymers improves the rigidity and phase-separated morphology of AEMs to increase the dimensional stability and ion conductivity. Moreover, AEIs with rigid FLN groups are expected to improve the water vapor permeability (or water diffusivity) and decrease the phenyl adsorption effect.

Results

Design of polymers and characterization. Our PFAP copolymers were synthesized by a facile acid-catalyzed condensation reaction (Supplementary Fig. 1). Poly(fluorene-co-biphenyl N,N-dimethylpiperidinium) (PFBP-x) and poly(fluorene N,N-dimethylpiperidinium-co-nonfluoride) (PFNP-x) are designed for AEIs (Fig. 1a, b), whereas poly(fluorene-co-terphenyl N,N-dimethylpiperidinium) (PFTP-x) is specifically considered for AEMs (Fig. 1c). Here, x is the molar ratio of the fluorenyl piperidinium segment in the copolymer. Structural analysis of PFAP-x can be confirmed by 1H nuclear magnetic resonance (1H NMR) spectra (Supplementary Figs. 2–12).

PFAP AEIs were rationally designed to combine the merits of currently representative BTMA-ETFE29,30, alkyl ammonium PF34, and PAP ionomers17,36, and overcome their drawbacks. They have advantages including (1) PFAP AEIs containing DMP and FLN groups possess high ex-situ durability, rigidity, and low ionomer phenyl adsorption. Torsional rotation calculations demonstrated that FLNs had much smaller dihedral angle in the optimized

<insert Fig. 1: The chemical structure of representative polyelectrolytes with IEC and intrinsic viscosity. a) PFBP-x, b) PFNP-x, and c) PFTP-x.>
Water diffusion or water permeability related to AEMs41,42. Three of those of PFBP-0 and PFTP-0 AEMs, respectively, due to the presence of rigid FLN groups. Solubility testing of these polymers demonstrated that PFBP ionomers showed the best solubility in IPA/DI water (Supplementary Table 1), which is beneficial for catalyst slurry preparation.

As for the advantages of PFAP AEMs, (1) FLNs increase the rigidity of PFTPT AEMs, which simultaneously improves the ion-conducting capability and dimensional stability (Supplementary Fig. 15). PFTPT-13 AEMs with high IEC show lower water SRs than those of PFTPT-0 AEMs (Supplementary Table 2). (2) PFAP copolymers have facile synthetic processes (two steps, no heating, short synthetic period). PFAP AEIs and AEMs possess significantly different intrinsic viscosities (η) depending on the FLN content (Supplementary Table 3), which is related to the differences in their molecular weights. PFBP-14 (2.32 dL g\(^{-1}\)), PFTPT-13 (4.08 dL g\(^{-1}\)), PFPN-0 (5.25 dL g\(^{-1}\)), and PFTP-0 (4.875 dL g\(^{-1}\)) possess a high η that provides excellent film-forming properties. PFAP-x and PFPN-x copolymers with high FLN contents exhibit low η resulting in limited film-forming properties, while the η of PFPN (−0.38 dL g\(^{-1}\)) is still close to Olsson et al.’s PAPs44 (−0.2 to −0.47 dL g\(^{-1}\)). PFAP copolymers with high η exhibit preferable film-forming properties.

**Water sorption and transport behavior and gas permeability.** Water management plays a crucial role in AEMFCs. Water is a reactant in the cathode and a product in the anode, and the amount of water generated in the anode is two times faster than the electrochemical consumption of water in the cathode (Fig. 2a). This is why it is easy to flood the anode, while the cathode is inclined to dry out. Different PFAP-x polymers exhibit significantly different water uptake (WUs) and swelling ratios (SRs) with different counterions (Fig. 2b, Supplementary Fig. 16a, b). PFTPT-13 (WU: ~45%, SR: ~16%) and PFTP-0 (WU: ~55%, SR: ~24%) membranes exhibited much lower WU and SR in liquid water at 30 °C compared to PFBP-14 (WU: ~300%, SR: ~100%) and PFPB-0 (WU: ~350%, SR: ~110%) due to lower IEC values. Meanwhile, the PFTPT-13 membrane with higher IEC displayed lower SR and enhanced dimensional stability compared to the PFTPT-0 membrane due to the presence of rigid FLN groups.

Dynamic water vapor sorption (DVS) of PFAP-x membranes is significantly lower than their liquid WU (in equilibrium) at different RHs (Fig. 2c). PFBP-14 and PFTPT-13 films exhibited lower water vapor sorption than PFPB-0 and PFTP-0 films, respectively, which is consistent with liquid WU behavior. Notably, WU represents the water sorption capacity of AEIs or AEMs when liquid water is forming in AEMFCs, while it cannot represent the water transport behavior. Therefore, water diffusivity of AEIs at different RHs was automatically estimated by DVS, as shown in Supplementary Table 4. PFBP-14 and PFPB-0 AEMs with higher IEC values exhibited slightly higher water diffusivities than those of PFTPT-13 and PFTP-0 AEMs. PFBP-14 and PFTPT-13 AEMs also display higher water diffusivities than those of PFPB-0 and PFTP-0 AEMs, respectively, due to the existence of FLN blocks.

Currently, the water transport behavior can be referred to as water diffusion or water permeability related to AEMs41,42. Three small gas molecules—H\(_2\), O\(_2\), and water vapor—reach and participate in catalytic reactions, yet none of the current reports has accurately analyzed the water vapor permeability (P\(_{water}\)) through AEMs or AEIs at different RHs. Similar to diffusion behavior, water vapor permeabilities of PFBP-14 and PFBP-0 are 62,398 Barrer (where 1 Barrer = 10\(^{-10}\) cm\(^2\) s\(^{-1}\) cm Hg\(^{-1}\)) and 58,921 Barrer at 85% RH, respectively, and those of PFTPT-13 and PFTP-0 are 20,000–25,000 Barrer (Fig. 2d). Note that BP-containing copolymers (PFBP-0 and PFBP-14) showed high water vapor sorption and much higher P\(_{water}\) compared to TP containing AEIs (PFTPT-13 and PFTP-0). FLN-containing PFAP copolymers (PFPB-14 and PFTPT-13) with lower water vapor sorption and liquid WU exhibited similar or even higher water vapor permeability than that of PAP AEIs (PFBP-0 and PFTP-0) due to the rigid FLN groups, the unique phase-separated morphology, and large water channels (Supplementary Fig. 17). The detailed discussion of membrane morphology and water channels are presented in Supplementary information.

On the other hand, the H\(_2\) and O\(_2\) permeabilities of AEIs were measured and recorded at different RHs using Barrer as a unit that is well-known in gas separation communities43 (Fig. 2e and Supplementary Fig. 16c, d). PFTPT-13 and PFTP-0 exhibited much lower H\(_2\) (~10 Barrer) and O\(_2\) (~0.5 Barrer) permeabilities compared to PAP-TP-85 (H\(_2\) ~35 Barrer)47, commercial FAA-3-50 (H\(_2\): ~15 Barrer), indicating that the PFTP-13 and PFTP-0 AEIs possess superior gas barrier properties.

**Electrochemical and physical properties.** FLN-based PFAP copolymers exhibited superior ion conductivity compared to PAP AEIs (Fig. 3a, b). Among these AEIs, PFTP-13 AEIs with the lowest swelling ratio displayed the highest ion conductivities of 208 and 77 mS cm\(^{-1}\) in OH\(^-\) and Cl\(^-\) forms, respectively, at 98 °C. An appropriate FLN segment incorporated into the PFAP backbone is beneficial for improving ion conductivity. Supplementary Fig. 17 shows that PFTP-13 and PFBP-14 AEIs possess preferable microphase separated morphologies and larger water channels compared to PFTPT-0 and PFPB-0 AEIs, which improves their ion conductivity and water vapor permeability. The CO\(_3^{2-}\) conductivities of PFTPT-13 and PFPB-14 were over 65 mS cm\(^{-1}\) at 80 °C (Supplementary Fig. 18), meaning that the PFTPT-13 and PFPB-14 still possess high ion conductivity after carbonation13. Differential scanning calorimetry (DSC) analysis showed that excessive free water content (N\(_{free}\)) in PAP AEIs did not enhance the ion conductivity (Supplementary Fig. 19 and Table 2), indicating that the ion conductivity of swollen PAP AEIs does not always match well with IEC, but is related to the morphology and water transport behavior17,31.

PFTP-13 exhibits high tensile strength (TS, 84.6 MPa), elongation at break (EB, 25.6%), and Young’s modulus (YM, 1580 MPa) among these AEIs, and it can be easily fabricated into thin membranes (7–20 μm) (Fig. 3c–g and Supplementary Fig. 20). Supplementary Table 5 lists the mechanical properties of AEIs reported to date. The mechanical properties of the PFTP-13 AEIs without reinforcement are close to the best in current research. PFTP-13 AEIs possess high glass-transition temperatures (T\(_g\)) and an excellent storage modulus (SM) (E’\(\)) over 1500 MPa at 80 °C (Supplementary Figs. 21 and 22) that is the highest value so far in AEIs. This implies that PFTP-13 AEIs possess high rigidity and thermomechanical stability. Note that PFAP copolymers show two T\(_g\)s, which are due to the two different segments in the polymer backbone. In contrast, homopolymers such as PFTP-0 and PFBP-0 exhibit only one T\(_g\). On these grounds, the PFTP-13 copolymer with low SR, excellent dimensional stability, and high ion conductivity was chosen as representative AEIs, while PFBP-14 with high ion conductivity, high water permeability (or water diffusivity), but limited dimensional stability was selected as representative AEIs in this work.
Fig. 2 Gas and water sorption and transport behavior. a Schematic diagram of the membrane electrode assembly (MEA) in AEMFCs emphasizing fuel gas and water transport. b The WU of PFBP-0, PFBP-14, PFTP-0, and PFTP-13 membranes in OH$^-$ form in liquid water. c Dynamic water vapor sorption behavior of PFBP-0, PFBP-14, PFTP-0, and PFTP-13 membranes at different RHs measured in a DVS instrument (RH changes between 18%, 36%, 54%, 72%, 90% at a time interval of 60 min) at 25 °C. RH is controlled to automatically increase in a DVS instrument at a given time interval. Two hydration-dehydration cycles were recorded. d Water vapor permeability, and e H$_2$ permeability of different AEPs in I$^-$ form at 60 °C under 2.2 bar unilateral backpressure. H$_2$ permeability of reported PAP-TP-x$^{[17]}$ is presented for comparison.
Fig. 3 Physical properties of AEMs. a OH$^-$ and b Cl$^-$ conductivity of different AEMs as a function of temperature along with the picture of PFTP-13 membranes after testing at 98 °C. PFBP-14 and PFBP-0 membranes showed poor dimensional stability at high temperatures, and thus it was difficult to measure their OH$^-$ conductivities over 90 °C. c, d A picture of transparent PFTP-13 membranes 13.5 × 22.5 cm in size. e SEM image of a cross-section of PFTP-13 membrane with a thickness of ~15 µm. f The TS and EB of AEMs in I$^-$ form and commercial FAA-3-20 membranes at room temperature. Compared to the present PFTP-0 AEMs (TS: 71 MPa, EB: 45.7%, YM: 1.2 GPa) and reported PAP-TP-x AEMs (TS: 67 MPa and EB:117%)$^{17}$, PFTP-13 AEMs exhibit much higher TS and YM but lower EB, indicating that the PFTP-13 AEMs have a higher deformation resistance. g The tensile strength and elongation at break of PFTP-13 and PFTP-0 membranes at different temperatures and types. PFTM-13 is PFTP-14 before quaternization, whereas PFTP-13-I$^-$ and PFTP-13-OH$^-$ are in I$^-$ and OH$^-$ forms, respectively. PFTP-13 AEMs maintain their mechanical properties at 60 °C. Compared to Peng et al.’s PFTP-0 AEMs$^{36}$ (TS: 35 MPa and EB: 40%), the present PFTP-13 and PFTP-0 AEMs (TS: > 50 MPa and EB: ~60%) in OH$^-$ form exhibit much higher mechanical properties due to their higher intrinsic viscosity.
**AEMFC performance.** The effect of water behavior of AEIs on AEMFC performance was systematically investigated at different RHs based on the commercial FAA-3-20 and PFTP-13 AEMs with TKK Pt/C. At high anode/cathode (A/C) RHs (90%/100%) and low current density (<2.5 A cm⁻²), Supplementary Fig. 23a showed that PFTP-13 (WU: ~50%) and PFBP-14 (WU: ~300%) ionomers exhibited similar PPDs at 65 °C based on the commercial FAA-3-20 membrane, while those of FLN-based ionomers show higher PPDs than PFTP-0 (WU: ~350%) and PFTP-0 (WU: ~55%) ionomers due to the lower phenyl adsorption (Supplementary Fig. 23b) and higher ion conductivity. On the other hand, at high RH and moderate current density (~3.5 A cm⁻²) (Fig. 4a) or at low RHs (50%/80%) and high current density (>5 A cm⁻²) (Fig. 4b), PFBP-14 (1.42 W cm⁻²) and PFBP-0 (1.19 W cm⁻²) exhibited higher PPDs than PFTP-13 (1.06 W cm⁻²) and PFTP-0 (0.98 W cm⁻²) ionomers due to lower phenyl adsorption and higher P_water (or high water diffusivity). According to Matanovic et al.’s discovery, poly(biphenyl)-based ionomers showed higher PPDs than poly(terphenyl)-based ionomers due to lower phenyl adsorption, which is basically matching with our results. Moreover, high P_water of PFBP-14 AEMs with moderate WU contributed to rapidly dissolving the generated water in the anode which improved the water back diffusion or to maintaining the water content at low RH conditions. PFBP-14 ionomers (~300% WU at room temperature) showed much lower WU compared to the state-of-the-art PF ionomers (side-chain-type FLN-100, WU > 2000% at room temperature) at similar IEGs (~3.45 mmol g⁻¹). Therefore, PFBP-14 ionomers with moderate WU did not raise the anode flooding issues in the present AEMFCs. On the contrary, PFTP-13 ionomers with low WU and high conductivity showed limited AEMFC performance at low RH due to relatively low P_water. Meanwhile, AEMs also require reasonable water permeability. Note that PFTP-13 AEMs display higher PPDs than the commercial FAA series and PFTP-0 AEMs due to higher ion conductivity, mechanical properties, and P_water (or water diffusivity) (Supplementary Fig. 24).

Unfortunately, PFAPN-100 and PFAPN-85 AEMs with low phenyl adsorption and high rigidity (Supplementary Figs. 13 and 14) possess insufficient intrinsic viscosity (or molecular weight), which cannot tightly hold on catalyst particles, resulting in severe catalyst detachment from catalyst-coated membrane (CCM) during ion-exchange process. Therefore, AEMFC performance of PFAP-x ionomers (0.3–0.7 W cm⁻²) is limited. Figure 4c shows that the PPDs of AEMFCs are significantly impacted by the [n] of PFAP-x AEMs, and the detachment issue has been found when the [n] is lower than 1 dL g⁻¹ along with PPD decrease. Development of PFAP-x and PFPB-x ionomers with reasonable molecular weight will be our future work. These discoveries provide a clear information for the PAP family to rationally design AEIs with sufficient molecular weight. PFAP-x AEMs containing 14–30% FLNs displayed the highest PPDs (1.52–1.64 W cm⁻²) due to the reasonable [n] and high P_water. Based on PFPB-14 AEMs, PFTP-13 AEMs, and 75%/100% A/C RH, the PPDs of AEMFCs reached 1.67 W cm⁻² (0/0 bar back pressure) and 2.34 W cm⁻² (1/1.3 bar back pressure) at 80 °C based on Pt–Ru/C anode (Fig. 4d). A small applied back pressure (0.5/0.5 bar) shows significant effect on the cell performance due to the higher electrode reactions and optimizing water transport that decreases the mass transport resistance (Fig. 4d and Supplementary Fig. 24b). Under H₂-air (CO₂ free) conditions, the present AEMFCs reached PPDs of 1.25 and 1.01 W cm⁻² with 0.42 mg cm⁻² Pt–Ru/C anode and 0.33 mg cm⁻² Pt/C anode, respectively (Fig. 4e). Moreover, after replacing the expensive Pt/C cathode with a home-made cobalt catalyst (0.6 mg cm⁻² Co@C/C, 40 wt% Co), the PFAP-based AEMFCs still reached an impressive PPD of 0.891 W cm⁻² at 80 °C with a low back pressure (Fig. 4f).

**Optimized AEMFCs.** Based on the Co@C/C cathode will be presented in our following paper.

Supplementary Table 6 summarizes all the fuel cell performances with low catalyst loadings conducted in this work, and these are compared with those in the literature. Currently, the state-of-the-art PTFE-reinforced PNB (GT-x series: 3.2 W cm⁻² in H₂–O₂ and 1.75 W cm⁻² in H₂–air without back pressure), 3.5 W cm⁻² in H₂–O₂ and 1.25 W cm⁻² in H₂–air with 0.5/1.0 bar back pressure and BTMA-HDPE (2.35–2.5 W cm⁻² in H₂–O₂ and 1.06 W cm⁻² in H₂–air without back pressure) AEMs lead the current AEMFCs, while our present AEMFCs display comparable power density (2.34 W cm⁻² in H₂–O₂ and 1.25 W cm⁻² in H₂–air with 1.3/1.3 bar back pressure). On the other hand, compared to the state-of-the-art polyaromatics-based AEMFCs (<2.08 W cm⁻² in H₂–O₂ with 2.0/2.0 bar back pressure), our present AEMFCs showed higher PPDs. Note that GT-x series and BTMA-HDPE-based AEMFCs employed a high Pt–Ru/C loading of 0.7 mg cm⁻², while the present PFAP-based cells exhibited high performance with a low PGM loading of 0.33–0.42 mg cm⁻².

Figure 5 summarizes the PPD and OH⁻ conductivities of representative AEIs in current research. Compared to side-chain-type PF AEIs and poly(terphenylene) AEMs, PFBP-14 AEIs and PFTP-13 AEMs showed higher ion conductivity and PPDs. Although BTMA-ETFE ionomers displayed the slightly higher PPDs, the alkaline stability issues associated with the BTMA-ETFE still have not been well addressed. Our present ion conductivity and PPDs are the topmost values to date, compared to polyfluorene (PF), polyphenylene (PP) and PAP AEIs. This indicates that PFAP AEIs are good candidates for AEI and AEM applications.

**Ex-situ and in-situ durability.** Based on the high-throughput testing of current AEMs by the National Renewable Energy Laboratory (NREL), most AEMs show severe deformation of the membranes and even exhibit fracture along with color changes (in some cases) after testing in 1 M KOH at 80 °C for 1000 h. PFTP-13 AEMs are stable in 1 M NaOH at 80 °C for 2000 h and maintain transparency and mechanical toughness after ~200 h. On the other hand, the commercial FAA membranes and ionomer-based AEMFCs showed significant voltage loss (over 40% voltage decay) within 48 h (Supplementary Fig. 29). Peng et al. reported 120 h in-situ durability at a 0.2 A cm⁻² current density (~10% voltage decay, ~800 µV h⁻¹) at 80 °C based on PFTT-0 AEMs. Yan and coworkers presented 300 h in-situ durability (~11.5% voltage decay at 250 h, ~300 µV h⁻¹) at a 0.5 A cm⁻² current density at 95 °C based on PAP-TX-4 AEMs. Very recently, a few state-of-the-art AEMFCs reported ~1000 h in-situ durability (voltage decay 32–350 µV h⁻¹), and GT-x-based AEMFCs could even obtain 2000 h in-situ durability (only 3.65% voltage decay, ~15 µV h⁻¹) under a 0.6 A cm⁻² current density at 75 °C.
Fig. 4 Fuel cell performance. a The power density of AEMFCs with different AEIs and PFTP-13 AEMs (25 ± 3 μm) based on A/C TKK Pt/C catalysts (0.33 mg cm$^{-2}$): 1000/1000 mL min$^{-1}$ H$_2$–O$_2$ flow rate, 65 °C, 85%/100% A/C RH, and 0.5/0.5 bar back pressure. b The power density of AEMFCs with different AEIs and PFTP-13 AEMs (25 ± 3 μm) based on A/C TKK Pt/C catalysts (0.33 mg cm$^{-2}$): 80 °C, 50%/80% A/C RH, and 1.3/1.3 bar back pressure. c The relationship between the PPDs and the intrinsic viscosity of PFBP-x AEIs: PFTP-13 AEMs (25 ± 3 μm), H$_2$–O$_2$, A/C Hispec Pt/C catalysts (0.33 mg cm$^{-2}$), 80 °C, the A/C flow rate of 1000/1000 mL min$^{-1}$, 75%/100% A/C RH. Hollow circle symbols are PPDs without back pressure, while filled circle symbols are PPDs with 1.3/1.3 bar back pressure. d The power density of AEMFCs based on Pt–Ru/C anode with back pressure: PFBP-14 AEIs and PFTP-13 AEMs (20 ± 3 μm), 80 °C, 75%/100% A/C RH, 1000/2000 mL min$^{-1}$ H$_2$–O$_2$ flow rate, different back pressures, Pt–Ru/C anode (0.42 mg cm$^{-2}$), Hispec Pt/C cathode (0.33 mg cm$^{-2}$) for comparison. e The power density of AEMFCs in H$_2$–air (CO$_2$ free) with different anode catalysts: PFAP-14 AEIs and PFTP-13 AEMs (20 ± 3 μm), 80 °C, 75%/100% A/C RH, 1000/2000 mL min$^{-1}$ H$_2$–O$_2$ flow rate, 1.3/1.3 bar A/C back pressure, 0.33 mg cm$^{-2}$ A/C catalyst loading. f PFAP-based AEMFCs with 0.6 mg cm$^{-2}$ loading of Co@C/C cathode and Pt–Ru/C anode with 1000/1000 mL min$^{-1}$ H$_2$–O$_2$ flow rate at 60 and 80 °C. PPDs reached 0.769 cm$^{-2}$ and 0.891 W cm$^{-2}$ at 60 °C without back pressure and at 80 °C with 0.5/0.5 bar back pressure, respectively.
Discussion
In summary, a series of high-performance PFAP-x AEIs and AEMs have been developed in this work. PFTP-13 AEMs simultaneously possessed >80 MPa TS and ~1500 MPa SM, excellent dimensional stability, and over 200 mS cm\(^{-1}\) OH\(^{-}\) conductivity at 98 °C. AEMFC performance demonstrated that PFBP-14 AEIs with suitable water vapor permeability exhibited superior PPDs at moderate or low RHs, which improved the mass transport efficiency and water diffusion in AEMFCs. The present AEMFCs reach PPDs of 2.34 and 1.25 W cm\(^{-2}\) in H\(_2\)-O\(_2\) and H\(_2\)-air, respectively. In-situ durability demonstrated that the present AEMFCs can be operated stably under a 0.2 A cm\(^{-2}\) current density for ~200 h at 70 °C. All these results indicate that these rigid PFAP AEMs and AEIs are promising candidates for AEMFCs.

Methods
Synthesis of poly(fluorene-co-aryl methylpiperidine) (PFAM-x). A typical synthesis procedure of PF0.13T0.87M (or PFTM-13) is as follows: terphenyl (8.28 g, 36 mmol), 9,9′-dimethylfluorene (0.777 g, 4 mmol), and 1-methyl-4-piperidone (5.12 mL, 44 mmol) were added into a three-neck reactor, and then dichloromethane (CH\(_2\)Cl\(_2\), 32 mL) was added to dissolve the monomers with mechanical stirring, followed by N\(_2\) purge for 10 min. The color of the above solution immediately became dark red after adding TFOA. The reaction was kept at -3 °C by continuous mechanical stirring at ~10%
RH for 7–12 h depending on the viscosity of the solution. Subsequently, a very viscous polymer solution with a black-red color was carefully poured into a 1 M NaOH/DMSO solvent to produce white and stringy polymers. The polymer was washed by a blender, and carefully washed several times with DI water until the pH was neutral. Finally, the polymer was dried in a vacuum oven at 80 °C to obtain a pale yellow PFTM-13. Yield: >95%. 1H NMR (600 MHz, DMSO, δ): 7.29 – 7.07 ppm (Hα), 3.50 ppm (Hβ), 3.07 ppm (Hγ), 2.83 ppm (Hδ), 2.75 ppm (Hε), 2.29 ppm (Hζ), and 1.32 ppm (Hθ) (Supplementary Fig. 2).

A typical synthesis procedure of PF0.13T0.87M (or PFTM-13) is as follows: 4 g of PF0.13T0.87M (or PFTM-13) was dissolved in 40 mL of DMSO at 80 °C with 1 mL of TFA as a cosolvent. After PFTM-13 was completely dissolved in DMSO, the polymer solution was cooled to room temperature. Then, 2.5 g of potassium carbonate and 2 mL of CH3I (3eq) were added to the above solution. The quaternization reaction was kept at room temperature for 24 h with a tinfoil covering to avoid light. After reaction, the polymer solution was precipitated in ethyl acetate to obtain a polymer, and then the polymer was filtered and washed with twice with DI water to remove residual inorganic salt. Finally, the polymer was dried in a vacuum oven at 80 °C to obtain a pale yellow PFTM-13. Yield: >95%. 1H NMR (600 MHz, DMSO, δ): 7.29 – 7.07 ppm (Hα), 3.50 ppm (Hβ), 3.17 ppm (Hγ), 2.83 ppm (Hδ), 2.75 ppm (Hε), 2.29 ppm (Hζ), and 1.32 ppm (Hθ) (Supplementary Fig. 2).

Synthesis of PFAP-x copolymers. A typical synthesis procedure of PF0.13T0.87P (or PFTP-13) is as follows: 4 g of PF0.13T0.87P (or PFTP-13) was dissolved in 30 mL of DMSO at 80 °C to prepare a 3.33 wt% polymer solution. Subsequently, the polymer solution was cooled to room temperature with a tinfoil covering to avoid light. After reaction, the polymer solution was precipitated in ethyl acetate to obtain a polymer, and then the polymer was filtered and washed with twice with DI water to remove residual inorganic salt. Finally, the polymer was dried in a vacuum oven at 80 °C to obtain a yellow PFTP-13. Yield: ~70%.

Dynamic vapor sorption (DVS). The water sorption of AEM samples at different RHs was measured by a DVS (Surface Measurement Systems, UK) instrument at 25 °C. AEM samples were dried in a vacuum oven at 100 °C to remove residual water before testing. During testing, RH was automatically increased from 0% to 90% with six steps (0%, 18%, 36%, 54%, 72%, 90%), and then decreased from 90% to 0% step by step, and every RH stage was stable for 1 h to reach water equilibrium.

DFT calculations. Spin-polarized DFT calculations were performed for estimating the adsorption energy of 9,9-dimethylfluorene-dimethylpiperidinium (FDMP) and biphényl-dimethylpiperidinium (BDMP) on the surfaces of Pt (111) and Pt–Ru (111) using the Vienna Ab initio Software Package (VASP) code, which is based on density-functional principles. The Perdew–Burke–Ernzerhof (PBE) approach within the generalized gradient approximation (GGA) was adopted to examine the electronic exchange correlation function of the interacting electrons. Input parameters were set as follows: energy cutoff (400 eV), energy criteria (10−8 eV), force criteria (0.05 eV/Å), smearing method (Methfessel-Paxton), and broadening width (0.2 eV). In this study, adsorption reactions were described as a large scaled unit cell (a: 22 Å, b: 22 Å, c: 30 Å) to avoid direct interactions between the periodic images. The calculated adsorption energy was determined from the equation below:

$E_{\text{ad}} = E_{\text{ads}} - [E_{c} + E_{I}]$ (5)

Here, $E_{\text{ads}}$ denotes the adsorption energy of the molecule on the catalyst surface. $E_{c}$ denotes the total energy of the adsorbed system. $E_{I}$ denotes the total energy of the catalyst, and $E_{f}$ denotes the total energy of the adsorbate. Different adsorption directions of ionomers on the surface of catalysts were considered to optimize the calculated adsorption energies of phenyl and ammonium groups.

Torsional rotation calculation. The structural models were constructed by Material Studio 8.0 (Accelrys). Dihedral angles in the optimized geometry were determined by using the Dmol3 module (GGA/BLYP method and DND basis set). The relative energy variation of highlighted bonds with the torsional rotation angles was measured by the conformers package in Materials Studio 8.0. Energy minimizations of the structures of each conformer generated were done by using the Forcefiled Module (forcefield assigned COMPASS and Smart algorithm for iterations).

Mechanical properties and thermal stability. A universal testing machine (UTM, AGS-J 5000N, Shimazdu, Japan) was used for measuring the mechanical properties of membrane samples. The TSs and elongations at break (EB) of PFBB-14, PFBB-0,
PFTP-13, PFTP-0, and commercial FAA-2-30 membranes in halogen form were measured in the dry state. All membrane samples were cut into a dumbbell shape (2 x 10 mm), and the stretching rate was 1 mm/min. The thickness of the membranes was recorded using micrometer-scale calipers. In addition, the mechanical properties of PFTP-13 and PFTP-0 membranes in different forms and at different temperatures were also investigated. Moreover, the TS and EB of the PFTP-13 membrane after in-situ stability testing was investigated. The thermal stabilities of AEPs were measured using a thermogravimetric analysis instrument (TGA, Q500, TA Instrument, USA) connected to a mass spectrometer (MS, ThermoStar GSD 301T, Pfeiffer Vacuum GmbH, Germany). The temperature was increased from 30 to 800 °C at a 10 °C/min ramping rate under a nitrogen atmosphere. Mass spectroscopy was used to detect the thermally decomposed species released from AEPs at related temperatures.

**Dynamic mechanical analysis (DMA).** DMA (Q800, TA Instrument, DE, USA) was employed to measure the glass-transition (Tg) temperature, SM, and loss modulus (LM) of AEPs. Specifically, all membrane samples were cut into a 0.9 x 2 cm shape and were fixed with tension clamps in the DMA system. DMA testing was performed with a 1 Hz single-frequency strain mode, a preload force of 0.01 N and a force track of 125% under a nitrogen atmosphere. The target temperature was set to 450 °C along with a 10 °C/min ramping rate.

**Intrinsic viscosity.** The intrinsic viscosity ([η]) of AEPs was measured using an Ubbelohde viscometer in a DMso solution at 25 °C. The viscometry system is composed of a Schott Viscosystem (AVS 370, Germany). Ubbelohde viscometer (SI Analytik, Type 530 13: Capillary No. Ic, 50 μm (I) x 200 μm (L)) and the shearing rate was 0.03 s⁻¹. The obtained [η] values were used to calculate the following equations:

\[
\eta_{inh} = [\eta] \times \frac{1}{[\eta]_0}
\]

(6)

Here, \(\eta_{inh}\) is the intrinsic viscosity ([η]) of a polymer solution, \(\eta_{inh}\) is the obtained [η] value, and \(\eta_{inh}\) is calculated by obtaining the slope that can be plotted from a change in the heating temperature was gradually increased from −55 to 20 °C along with a 3 °C/min ramping rate. \(N_{free}\) and \(N_{bound}\) were determined by the following equations:

\[
N_{free} = \frac{H_1}{H_2} \times \lambda
\]

(8)

Here, \(H_1\) is the enthalpy obtained by the integration of the freezing peak calculated from the DSC program. \(H_2\) is the enthalpy of water fusion. \(M_{acid}\) and \(M_{base}\) are wet and dry masses of a membrane sample, respectively.

**Gas permeability.** H₂, O₂, and water vapor permeabilities of PFTP-13, PFBP-14, PFTP-0, PFBP-0, commercial FAA-2-30 and Nafion 212 membranes were measured using a laboratory made gas permeability testing system. The device, as shown in Supplementary Fig. 30, was connected to a gas chromatograph (GC, 490 Micro GC, Agilent Technologies, USA) and two mass flow controllers (MFC, M3030V, Line Tech, Korea) operating at different RHs (from 0% to 90% RH) at 60 °C (T) under a 2.2 bar unilateral back pressure. The gas permeability (P) can be calculated by the following equation:

\[
P = \frac{V_{m} \cdot \mu \cdot d_{p}}{P_{ref} \cdot R \cdot T \cdot A \cdot \Phi_{d}}
\]

(11)

Here, \(A\) is the effective area and \(d\) (μm) represent the thickness of membrane samples, respectively. \(P_{ref}\) and \(M_{meas}\) (g mol⁻¹) are the pressures of each gas (760 mmHg) and molecular weight of the permeating gas, respectively. V (cm³) is the volume of the measuring device at the bottom of the membrane samples. \(\mu\) is the density of water (0.9997 g cm⁻³) and \(R\) is the ideal gas constant. The permeation time, \(t\), is the slope that can be plotted from a change in permeated gas pressure as a function of time. The unit of P is Barrer where 1 Barrer = 10⁻¹⁰ cm³ (STP) cm⁻¹ cmHg⁻¹.

**Morphology analysis.** The surface and cross-section morphologies of AEMs and MEAs were observed using a scanning electron microscope (SEM, FE-SEM S-4800, Hitachi, Japan) at 15 kV. Membrane and MEA samples for observing the cross-section morphologies were fractured in liquid nitrogen, and all samples were coated with a thin platinum layer using an ion sputtering system (E-1045, Hitachi). Kilday et al. (2016). The force microscopy (AFM) was used to observe the surface microphase separation of AEMs on a MultiMode 8 AFM (Veeco) with a NanoScope V controller. AEMs were tested in OH⁻ form in the dry state.

**Fuel cell testing.** PFTP-13, PFTP-0, and commercial FAA-2-30 membranes were selected as AEMs. PFTP-13, PFBP-14, PFBP-0, PFTP-0, PFPN-100, PFPN-85, and FuMa-Tech Fumion ionomers were used as AEsIs. Pt/C (Titania Ketjen Cats Cloisite 15A, 46.5 wt% Pt/C, Pt/C (Johnson Mathey HiSpec 4000, 40 wt% Ru/C), Pt-Ru/C (Johnson Matthey HiSpec 10,000, 40 wt% Pt and 20 wt% Ru) and home-made Cof/C (40 wt% Co) were employed as catalysts. AEsIs were dissolved in DMSO to prepare a 5% polymer solution, and then the polymer solution was filtered using a 0.45 μm PTFE filter. The catalyst slurry was prepared by adding the 5% AEMs/DMSO solution and catalysts into IPA/DI water (10 to 1), and then the slurry was sonicated for 1 h. Subsequently, the catalyst slurry was sprayed onto both sides of AEMs (1 mm thick) using an airbrush to produce 5 cm² CCM. 12.5 mg Hispec Pt/C, or 8.33 mg Pt-Ru/C, or 11.1 mg TkK Pt/C can produce the catalyst loading of 0.4 ± 0.05 mg cm⁻² in a dry CCM. The ratio of catalysts to ionomers is 3.3:1. CCMs were immersed in 1 M NaOH at room temperature overnight, and then they were then washed with DI water three times. CCMs in the wet state were directly assembled with two gas diffusion layers (GLDs), fluorinated ethylene propylene (FEP) gaskets, and graphite bipolar plates with a 5 cm² flow field to obtain a complete AEMFC using a torque of 70 in-lb. The actual catalyst loading of MEAs was slightly adjusted by the area swelling of wet CCMs.

AEMFC performance was measured using a fuel cell test station (CNL, Seoul, Korea). Single cells were activated by scanning the current from 0 to 3 A cm⁻² with a 1000 mV min⁻¹ flow rate at 80 °C for two cycles without backpressure, and the polarization curve and power density curve were recorded after activation. Fuel cell performance was tested under different conditions, including temperature, RH, back pressure, flow rate, and feed gas.

**Ex-situ and in-situ durability.** The ex-situ durability of the PFTP-13 membrane was measured in 1, 5, and 10 M NaOH at 80 °C for 2000 h. The degradation ratio of PFTP-13 was calculated by the changes in chemical structure detected by 1H NMR and Cl⁻ -conductivity at room temperature. Changes in the mechanical properties and thermal stability were also investigated after alkaline treatment in 10 M NaOH at 80 °C for 168 h. Moreover, the in-situ durability was measured at a 0.2 A cm⁻² current density at 70 °C under H₂-O₂ conditions based on A/C PPFB-14 ionomers and a PFTP-13 membrane.

**Data availability**

The data that support the plots within this paper and other findings of this study are available from the corresponding author upon reasonable request.

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**References**

1. Park, C. H. et al. Nanocrack-regulated self-humidifying membranes. Nature 532, 480–483 (2016).
2. Hassan, N. U. et al. Achieving high—performance and 2000 h stability in anion exchange membrane fuel cells by manipulating ionomer properties and electrode optimization. Adv. Energy Mater. 10, 2001986 (2020).
3. Peng, X. et al. Using operando techniques to understand and design high performance and stable alkaline membrane fuel cells. Nat. Commun. 11, 3561 (2020).
4. Ramesh, K. S. et al. Synthesis of CeO₂-decorated Pd/C catalysts by controlled surface reactions for hydrogen oxidation in anion exchange membrane fuel cells. Adv. Funct. Mater. 30, 2002087 (2020).
5. Lee, K. H. et al. Highly conductive and durable poly(arylene ether sulfone) anion exchange membrane with end-group cross-linking. Energy Environ. Sci. 10, 275–285 (2017).
6. Chen, N. J. & Lee, Y. M. Anion Exchange Polyelectrolytes for membranes and ionomers. Prog. Polym. Sci. 113, 103431 (2020).
7. Thompson, S. T., Peterson, D., Ho, D. & Papageorgiou, D. Perspective—the next decade of AEMFCs: near-term targets to accelerate applied R&D. J. Electrochem. Soc. 167, 084514 (2020).
10. Park, E. J. et al. Alkaline stability of quaternized Diels–Alder polyphenylenes. *Macromolecules* **52**, 5419–5428 (2019).

11. Chen, N. J., Long, C., Li, Y., Lu, C. & Zhu, H. Ultrastable and high ion-conducting polyelectrolyte based on six-membered N-spirocyclic ammonium for hydroxide exchange membrane fuel cell applications. *ACS Appl. Mater. Interfaces* **10**, 15720–15732 (2018).

12. Wang, L. et al. Non-fluorinated pre-irradiation-grafted (peroxodized) LDPE-based anion-exchange membranes with high performance and stability. *Energy Environ. Sci.* **10**, 2154–2167 (2017).

13. Zheng, Y. et al. Quantifying and elucidating the effect of CO2 on the thermodynamics, kinetics and charge transport of AEMFCs. *Energy Environ. Sci.* **12**, 2806–2819 (2019).

14. Cha, M. S. et al. Poly(carbazole)-based anion-conducting materials with high performance and durability for energy conversion devices. *Energy Environ. Sci.* **13**, 3633–3645 (2020).

15. Fan, J. et al. Poly(bis-aryl imidazolium) possessing high hydroxide ion exchange capacity and high alkaline stability. *Nat. Commun.* **10**, 2306 (2019).

16. Wright, A. G. et al. Hexamethyl-p-terphenyl poly(benzimidazolium): a universal hydroxide-conducting polymer for energy conversion devices. *Energy Environ. Sci.* **10**, 2310–2312 (2017).

17. (a) Wang, J. et al. Poly(aryl piperidinium) membranes and ionomers for hydroxide exchange membrane fuel cells. *Nat. Energy* **4**, 392–398 (2019). (b) Wang, T. et al. High-performance hydroxide exchange membrane fuel cells through optimization of relative humidity, backpressure and catalyst selection. *J. Electrochem. Soc.* **166**, F3305–F3310 (2019).

18. Guo, S. et al. A stable and highly conductive ionomer for high-performance hydroxide exchange membrane fuel cells. *Angew. Chem. Int. Ed. Engl.* **48**, 6499–6502 (2009).

19. Zhang, B. et al. Tertiary sulfonium as a cationic functional group for hydroxide exchange membranes. *RSC Adv.* **2**, 12683–12685 (2012).

20. Chen, N. J. et al. Cobaltocene-containing polybenzimidazole polymers for alkaline anion exchange membrane applications. *Polymer* **8**, 1381–1392 (2017).

21. Zha, Y., Disabb-Miller, M. L., Johnson, Z. D., Hickner, M. A. & Tew, G. N. Metal-cation-based anion exchange membranes. *J. Am. Chem. Soc.* **134**, 4493–4496 (2012).

22. Kim, Y. et al. Ionic highways from covalent assembly in highly conducting and stable anion exchange membrane fuel cells. *J. Am. Chem. Soc.* **141**, 18152–18159 (2019).

23. Liang, X. et al. Ionomer cross-linking immobilization of catalyst nanoparticles for high performance alkaline membrane fuel cells. *Chem. Mater.* **31**, 7812–7820 (2019).

24. Isson, J. S., Pham, T. H. & Jannasch, P. Poly(arylene piperidinium): a universal hydroxide ion exchange membrane for high performance alkaline fuel cells. *Polym. Chem.* **10**, 1893–1903 (2019).

25. Omasta, T. J. et al. Strategies for reducing the PGM loading in high power AEMFC anodes. *J. Electrochem. Soc.* **165**, F710–F717 (2018).

26. Leonard, D. P. et al. Asymmetric electrode ionomer for low relative humidity operation of anion exchange membrane fuel cells. *J. Mater. Chem. A* **8**, 14135–14144 (2020).

27. Chen, G. Q., Scholes, C. A., Qiao, G. G. & Kentshi, S. E. Water vapor permeation in polyimide membranes. *J. Membr. Sci.* **379**, 479–487 (2011).

28. Choi, J. et al. Application of spiribindane-based microporous poly(ether sulfone) as polymeric binder on solid alkaline exchange membrane fuel cells. *J. Membr. Sci.* **568**, 67–75 (2018).

29. Wang, Y. et al. Pt–Ru-catalyzed hydrogen oxidation in alkaline media: oxophilic effect or electronic effect? *Energy Environ. Sci.* **8**, 177–181 (2015).

30. Zhu, L. et al. Multication side chain anion exchange membranes. *Macromolecules* **49**, 815–824 (2016).

31. Gao, X. et al. Enhanced water transport in AEMs based on poly(ethylene–ethylene–butylene–styrene) triblock copolymer for high fuel cell performance. *Energy Environ. Sci.* **12**, 75 (2018).

32. Jeon, J. Y. et al. Synthesis of aromatic anion exchange membranes by Friedel–Crafts bromoaikylation and cross-linking of polystyrene block copolymers. *Macromolecules* **52**, 2139–2147 (2019).

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**Author contributions**

Y.M.L. and N.I.C. conceived of the idea. N.I.C. wrote the draft. Y.M.L. guided the work and edited the manuscript. N.I.C. synthesized the polymers, fabricated the membranes, and measured ion conductivity and alkaline stability. N.I.C., H.H.W., and H.M.K. performed TGA and mechanical property measurements. H.H.W. and H.M.K. tested the intrinsic viscosity and performed DSC and DMA measurements. Y.-C.C. and E.S.S. performed the DFT calculations. H.H.W. performed SEM and TEM measurements. S.P.K. prepared MEA. N.I.C. and S.P.K. tested fuel cells and in-situ durability. C.H. and Y.-S.L. performed water and gas permeabilities. Torsional rotation calculations were done by Y.Z. Co@C/Cathode based AEMFCs were measured by S.J.Y. and J.-H.J. AEMFCs were measured by S.J.Y. and J.-H.J. S.P.K. prepared MEA. N.J.C. and S.P.K. tested fuel cells and in-situ durability. C.H. and Y.-C.C. and E.S.S. performed TGA and mechanical property measurements. H.H.W. and H.M.K. tested the intrinsic viscosity and performed DSC and DMA measurements. Y.-C.C. and E.S.S. performed the DFT calculations. H.H.W. performed SEM and TEM measurements. S.P.K. prepared MEA. N.I.C. and S.P.K. tested fuel cells and in-situ durability. C.H. and Y.-S.L. performed water and gas permeabilities. Torsional rotation calculations were done by Y.Z. Co@C/Cathode based AEMFCs were measured by S.J.Y. and J.-H.J.

**Competing interests**

The authors declare no competing interests.
