Supplementary Information

Boosting hydrogen evolution reaction catalytic activity of Pt/C via well-designed anion-exchange ionomers

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Experimental section

Materials: 3,3’-(2,7-Dichloro-9H-fluorene-9,9-diyl)bis(N,N-dimethylpropan-1-amine) (AF), bis(3-chlorophenyl)perfluorohexane (PAF) were synthesized according to our previous reports [1-2].

N,N-Dimethylacetamide (DMAc) (> 99.0%, Kanto Chemical), dimethyl sulfoxide (DMSO) (> 98.0%, Kanto Chemical), chloroform (> 99.0%, Kanto Chemical), hydrochloric acid (35-37%, Kanto Chemical), potassium hydroxide (> 86.0%, Kanto Chemical), 2,2’-bipyridine (BPY, >99.0%, TCI), Cycloheptanone (>98.0%, TCI), aniline (>98.0%, TCI), 9,9'-Spirobi[9H-fluorene] (>98.0%, TCI), $FeCl_3$ (> 96.0%, Kanto Chemical), anhydrous $MgSO_4$ (> 98.0%, Kanto Chemical), bis(1,5-cyclooctadiene)nickel(0) ($Ni(COD)_2$) (> 95.0%, Kanto Chemical), dimethyl sulfate (> 99%, Kanto Chemical) and other solvents and chemicals were used as received. Nafion NRE 211 membrane (25-um thick and ion exchange capacity = 0.98 mmol g^{-1}; Du Pont) and Nafion dispersion (ion-exchange capacity = 0.95–1.03 mmol g^{-1}, D-521; DuPont) were purchased from the Chemours Company (Wilmington, DE, USA). Pt/C catalyst (TEC10E50E) was purchased from Tanaka Precious Metals Co. (Tokyo, Japan). Tokuyama AS-4 binder was kindly supplied by Tokuyama Corp.

Synthesis of QPAF-4-1.5: PAF-4-1.5 and QPAF-4-1.5 polymers were synthesized according to our previous reports.[1,2] The ^1H NMR spectrum of QPAF-4-1.5 is given in **Fig. S1**.

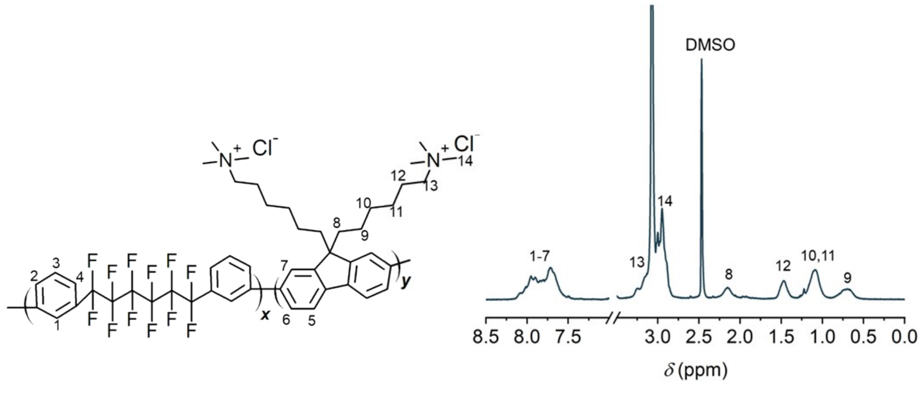
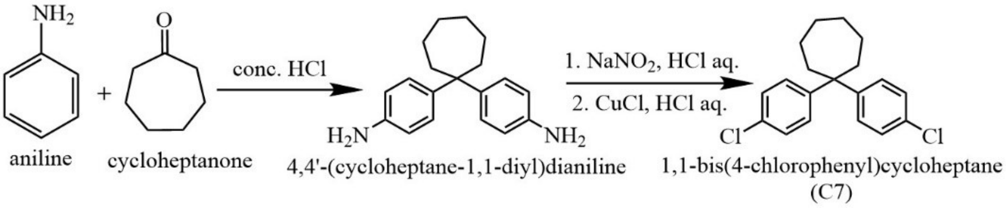


Fig. S1. ^1H NMR spectrum of QPAF-4-1.5 in Cl^- form in DMSO-d_6.

Synthesis of 1,1-bis(4-chlorophenyl)cycloheptane (C7) monomer: Prior to the synthesis of C7 monomer, 4,4'-(cycloheptane-1,1-diyl)dianiline was synthesized. Cycloheptanone (10.30 g, 91.80 mmol), aniline (30 mL, 330.00 mmol) and 33 mL of concentrated hydrochloric acid were added in a flask with a magnetic stirring bar. The mixture was heated at 150 °C for 48 h. After cooling to r.t., NaOH aqueous solution was added to the reaction mixture. The oil layer was separated, and unreacted aniline was removed by distillation. The residue was purified by silica gel column chromatography (hexane: ethyl acetate = 4: 1 and then 1: 1). After drying in a vacuum oven at 50 ^{o}C, 4,4'-(cycloheptane-1,1-diyl)dianiline was obtained as a pale brown solid (6.44 g, 25% yield).

4,4'-(Cycloheptane-1,1-diyl)dianiline (3.00 g, 10.7 mmol) in concentrated HCl (10 mL) was suspended in an ice-water bath, followed by the addition of $NaNO_2$ (1.90 g, 27.6 mmol)/water (5 mL) solution with continuous stirring. After 30 min, a pre-cooled solution of CuCl (3.81 g, 38.5 mmol) in concentrated HCl (20 mL) was added. After stirring for 1 h at r.t., the mixture was extracted with chloroform and washed with brine. The organic layer was filtered through a celite plug, and then washed with water and evaporated. The residue was purified by silica gel column chromatography (*n*-hexane). The obtained product was dried in a vacuum oven to yield C7 monomer as a white solid (1.60 g, 47% yield).



Scheme S1. Synthesis of C7 monomer.

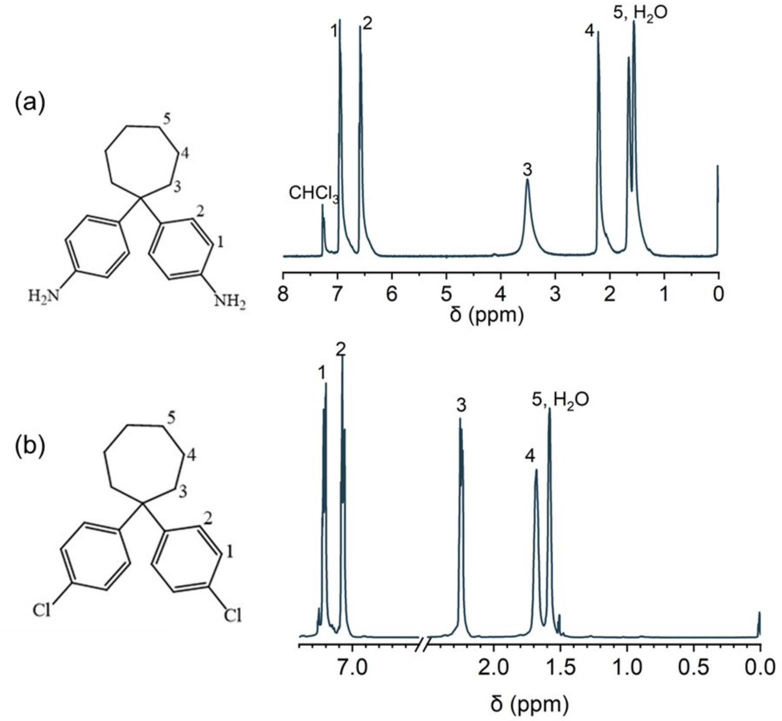


Fig. S2. ^{1}H NMR spectra of (a) 4,4'-(cycloheptane-1,1-diyl)dianiline and (b) 1,1-bis(4-chlorophenyl)cycloheptane (C7) monomer in $CDCl_3$.

Synthesis of C7-QAF-3.0: C7-AF-3.0 polymer was synthesized by $Ni(COD)_2$ (5.66 mmol) promoted polycondensation of C7 (0.88 mmol) and AF (1.01 mmol) in the presence of BPY (5.94 mmol) in DMAc (5 mL). The reaction solution was stirred at 80 °C for 3 h. The obtained mixture was poured into HCl and then washed sequentially with HCl, K_2CO_3 aqueous solution and deionized water, and finally dried under vacuum oven to obtain pale-yellow powder (0.69 g, 108% yield). The quaternization of C7-AF-3.0 polymer was conducted by dissolving the above polymer in DMAc (16 mL), followed by the addition of dimethyl sulfate (6 mL) and stirred for 48 h at 60 °C. The obtained mixture was dropped into deionized water, and then washed twice with deionized water and dried in a vacuum oven at 50 °C. The ^{1}H NMR spectrum of C7-QAF-3.0 is given in **Fig. S3**.

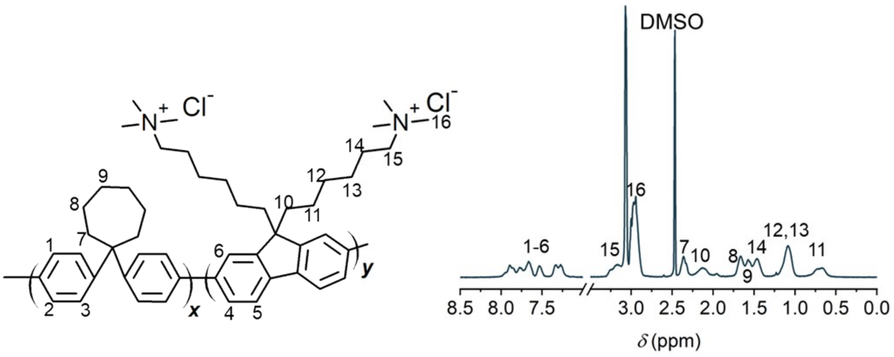
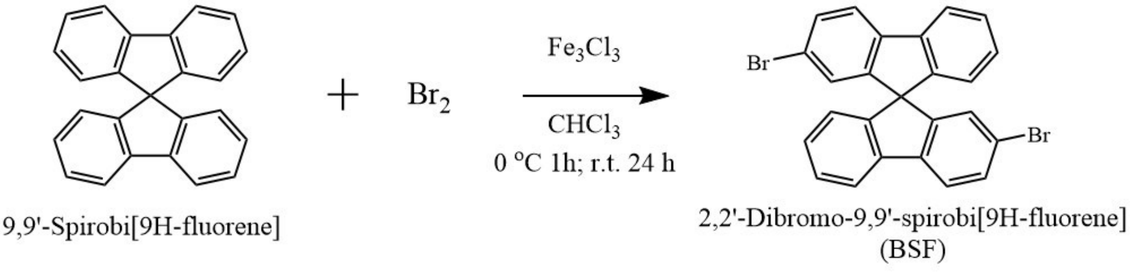


Fig. S3. ^{1}H NMR spectrum of C7-QAF-3.0 in Cl^- form in DMSO-d_6.

Synthesis of 2,2'-Dibromo-9,9'-spirobi[9H-fluorene] (BSF): BSF monomer was synthesized following a reported method with minor modifications.[3] Specifically, 9,9'-spirobi[9H-fluorene] (5.0 g, 15.80 mmol) was dissolved in chloroform (45 mL) and the solution was cooled to 0 °C under stirring. Then, $FeCl_3$ (7.67 mg, 47.29 μmol) was added as a catalyst. A solution of bromine (1.71 mL, 31.60 mmol, 2 equivalents) in chloroform (7 mL) was added dropwise over 1 h using a syringe. After the addition, the reaction mixture was allowed to warm to r.t. and stirred for 24 h. The reaction was quenched by the addition of a saturated aqueous solution of $Na_2S_2O_3$. The organic layer was separated, dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The resulting solid was purified by recrystallization three times from cyclohexane (or by washing with hot hexane), yielding the target product as a white solid (6.5 g, 87% yield). The purity was confirmed by ^{1}H and ^{13}C NMR spectra, respectively, as shown in **Fig. S4**.



Scheme S2. Synthesis of BSF monomer.

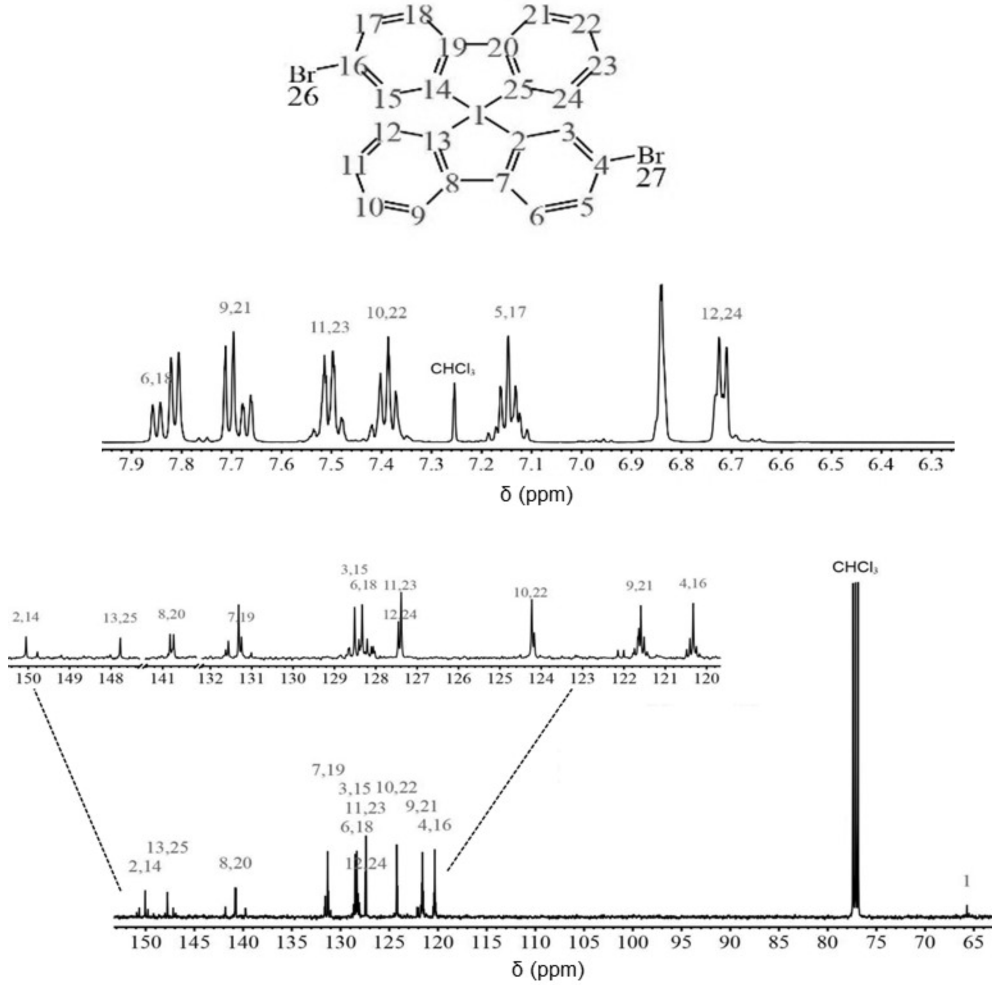


Fig. S4. ^{1}H (top) and ^{13}C (bottom) NMR spectra of BSF in CDCl$_3$.

Synthesis of C7-SF25-QAF-3.0: In the synthesis of C7-SF25-AF-3.0, BSF monomer was introduced into the C7-AF-3.0 polymer system in a 1:3 ratio of BSF to C7. Specifically, AF (1.5 mmol), C7 (0.80 mmol), BSF (0.27 mmol) and BPY (8.08 mmol) were dissolved in 6 mL of DMAc at 80 °C. Then, Ni(COD)$_2$ (7.69 mmol) was added to the above mixture, followed by polymerization for 3 h at 80 °C. The obtained mixture was poured into hydrochloric acid and washed with potassium carbonate aqueous solution and deionized water to obtain pale-yellow powder (0.91 g, 95% yield). The quaternization procedure of C7-SF25-AF-3.0 was the same as for C7-AF-3.0 polymer. The ^{1}H NMR spectrum of C7-SF25-QAF-3.0 is given in **Fig. S5**.

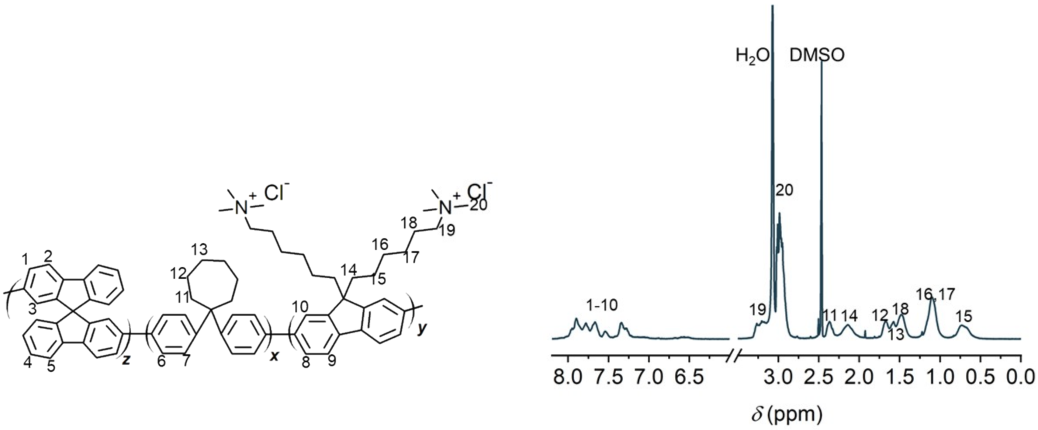


Fig. S5. ^{1}H NMR spectrum of C7-SF25-QAF-3.0 in Cl$^-$ form in DMSO-d_6.

Characterization: The proton (^{1}H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-ECA/ECX500 spectrometer, with deuterated dimethyl sulfoxide (DMSO-d_6) or deuterated chloroform ($CDCl_3$) containing an internal reference (tetramethylsilane, TMS) as the solvent. The surface area of the ionomers was evaluated using the Brunauer–Emmett–Teller (BET) method with an Autosorb-iQ instrument (Anton Paar GmbH, Austria). The Pt/C–ionomer inks were directly drop-cast onto copper grids and dried for transmission electron microscopic (TEM, Hitachi HT-7700) and scanning electron microscopic (SEM, Hitachi SU-9000) observations.

OH$^-$ conductivity, water uptake, and swelling ratio: A solution of 0.2 g of the quaternized polymer in 4 mL of DMSO was filtered and cast onto a flat glass plate (5 × 5 cm) at 50 °C for 12 h to produce a transparent membrane (in $MeSO_4^-$ form). Then, the membranes were soaked in 1 M KOH at 80 °C for 48 h to ion-exchange into OH$^-$ form and then washed with degassed water for more than 1 day. A 4-probe conductivity cell equipped with a Solartron 1255B AC impedance apparatus was used to measure the ion conductivity of the membranes under different temperatures. The OH$^-$ conductivity (σ, mS cm^{-1}) of the membranes was calculated as follows: $\sigma = l \times 1000/(A \times R)$, where l, A, and R are electrode distance (cm), conducting area (cm^2) and resistance (Ω), respectively. The membranes were immersed in 3 M NaCl aqueous solution for 48 h at r.t. for the ion exchange process and then the water uptake and swelling ratio of the membranes (in Cl$^-$ form) were measured.

Preparation and electrochemical testing of catalyst inks: The catalyst inks for hydrogen evolution reaction (HER) test were prepared by ultrasonically mixing 1 mg of Pt/C catalyst with a mixture including 20 μL of H_2O and 3.98 mL of ethanol. The ink was then dropped onto a glassy carbon rotating disk electrode (RDE, 5 mm diameter, Meiden Hokuto Co., Japan) as the working electrode, maintaining a loading of 10 μg_{Pt} cm^{-2}. 2 μL of 0.2 wt% binder solution (H_2O: methanol=3:2) was pipetted over the catalyst layer. A Pt mesh and reversible hydrogen electrode (RHE) were used as the counter and reference electrodes, respectively. The electrochemical measurements were carried out in a three-electrode glass cell using a potentiostat (HZ-5000, Meiden Hokuto Co., Japan) and rotation system (HR301, Meiden Hokuto Co., Japan) with 1 M KOH electrolyte solution. Cyclic voltammograms (CVs) were measured in N_2-saturated electrolyte at a scan rate of 50 mV s^{-1}. Polarization curves of HER were recorded at 3000 rpm and 10 mV s^{-1} scanning conditions.

Table S1. Molecular weights of the copolymers.

Copolymers	Molecular weight		
	M_w (kDa)	M_n (kDa)	PDI
QPAF-4-1.5	245.6	20.3	12.1
C7-QAF-3.0	87.3	21.8	4
C7-SF25-QAF-3.0	106.8	22.4	4.8

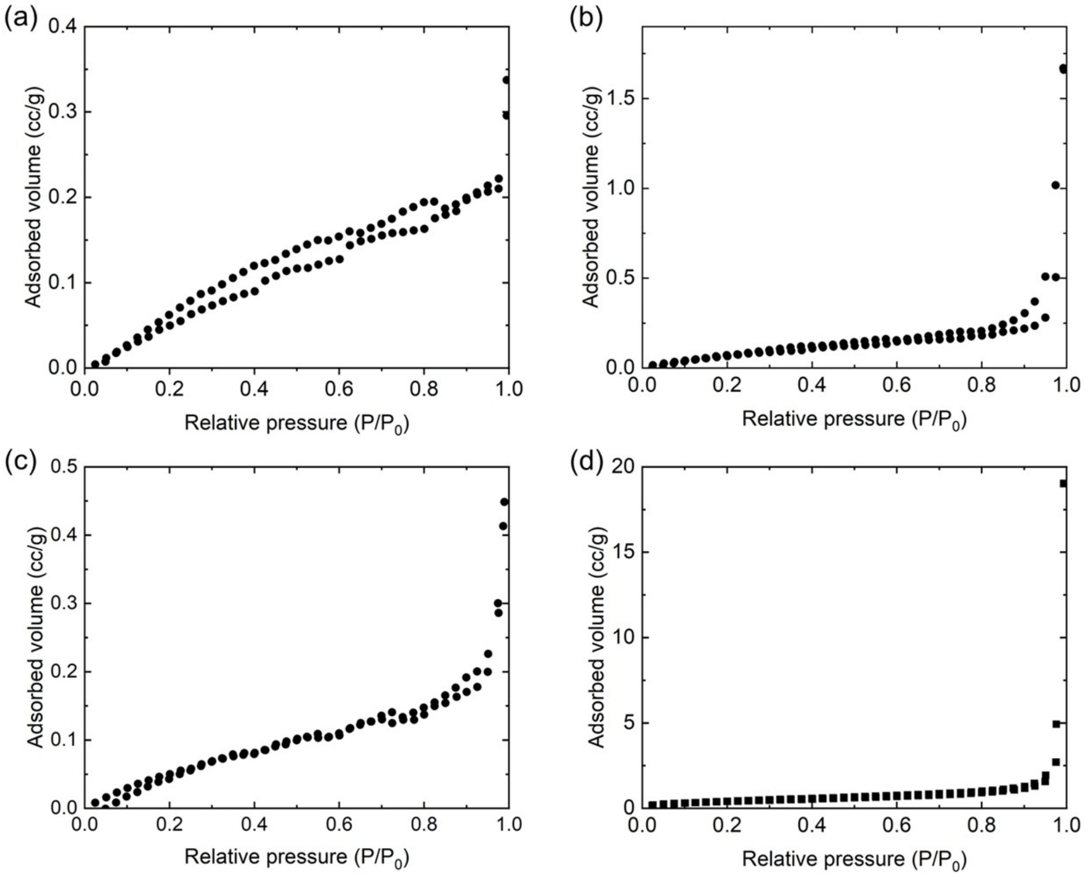


Fig. S6. N_2 adsorption–desorption isotherms of (a) Nafion, (b) QPAF-4-1.5, (c) C7QAF-3.0 and (d) C7-SF25-QAF-3.0 ionomers.

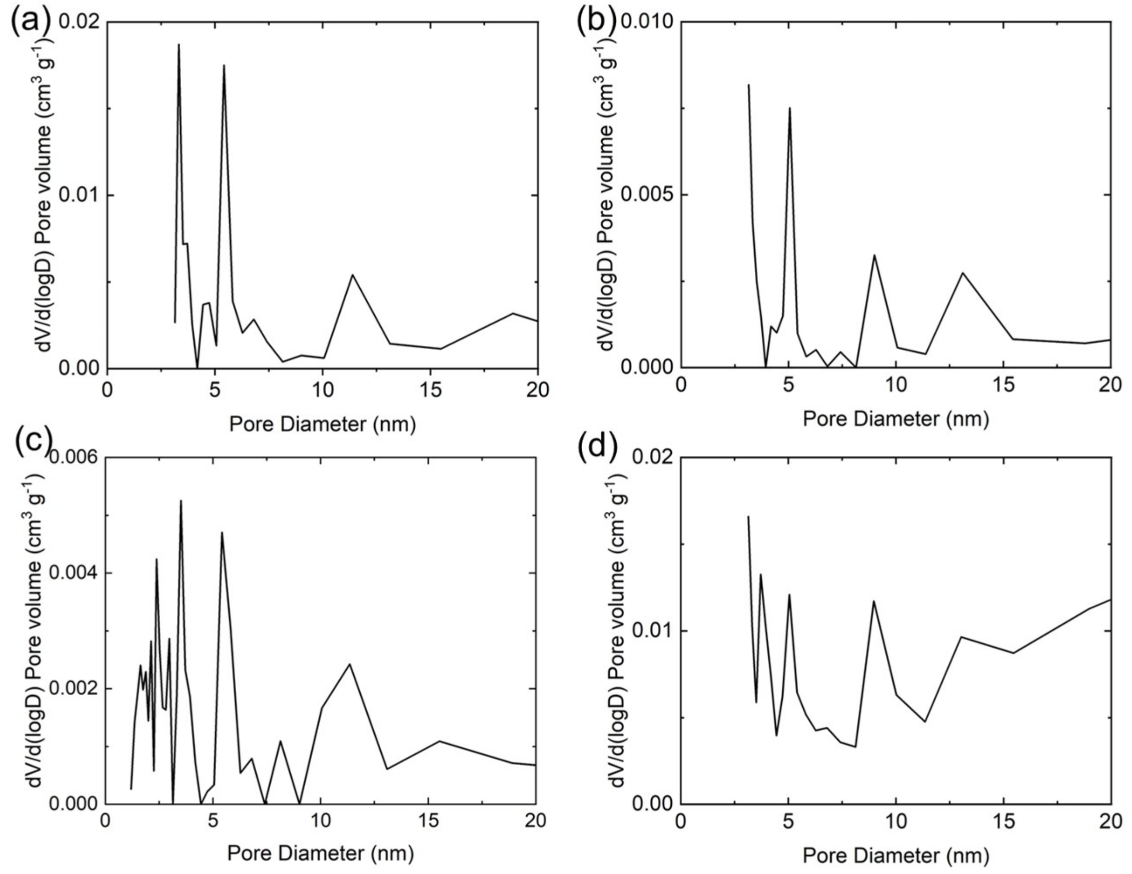


Fig. S7. Pore size distribution of (a) Nafion, (b) QPAF-4-1.5, (c) C7QAF-3.0 and (d) C7-SF25-QAF-3.0 ionomers.

Table S2. Summary of the BET analysis of different ionomer binders: surface area, pore volume and diameters.

Ionomers	BET Surface Area (m^2 g^{-1})	Cumulative Pore Volume (cm^3 g^{-1})	Pore Diameter (nm)
Nafion	6.89	0.005	3.32
QPAF-4-1.5	2.24	0.016	3.14
C7-QAF-3.0	1.54	0.003	2.39
C7-SF25-QAF-3.0	15.363	0.292	3.14

Table S3. Comparison of ion conductivity and alkaline stability of fluorine-free anion exchange membranes reported in literature.

Sample	Conductivity[a] (mS cm^{-1})	Alkaline stability				Reference
		Test conditions[b]			% σ loss[c] or NMR[d]	
		Conc.	T	Duration		
CGAEM-10%	~130 at 80^{o}C	2M NaOH	80^{o}C	2500h	9(σ)	4
PS-PiQpi-1.3	~38 at 80^{o}C	2M NaOH	90^{o}C	720h	~10(NMR)	5
di-QDPEEKOH	35.3 at 25 °C	2M KOH	60^{o}C	120h,	39.7 (σ)	6
PAQ-5	186.54 at 80 ^{o}C	1 M KOH	80^{o}C	2500 h	No change (NMR)	7
Lightly branched PTP membranes	126.4at 80°C	1 M NaOH	80°C	60 days	No change (NMR)	8
QPAF-4-1.5	86.9 at 80°C	4M KOH	80°C	402h	No change (NMR)	This work
C7-QAF-3.0	165.8 at 80°C	4M KOH	80°C	402h	No change (NMR)	This work
C7-SF25-QAF-3.0	196.3 at 80°C	4M KOH	80°C	402h	No change (NMR)	This work

[a] Refers to OH^{-} ionic conductivity

[b] Measured with AEMs soaked in alkaline solution at a certain temperature for a certain period

[c] Ratio of hydroxide conductivity losing after alkaline stability.

[d] Ratio of cationic loss measured by ^{1}H NMR

Table S4. Electrochemically active surface area (ECSA) of Pt using different ionomer binders measured in 1 M KOH.

Ionomers	ECSA / $m^2\ g^{-1}{}_{Pt}$
Nafion	58.3
QPAF-4-1.5	46.8
C7-QAF-3.0	54.4
C7-SF25-QAF-3.0	56.6

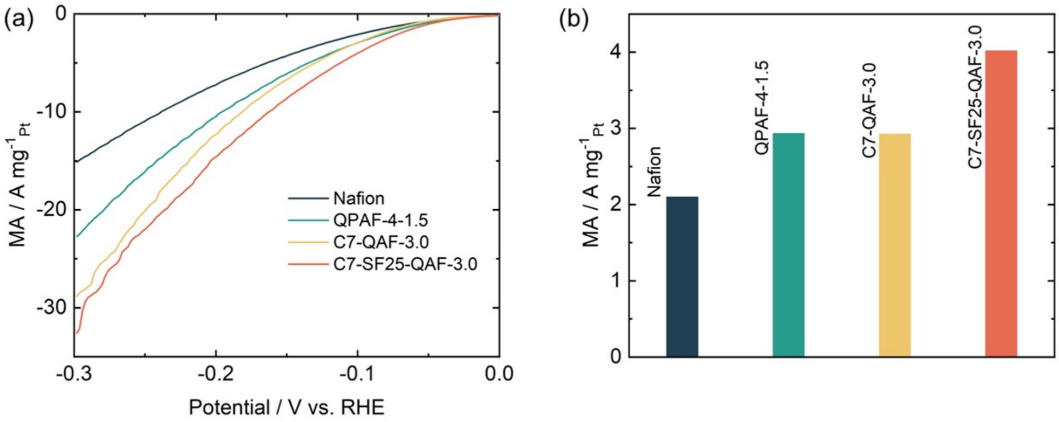


Fig. S8. (a) HER polarization curves with the y-axis plotted as mass activity (MA). (b) Comparison of mass activity using different ionomers at -0.1 V.

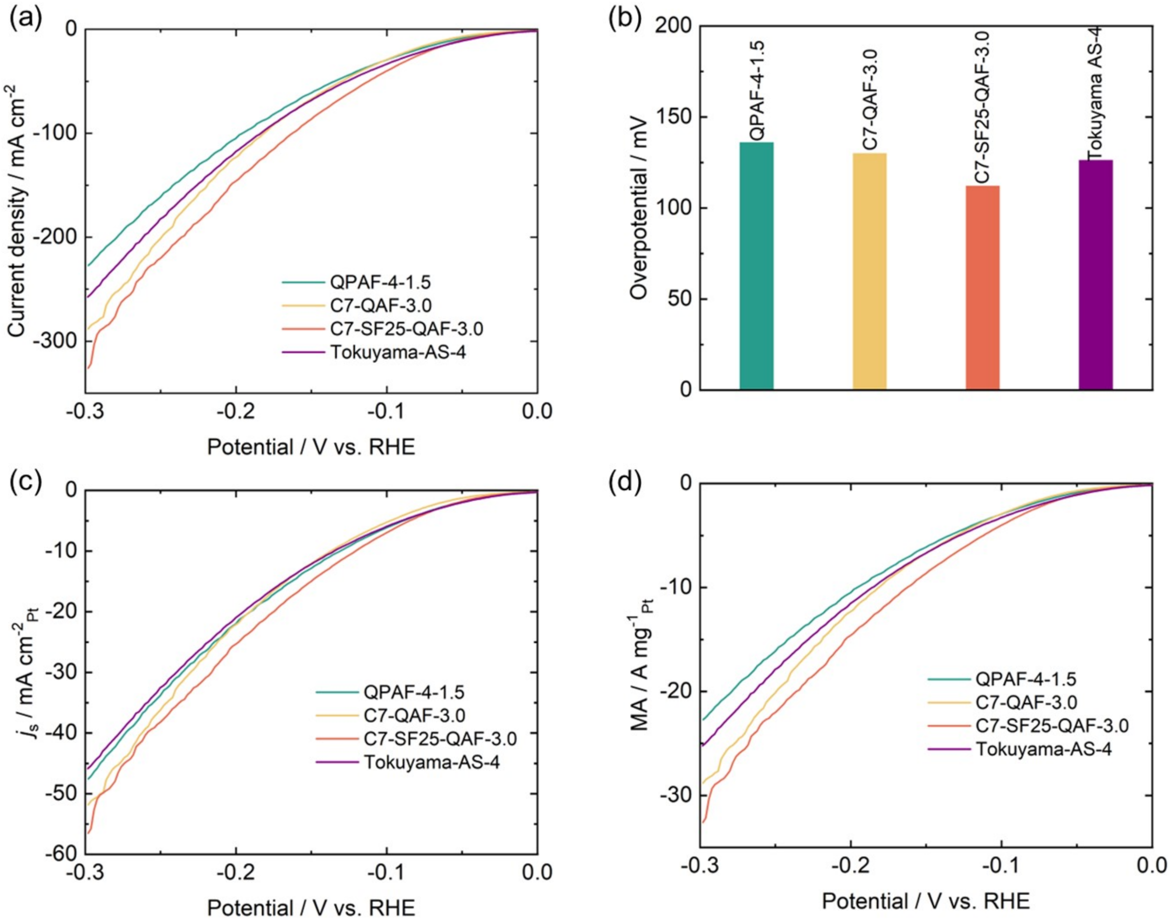


Fig. S9. (a) Linear sweep voltammograms (LSVs) of Pt/C catalyst covered with different ionomer binders in 1 M KOH at 10 mV s^{-1} and 3000 rpm. (b) HER overpotential at −50 mA cm^{-2}. (c) LSVs of Pt/C catalyst covered with different ionomer binders normalized with Pt surface area. (d) HER polarization curves with the y-axis plotted as mass activity (MA). (b) Comparison of mass activity using different ionomers at -0.1 V.

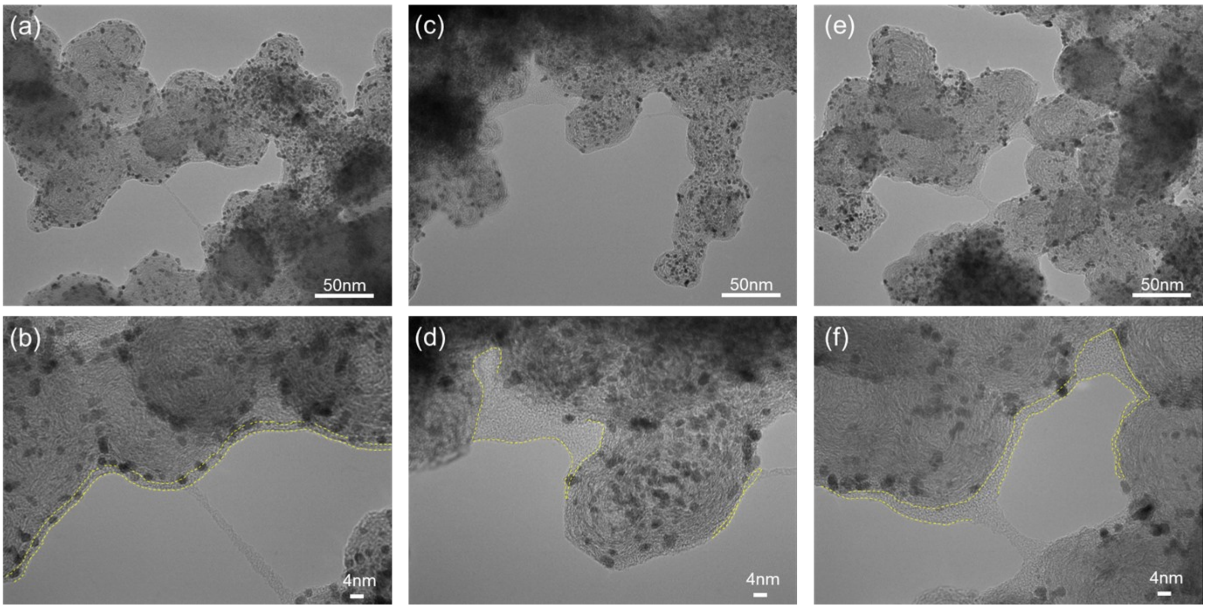


Fig. S10 TEM images of Pt/C catalyst coated by (a,b) C7-SF25-QAF-3.0, (c,d)QPAF-4-1.5, and (e,f)Tokuyama AS-4.

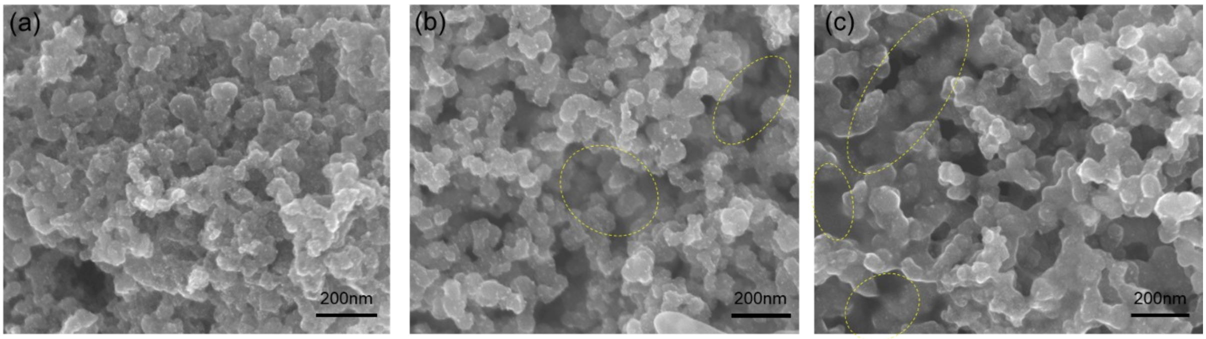


Fig. S11 SEM images of Pt/C catalyst coated by (a) C7-SF25-QAF-3.0, (c)QPAF-4-1.5, and (c)Tokuyama AS-4.

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