Electronic Supplementary Information (ESI)

Ultra-thin quaternized polybenzimidazole anion exchange membranes with throughout OH⁻ conducive highway networks for high performance fuel cell

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1. Experimental section

1.1 Materials.

Polybenzimidazole was purchased from Shanghai Shengjun Plastics Company. 2-chloroethyl ether (ClOCl), bis(2-dimethylaminoethyl) ether, ethanol, acetone, dimethyl sulfoxide (DMSO), N, N-Dimethylacetamide (DMAc), ethyl acetate, trimethylamine aqueous solution (33%), potassium hydroxide (KOH) and sodium iodide (NaI) were purchased and directly used without purification. The deionized water used in this work has been boiled in advance to remove CO_2.

1.2 Synthesis of tri-cationic grafting agent NON^+ON^+

The synthesis of tri-cationic grafting agent NON^+ON^+ is shown in Scheme S1 (a). 10.0 g of 2-chloroethyl ether (0.07 mol), 5.0 g of trimethylamine aqueous solution (0.028 mol) and 30 mL of acetone were added into a hydrothermal reactor, sealed and stirred at 80 °C for two days, and then cooled to room temperature in air. After centrifuging the mixed solution, the yellow down layer liquid was separated by centrifugation and washed repeatedly with acetone to obtain the precursor of grafting agent, $ClON^+$, with a yield of about 73%.

1 g of $ClON^+$ (0.005 mol) was dissolved in 20 mL ethanol, and then 8 g bis(2-dimethylaminoethyl) ether (0.05 mol) was added, refluxed at 78 °C for two days. The mixed solution was taken out and dried in an oven at 80 °C for 3 days to fully evaporate the ethanol and liquid reactant. After dried in a vacuum oven at 80 °C for 48 h, the NON^+ON^+ was prepared with a yield of about 80%.

1.3 The preparation of tri-cationic side chain grafted PBI (Tec-PBI-X) membrane

Tec-PBI-X was prepared by the method showed in Scheme S1 (b), where X represents the grafting ratio of flexible tri-cationic side-chain. The flexible non-cationic side chain grafted PBI material, PBIOCl was prepared as follow: 1 g PBI (0.0025 mol), 10 g KOH (0.179 mol) and 30 g 2-chloroethyl ether (0.211 mol) were dissolved in 90 mL DMAc. The mixture was stirred at room temperature for 7 days. The color of the solution changed from reddish brown to bright yellow, indicating the end of reaction. The reaction solution was precipitated in water to obtain a white precipitate. After washed with deionized water and acetone repeatedly and dried at room temperature, the flexible non-cationic side chain grafted PBI material, PBIOCl was obtained with a yield of about 94%.

The material with 50% tri-cationic side chain grafting ratio (Tec-PBI-50) was taken as an example. 0.5 g PBIOCl (0.817 mmol), 0.8 g tri-cationic graft agent NON^+ON^+ (2.285 mmol) and 3.28 g NaI (0.0218 mol) were dissolved in 30 mL DMSO, heated and stirred at 80 ^{o}C. After reacting for 2 days, the reaction solution was slowly precipitated in ethyl acetate to obtain white precipitate, followed by washing with deionized water and dried at room temperature for 24 h. The Tec-PBI-50 was obtained with a yield of 83%. Tec-PBI-X materials with different tri-cationic side chain grafting ratio were prepared by the similar method. The corresponding grafting ratio and IEC were shown in Table 1.

To prepare Tec-PBI-X membrane, 0.06 g Tec-PBI-X was dissolved in 6 mL DMSO and casted onto a glass plate. The Tec-PBI-X membrane was obtained by placing the glass plate in an oven at 60 °C for 2 days, and then soaked in 1 M KOH at room temperature for 2 days. After washed with deionized water for several times, the Tec-PBI-X membrane in OH⁻ form was obtained.
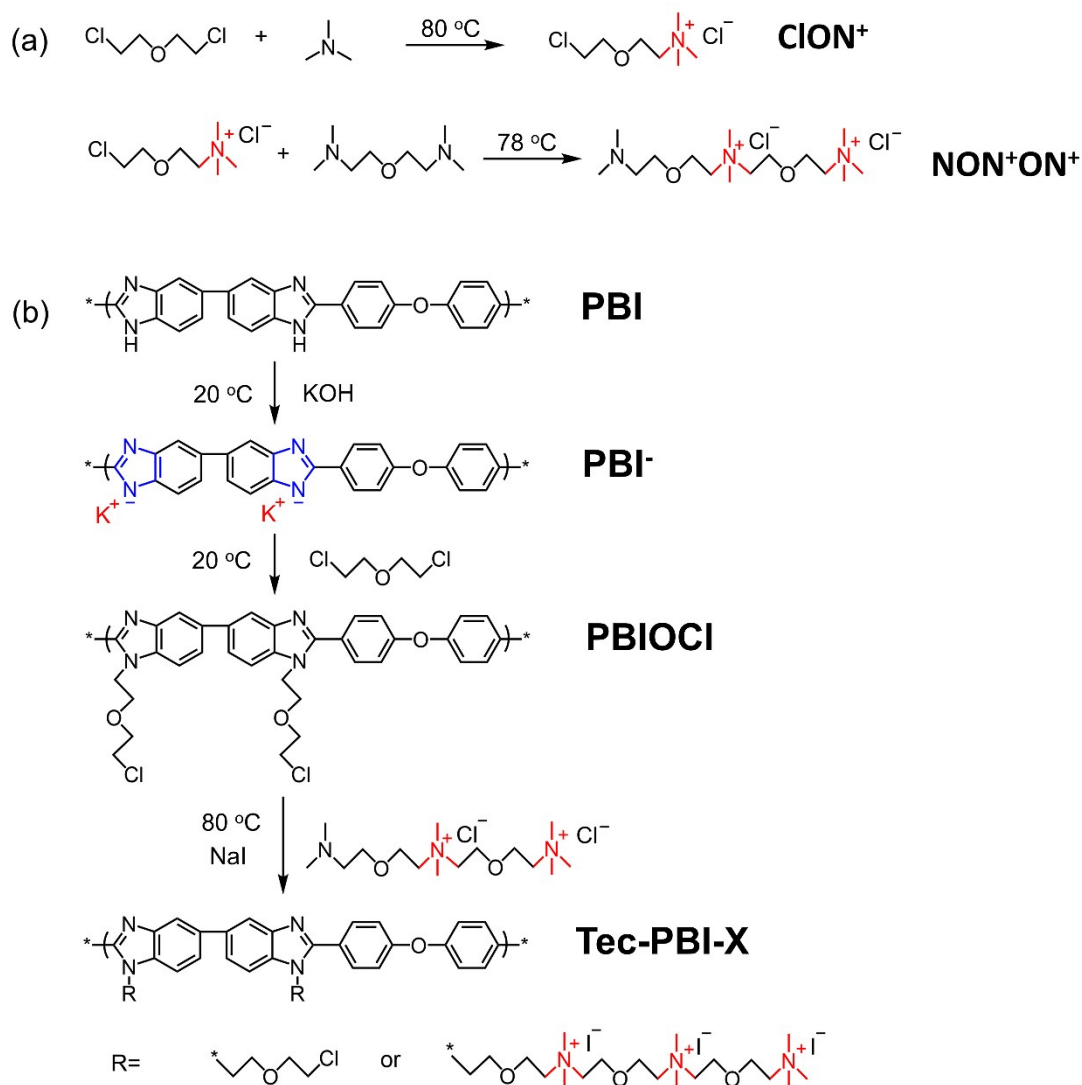
Scheme S1. Synthesis of tri-cationic graft agent NON⁺ON⁺ and Tec-PBI-X.

1.4 Characterization

The successful synthesis of Tec-PBI-X was confirmed by ^{1}H NMR with Varian Unity Inova 500 spectrometer and DMSO-d_6 as solvent.

SANS CMT8102 stretching tester was employed to test the mechanical properties of hydrated Tec-PBI-X membranes with the stretch rate of 10 mm min^{-1}.

Ion exchange capacity (IEC) of Tec-PBI-X membranes in OH$^-$ form was measured by back titration. The membranes were soaked in 25 mL 0.01 mol L^{-1} HCl solution for 24 h with stirring. After all the OH$^-$ in Tec-PBI-X membranes was exchanged by Cl$^-$, the solution was then back titrated by 0.01 mol L^{-1} NaOH with phenolphthalein as indicator. Each sample was tested three times and the testing results were averaged. The IEC of Tec-PBI-X membranes was calculated as eqn. (1):

$$IEC = \frac{C_1 V_1 - C_2 V_2}{m} \tag{1}$$

where C_1 and V_1 represent the concentration and the volume of HCl solution, respectively; C_2 and V_2 represent the concentration and the volume of NaOH solution, respectively; m represents the dry membranes weight.

The morphology of Tec-PBI-X membranes was investigated by transmission electron microscopy (TEM) and small angle X-ray scattering (SAXS). To test the TEM images, Tec-PBI-X

membranes were first stained by immersed in 2.5 M NaI for 48 h at 80 °C, then washed several times with deionized water to remove all the residual NaI and dried completely, and then TEM images were taken by JEOL JEM-2000EX microscope. Small angle X-ray scattering (SAXS) curves of hydrated Tec-PBI-X membranes (OH⁻ form) was tested by PANalytical X'Pert Powder X-ray diffraction system with a scattering angle of 0.6-5 ° and a scattering rate of 1 ° min⁻¹. The scattering vector can be calculated as eqn. (2):

$$q = \frac{4\pi \sin\theta}{\lambda} \tag{2}$$

where $\lambda=0.154$ nm represents the scattering wavelength and 2θ represents the scattering angle. The Bragg spacing was calculated by eqn. (3):

$$d = \frac{2\pi}{q} \tag{3}$$

To test the water absorption behavior of Tec-PBI-X, membranes were first saturated via immersion in deionized water for 24 h at room temperature. The residual water on the surface was then wiped away with filter paper, and the length and weight of the saturated membrane were quickly recorded (L_{wet} and W_{wet}). The samples were then placed in a vacuum oven at 100 °C for 24 h, after which the length and weight of the dried membranes were tested (L_{dry} and W_{dry}). Each sample was tested three times and the testing results were averaged. The water uptake and swelling ratio of Tec-PBI-X membranes were calculated by eqn. (4) (5)

$$\text{Water uptake (\%)} = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\% \tag{4}$$

$$\text{Swelling ratio (\%)} = \frac{L_{wet} - L_{dry}}{L_{dry}} \times 100\% \tag{5}$$

The number of water molecules per ionic group, hydration number λ, was calculated as eqn. (6):

$$\lambda = \frac{1000 \times WU}{IEC \times 18} \tag{6}$$

The conductivity of the Tec-PBI-X membranes in deionized water was measured using an electrochemical workstation (IviumTechnologies A08001) by the four-electrode AC impedance method over the frequency range from 1 to 10^5 Hz. Ionic conductivity (σ) was measured in deionized water at temperatures from 30 to 80 °C or in different relative humidity (RH) at 80 °C. Each sample was tested three times and the testing values were averaged. The conductivity can be calculated by eqn. (7):

$$\sigma = \frac{L}{RA} \tag{7}$$

where L is the distance between the two electrodes, R is the membrane resistance and A is the cross-sectional area of the tested membrane.

Alkaline stability of the Tec-PBI-X membranes was determined by monitoring the changes of the conductivity, IEC and chemical structure after immersing the membrane in 2 M KOH at 60 °C for different times. Then the membrane was immersed in deionized (DI) water for 24 h and then washed with DI water several times to remove the residual KOH; the residual hydroxide conductivity and IEC was measured at room temperature. Each sample was tested three times and the testing results were averaged. The chemical structure change was characterized by FTIR.

1.5 Fuel cell performance

Pt/C catalyst (70 wt. %), deionized water, ethanol and ionomer (Tec-PBI-50) were mixed to prepare a catalyst ink. The mixture was sonicated for 1 h in ice bath. The catalyst-coated membranes (CCM) were prepared by spraying the ink onto both sides of the membranes. The effective area of the electrodes and the catalyst loading is 4 cm^2 and 0.5 mg cm^{-2}, respectively. Before assembling, the CCM was immersed in 1 M KOH for 48 h and then placed in deionized water for another 48 h. To prepare the membrane electrode assembly, the final CCM was placed between two pieces of hydrophobic carbon paper.

Single fuel cell performance was tested by the 890e Multi Range fuel cell test station at 80 °C. The optimized dew points for the anode gas H_2 was controlled between 78 °C-80 °C, while the cathode O_2 gas was controlled between 80 °C-85 °C. The fuel was supplied to cell with a flow rate of 1 L min^{-1} with 0.15 MPa backpressure on both sides.

1.6 Molecular dynamics (MD) simulation details

Molecular dynamics (MD) simulations on Tec-PBI-50 were carried out by the Supercomputer Center of Dalian University of Technology. The binding energy between water molecule and side chains with different structure was calculated. The interactions and microstructure of Tec-PBI-X with different water uptake at room temperature were studied. In this work, the models comprise five polymer chains, and each chain is composed of 10 functionalized repeat units. To fully

equilibrate the amorphous cells, an annealing procedure was employed to treat the polymer chains.

The local probability density of finding B atoms at a distance r from A atom is calculated by radial

distribution function (RDF), g(r). Its corresponding coordination number (CN) is also calculated

by integrating RDF, which reveals the number of B atoms around A atoms. RDF and CN were

obtained by the eqn (8) (9)

$$g_{A-B}(r) = \frac{n_B(r)}{\rho_B 4\pi r^2 \Delta r} \qquad (8)$$

$$CN = \int_0^r \rho_B 4\pi r^2 g_{A-B}(r) dr \qquad (9)$$

where $n_B(r)$ is the number of B atoms within a distance r of a central A atom, and ρ_B represents for

the bulk number density of B atoms.

2. ^1H NMR spectra of synthesized compounds

As shown in Fig. S1, the quaternary ammonium cation is formed after the reaction of 2-

chloroethyl ether with trimethylamine, so the characteristic peak of quaternary ammonium cation

(H_5-H_7 at δ=3.10 ppm) can be observed in the ClON$^+$ spectrum. NON$^+$ON$^+$ was synthesized by

the reaction of bis (2-dimethylaminoethyl) ether and the ClON$^+$. The area of characteristic peaks

of quaternary ammonium cation (H_7''-H_8'' , H_{13}''-H_{15}'' at δ=3.10 ppm) can be observed in the ^1H

NMR spectrum of NON⁺ON⁺, and the characteristic peaks of tertiary amine (H$_1$'', H$_2$'' at δ=2.17 ppm, H$_3$''at δ=2.42 ppm) can also be observed, indicating the successful synthesis of NON⁺ON⁺.
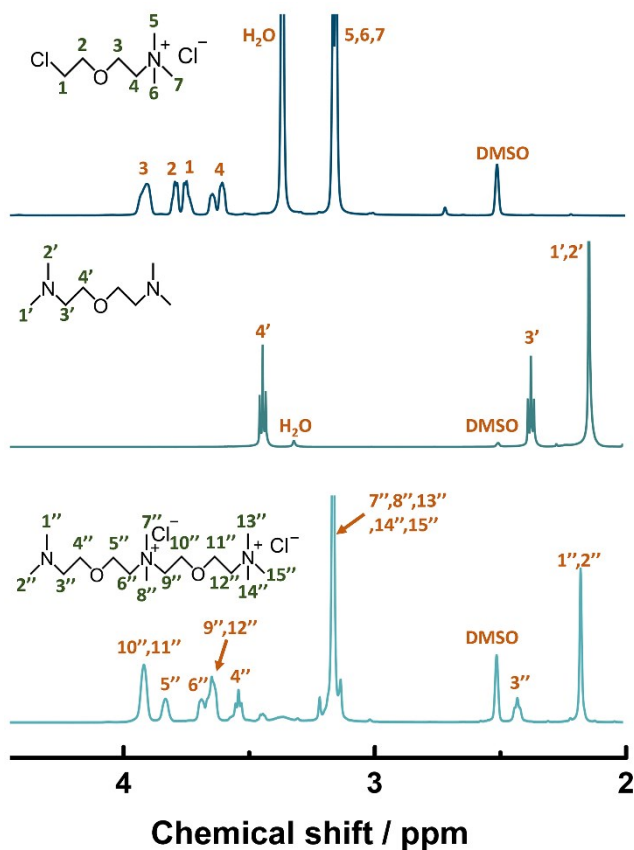

Fig. S1 ¹H NMR spectra of tri-cationic graft agent NON⁺ON⁺ and its reaction intermediates

3. Molecular dynamics simulation study on cation aggregation

The effects of different side chain structures (the different number of cationic groups and ether bonds) on the aggregation of cationic groups in AEM, i.e. the ability to form ion clusters, was investigated by molecular dynamics simulation. In addition to the Tec-PBI-50 structure, three quaternized PBI with different side chain structure (Tec only PBI, TC PBI and Sec PBI as shown in Fig. S2) were designed. The grafting ratio, structure and molecular dynamics simulation results of RDF and CN of (N^+ & N^+) were shown in Fig. S2 and Table S1.

By comparing the RDF and CN of (N^+ & N^+) in Tec-PBI-50 and Sec PBI, it can be seen that the tri-cationic side chain contributes more to the aggregation ability of ion cluster than the single cation side chain. The RDF peak radius of quaternary ammonium cation in Tec-PBI-50 is lower than that of Sec PBI (6.8 Å vs. 9.0 Å), and the corresponding CN is larger in 5-10 Å, which indicates a stronger cationic group aggregation ability, which is because the cations in the same side chain are closer and easier to aggregate.

By comparing the RDF and CN of (N^+ & N^+) in Tec-PBI-50 and Tc-PBI, it reveals the effect of ether bond on the aggregation of ion clusters. The RDF of Tec-PBI-50 still has a smaller peak position (6.8 Å vs. 7.1 Å), and the CN is larger in the range of 5 Å-10 Å, which is because the side chain of Tec-PBI-50 contains ether bond, which is more flexible and significantly enhances the mobility of the side chain and the cationic group, makes them easier to aggregate.

The RDF and CN analysis of (N^+ & N^+) in Tec-PBI-50 and Tec only PBI shows that the grafted non-ionic side chain also plays an important role in the formation of ion clusters. Although both of them were grafted with 50% of the tri-cationic side chains, there are 50% more ether-

containing non-ionic side chains in Tec-PBI-50. The peak of RDF of (N^+ & N^+) in Tec-PBI-50

appears slightly shorter than that of Tec only-PBI (6.8 Å vs. 6.9 Å), and the corresponding CN is

larger in the range of 5 Å -10 Å. The ether bonds on these non-ionic side chains can form hydrogen

bond networks with water molecules, thus slightly narrowing the distance between the three ion

side chains containing ether bonds. At the same time, the ether-containing non-ionic side chains

also show some hydrophilicity. Therefore, the grafting of these side chains will promote the

aggregation of cationic groups and the micro phase separation in the membrane. As a conclusion,

Tec-PBI-50 has the strongest cationic group aggregation ability, i.e. the ability to form ion clusters.
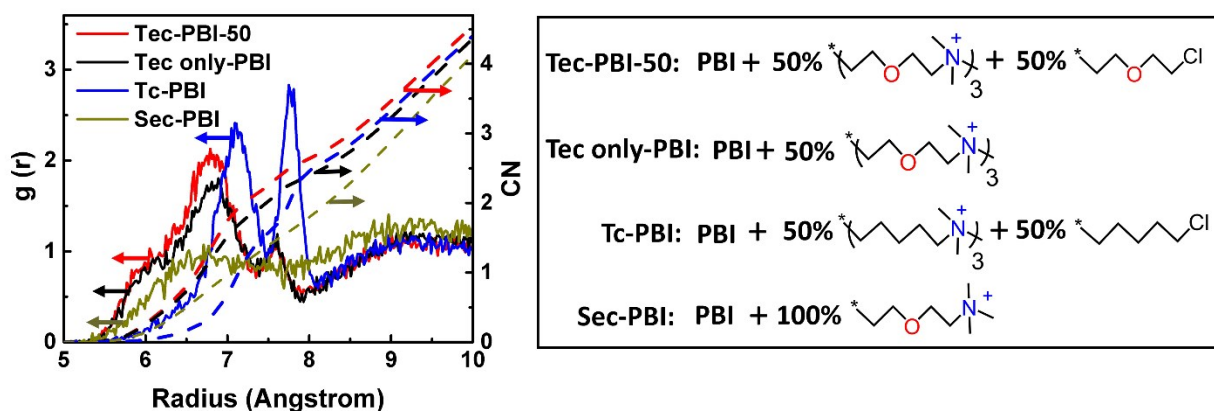

Fig. S2 Molecular dynamics simulation study on cation aggregation ability (RDF and CN of N^+ &

N^+) of AEMs with different side chains.

Table S1 Radial distribution function and coordination number of cationic groups (N^+ & N^+) for

AEMs with different side chains

	Tec-PBI-50	Tec-only-PBI	Tc-PBI	Sec-PBI

Peak position of RDF (Å)	6.8	6.9	7.1	9.1
CN (at 7.0 Å)	1.75	1.53	0.70	0.90

4. Water uptake (WU) and hydration number (λ) of Tec-PBI-X membranes

Table S2 Water uptake (WU) and hydration number (λ) of Tec-PBI-X membranes at different temperature.

	WU / % (30 °C)	WU / % (50 °C)	WU / % (80 °C)	λ (30 °C)	λ (50 °C)	λ (80 °C)
Tec-PBI-30	30.7	35.4	44.6	6.8	7.9	10.0
Tec-PBI-40	58.1	64.1	80.6	10.9	12.0	15.1
Tec-PBI-50	67.7	77.6	101.3	11.3	12.9	16.8
Tec-PBI-60	98.1	114.2	160.6	14.9	17.4	24.4

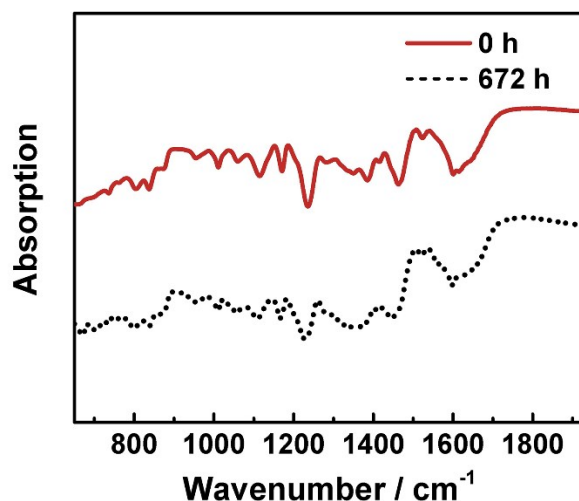## 5. FTIR spectra of the Tec-PBI-50 before and after alkali treatment

Fig. S3 FTIR spectra of the Tec-PBI-50 before and after alkali treatment

6. Properties of quaternized PBI and multi-cation side chain type AEMs reported in literatures

Table S3 Properties of quaternized PBI and multi-cation side chain type AEMs reported in literatures.

AEMs	Polymer matrix	Cationic group/ Number[a]	IEC_m[b] (mmol g^{-1})	HC[c] 30/80 °C (mS cm^{-1})	SR[d]/WU[e] (%)	Tensile strength[f] (MPa)/Elongation at break[g] (%)	OCV(V)/Peak power density[h] (mW cm^{-2})	Alkaline stability[i]	Ref.
Tec-PBI-50	PBI	TMA[s]/3	3.10	63.2/131.8	20.3/67.7	14.0/65.9	1.0/1162.3 (80 °C 0.15 MPa)	78.0% (2 M KOH 672 h 60 °C)	This work
QPBI-2/1[j]	PBI	Morpholin cation	1.94	13.0/56.0	34.0/85.0 (60 °C)	45.0/6.0	0.93/3.1(30 °C)	46.0% (6 M NaOH 60 °C 7 days)	37
msQPBI[k]	PBI	Imidazolium/1	1.49	5.1/27.2	4.1/43.8	19.2/8.0	-	28.6% (1 M KOH 30 °C 4 days)	36
OBImPPO[l]	PPO	Imidazolium/2	2.10	44.0/64.0 (65 °C)	27.0/82.0	5.8/104.8	0.93/437.0(65 °C)	72.7% 1 M NaOH 4 days 60 °C	43
Tri-QPESOH[m]	PES	DABCO/3	2.31	55.0/130.9	18.0/48.0	10.3/4.3	-	70.0% 4 M NaOH 144 h 25 °C	12

Sample	Polymer	Cation/[a]	IEC[b]	[c]	[d]	[e]	[h]	[i]	Ref
DPM/DMBP-QTB-11.5[n]	DPM/DMBP	TMA/4	1.67	43.3/103.9	14.6/41.2	29.7/4.86	0.94/158.0(60°C)	81.6% 1 M NaOH 720 h 60°C	50
T20NC6NC5N[o]	PPO	TMA/3	2.74	72.0/175.0	28.0/140.0	-	1.0/364.2(80°C 0.1 MPa)	90% 1 M NaOH 500 h 80°C	51
trimPES-0.4[p]	PES	Imidazolium/3	2.31	48.0/120.0	25.5/48.10	19.1/19.7	1.0/134.4(60°C)	75.8% 1 M NaOH 500 h 60°C	52
x(QH)3QPPO-40[q]	PPO	TMA/4	3.59	58.0/110.0	18.6/101.2	17.0/34.4	0.98/302.0(60°C 0.1 MPa)	61.2% 1 M NaOH 720 h 80°C	53
TQAPEK-0.5[r]	PEK	TMA/3	1.94	58.3/132.8	23.3/50.0	19.6/10.0	1.0/206.0(60°C)	77.6% 2 M KOH 600 h 60°C	54
HBPAEK-28-18[s]	HBPAEK	TMA/3	2.21	67.0/122.5	26.5/47.1	18.5/17.4	0.98/188.6(60°C)	85.1% 2 M KOH 500 h 80°C	55
15-CQP-3[t]	PPO	TMA/4	2.00	18.0/34.0 (25°C/60°C)	6.4/12.4 (25°C)	-	0.98/77.0(60°C)	51.0% 1 M KOH 480 h 60°C	56
M-OH-1:1[u]	SEBS	TMA/2	1.88	14.9/28.2	4.9/6.5	35.0/49.4	1.0/416.0(60°C 0.2 MPa)	95.2% 1 M KOH 480 h 60°C	26

[a]The number of cationic groups in side-chain; [b]The measured IEC; [c]Conductivity in water; [d]Swelling ratio at 30 °C; [e]Water uptake at 30 °C; [f,g]Fully hydrated membrane; [h]H_2/O_2 fuel cell assembled with AEM; [i]Alkaline stability: percentage of remained conductivity after soaking in alkaline solution; [i]Quaternized polybenzimidazole having imidazolium moiety in the side chains; [j]Quaternized polybenzimidazole having imidazolium moiety in the main-chains; [k]Quaternized polybenzimidazole having imidazolium moieties in both the main-chains and side chains; [l]polyelectrolyte containing rotatable ethylene oxide side-chains; [m] triquaternized poly (ether sulfone) AEMs; [n]Multi-cation quaternized random copolymer synthesized from monomers 4,4'-diaminodiphenylmethane (DPM) and 4,4'diamine-3,3'-dimethyl-biphenyl (DMBP) ; [o]poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)-based AEMs with different kinds of cationic side chains; [p]Fluorene-based poly (arylene ether sulfone) grafted with three imidazolium cations and hexyl spacers side chains; [q]Poly(2,6-dimethylphenylene oxide) -based AEMs containing flexible, long-chain, multication cross-links; [r]Poly(ether ketone)s bearing multication side chains; [s]Hyperbranched poly(arylene ether ketone) anion exchange membranes; [t]Poly(2,6-dimethyl-1,4-phenylene oxide with tris[2-(dimethylamino)ethyl]amine) anion exchange membranes; [u]poly(styrene-b-(ethylene-co-butylene)-b-styrene) triblock copolymer based crosslinked membranes.