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Supporting Information for

Tuning thePropertiesof Poly(2,6-dimethyl-1,4-phenylene oxide) Anion Exchange Membranesand Their Performance in H_2/O_2 Fuel Cells

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Experimental Section

Materials. Commercially availablepoly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was obtained from Sigma-Aldrich (M_n=20,000). *N*-Bromosuccinimide (NBS), 2,2'-azobis-isobutyronitrile (AIBN), *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA), cuprous bromide (CuBr), trimethylamine, 6-chloro-1-hexyne, propargyl bromide, N,N-dimethyl-butylamine, and N,N-dimethyloctadecylamine were purchased from ENERGY CHEMICAL (China). The azide-functionalized PPOs(PPO-N_3) with various degrees of functionalization (DF) (14-40 %) were synthesized according to our previous reports.[1,2]

Synthesis of Alkyne-functionalized Quaternary Ammoniums. The Menshutkin reaction has been employed to synthesize thealkyne-functionalized quaternary ammoniumsmoieties by reacting between6-iodohex-1-yne or propargyl bromide and a corresponding tertiary amine, as shown in Scheme S1. In order to increase the reactivity of6-chlorohex-1-yne, a commonly available reagent, 6-chlorohex-1-yne was converted to 6-iodohex-1-yneby treatment with NaI in acetone according to the reported procedure.[3] Subsequently, the obtained 6-iodohex-1-yne and trimethylamine were dissolved in toluene. The mixture was heated at 80 °C for 24 h. After cooling to room temperature, the resulting white solid was filtered, washed with diethyl ether several times, and dried at room temperature *in vacuo* to obtainN,N,N-trimethylhex-5-yn-1-aminium chloride (QA-2) with a yield of 90 %.

N,N-dimethyl-N-(prop-2-yn-1-yl)butan-1-amonium bromide (QA-1), N-butyl-N,N-dimethylhex-5-yn-1-amonium iodide (QA-4), and N-(hex-5-yn-1-yl)-N,N-dimethyloctadecan-1-amonium iodide (QA-18), were synthesized using the similar procedure as mentioned above. The yields of QA-1, QA-4, and QA-18 were 95 %, 86 % and 75 %, respectively.

Synthesis of Quaternized PPO Copolymers. QuaternizedPPO copolymers were synthesized using a Cu(I) catalyzed azide−alkyne cycloaddition (CuAAC) reaction following previous reports.[1]As a typical procedure: to a 25 mL Schlenk flask with a magnetic stirring bar, PPO-N_3 (DF=0.3) (0.5 g, 1.13mmolazide groups), QA-1 (0.300

g, 1.36mmol), ligand (PMDETA, 0.68mmol), catalyst (CuBr, 0.34mmol) were dissolved in 7 mL of NMP. The flask was degassed by three freeze-pump-thaw cycles to remove the oxygen. The click reaction was then carried out at 50 °C for 12 h. The CQA-30 copolymer was obtained by precipitatingthe resulting reaction into water, washing with water three times, and dried at 60 °C for 24 h *in vacuo*.

The LSCQA-x, SCCQA4-x and SCCQA18-x copolymer were synthesized according to the aboveprocedure where x denotes the degree of functionalization, but using the QA-2, QA-4, and QA-18 as starting materials instead of QA-1 respectively. BTMA-30 and SCQA-30 copolymers were also synthesized following our previous reports.[1]

Membrane Fabrication and Anion Exchange. The quaternized PPO copolymers were dissolved in NMP (10 wt %). The brown-colored membranes were then obtained by solution casting at 80 °C for 12 h. The membranes in hydroxide form or bicarbonate form were obtained by treating membranes in 1 M NaOH or 1M $NaHCO_3$ at room temperature for 48 h, respectively.

Characterization and Measurements. NMR spectra were recorded on a Bruker DPX spectrometer (400 MHz or 600 MHz) at room temperature using $CDCl_3$or DMSO-d_6 as solvents. Small-angle X-ray scattering (SAXS) of dry membranes were obtained using a SAXSess mc^2 instrument (Anton Paar, Austria), equipped with a Cu-Kα slit-collimated X-ray source operating at 40 kV and 50 mA.Atomic force microscopy(AFM) phase images of PPO AEMs were recorded on a Multimode V

(Veeco Co., USA) in tapping mode at ambienttemperature. Tensile measurements of PPO AEMs in the dry state werecarried out with an Instron-1211 (Instron Co., USA)mechanical testing instrumentat a crosshead speed of 1 mm/min.The thermal stability of membranes was determined by thermogravimetric analysis (TGA) (PerkinElmerTGA-7, USA) under a N_2 flow with the heating rate of 10 °C/min, and all the samples was pre-dried at 60 °C for 24 h under vacuum.

Water uptake (WU) of membranes in hydroxide form was measured by a typical method. After drying the membrane at 60 °C in vacuum for 24 h, the dried membrane was immersed in water at given temperature for 24 h, and weighed on an analytical balance until a constant mass was obtained. Water uptake was calculated by the equation:

$$\mathrm{WU} = \frac{\mathrm{W_{wet}} - \mathrm{W_{dry}}}{\mathrm{W_{dry}}} \times 100\%$$

where w_{wet} and w_{dry} are the mass of wet and dried membrane, respectively.

The hydration number (λ), defined as the number of absorbed H_2O per quaternary ammonium group, was calculated from:

$$\lambda = \frac{\left(\mathrm{w_{wet}} - \mathrm{w_{dry}}\right) \times 1000}{IEC \times \mathrm{w_{dry}} \times 18}$$

where 18(g/mol)is the molar mass of water

The experimental *IEC* values (IEC_{exp}) of membranes were determined by backtitration methods. Typically, the membrane in hydroxide form was immersed into 10 mL of HCl solution (0.01 M) for 24 h in order to fully neutralize the hydroxide ions in the membrane. The unreacted HCl was titrated by a standardized NaOH solution (0.01 M) using phenolphthalein as an indicator. Every membrane was tested in triplicate. The IEC_{exp} values were calculated as:

$$IEC_{exp} = \frac{\mathrm{V_{HCl}} \times \mathrm{c_{HCl}} - \mathrm{V_{NaOH}} \times \mathrm{c_{NaOH}}}{\mathrm{w_{dry}}}$$

where V_{HCl} and c_{HCl} are the volume and concentration of the standardized HCl solution; V_{NaOH} and c_{NaOH} are the volume and concentration of the standardized NaOH solution; W_{dry} is the weight of dry membrane.

The volumetric IEC_{v} values were calculated from:

$$IEC_{v} = \frac{IEC_{\mathrm{w}}}{\frac{1}{\rho_{\mathrm{polymer}}} + \frac{WU(\mathrm{wt\%})}{100 \times \rho_{\mathrm{water}}}}$$

where IEC_{w} is the gravimetric IEC (meq/g) and ρ_{polymer} (g/cm^3) refers to the density of membrane.

The diffusion coefficients of the mobile ions for membranes were calculated from the Nernst−Einstein equation:

$$D = \frac{\sigma \mathrm{RT}}{\mathrm{cF}^2\mathrm{Z}^2}$$

where σ is the measured conductivity, R is the ideal gas constant, T is the absolute temperature (K), c is the concentration of ions, F is Faraday'sconstant and Z is number of charges.

The swell ratio (SR) was calculated from the equation SR=$((L_{wet}-L_{dry})/L_{dry})$, where L_{wet} and L_{dry} are the lengths of the wet and dry membrane at room temperature, respectively.

Ionic conductivity (σ, mS/cm) of each membrane (size: 1 cm×4 cm) was obtained from$\sigma=d/LWR$ (*d*is the distance between reference electrodes, and *L* and *W* are the thickness and width of the membrane, respectively). The resistance value (*R*) was measured over the frequency range from 50mHz to 100 kHz by two-point probe alternating current (ac) impedance spectroscopy using an electrode system connected with an impedance/gain-phase analyzer (Bio-Logic VSP-300, FR). The membranes were secured in a Teflon cell, and the conductivity measurements under fully hydrated conditions in the longitudinal direction were carried out with the cell immersed in deionized water, which was degassed and blanketed with flowing Ar gas.

The alkaline stability of membranes was evaluated at 80 °C in 2M, 5M or 10 M NaOH, and fresh alkaline solution was added every three days. After 200 h, membranes were washed with deionized water several times to remove residual NaOH, and the changes of hydroxide conductivity of membrane before and after alkaline stability test wererecorded.

Membrane Electrode Assembly (MEA) Fabrication and Fuel Cell Testing

The catalyst-coated membrane (CCM) method was adopted to prepare the membrane electrode assemblies for fuel cell testing. Pt/C (40 wt%, Johnson Matthey Co.) was mixed deionized water, 1-propanol, and ionomer solution (5 wt%, AS-4, Tokuyama, Japan) using magnetic stirring and ultrasonication to obtain a well-dispersed catalyst ink. To obtain a CCM, the as-prepared ink was sprayed onto both sides of membranes (about 50 μm in thickness) using an air spray gun. The Pt loading and ionomer content in catalyst layer were calculated to be 0.5 mg/cm^2 and 20 wt% respectively. The area of the electrodes was 5 cm^2. The MEA was fabricated by assembling CCM and carbon paper (HCP120, HESEN, China) together without hotpressing.

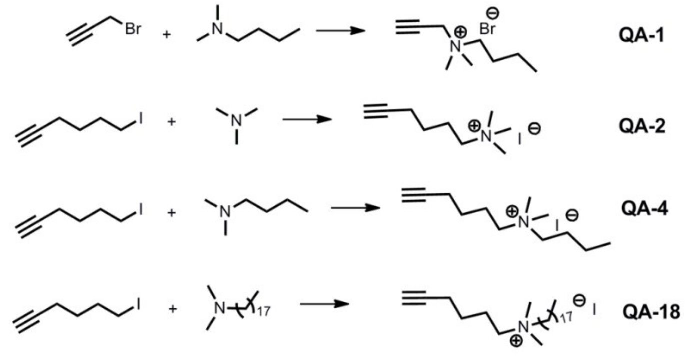
Fuel cell testing was conducted with a commercial fuel cell testing system (Smart2 PEM/DM, WonATech, Korea). The fuel cell performance was measured at 60 °C with a flow rate of 200 sccm for both H_2 and O_2 under full humidification with no backpressure. The MEA was activated under potentiostatic mode at 100 mV until the current density increased to a maximum and became constant for 30 min. After full activation, the polarization curve was measured under galvanostatic mode by holding the fuel cell at serial constant currents for 30 s. The durability test was conducted at 60 °C with a flow rate of 200 sccm for both H_2 and O_2 under full humidification with no backpressure. A current density of 100 mA/cm^2 was applied to the fuel cell, and the cell voltage as a function of time was recorded.

References

(1) Li, N.; Guiver, M. D.; Binder, W. H. *ChemSusChem*, **2013**, *6*, 1376-1383.

(2) Liu L.; He S.; Zhang S.; Zhang M.; Guiver M. D.; Li N. *ACS Appl. Mater. Interfaces*, **2016**, *8*, 4651-4660.

(3) Trost, B. M.; Breder, A.; Kai, B. *Org. Lett.*, 2012, 14, 1708-1711.



Scheme S1 Synthesis of alkyne-functionalized QAs.

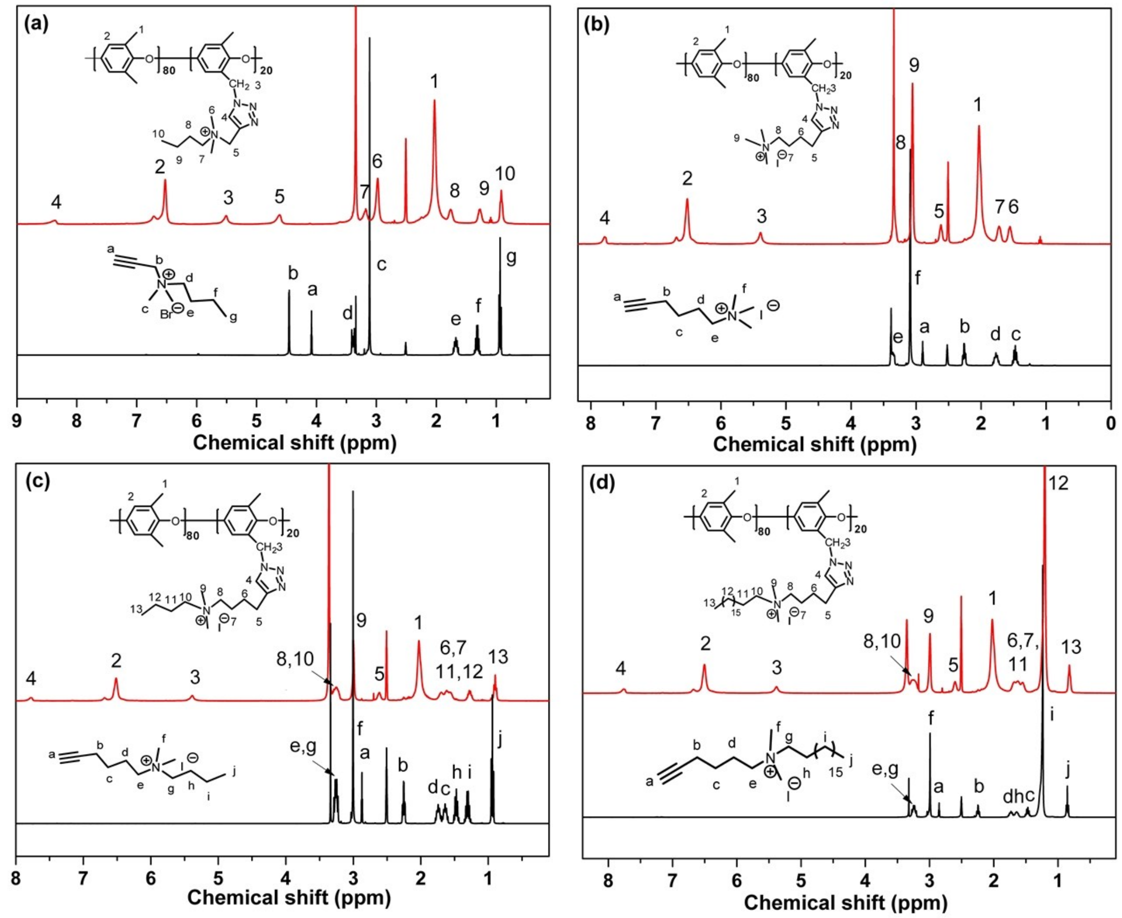


Fig. S1 ^{1}H NMR spectra of (a) CQA-20 copolymer and QA-1, (b) LSCQA-20 copolymer and QA-2, (c) SCCQA4-20 copolymer and QA-4, and (d) SCCQA18-20 and QA-18 in DMSO-d_6.

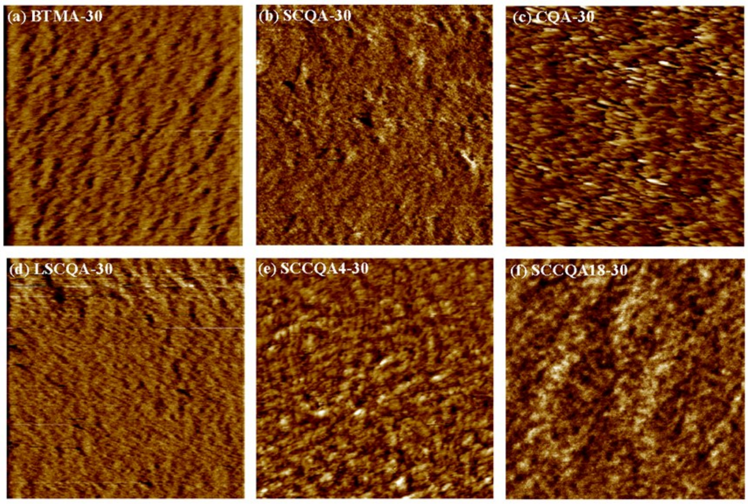


Fig. S2 AFM phase images of PPO AEMs in a taping mode. Scan box: 500 nm×500 nm.

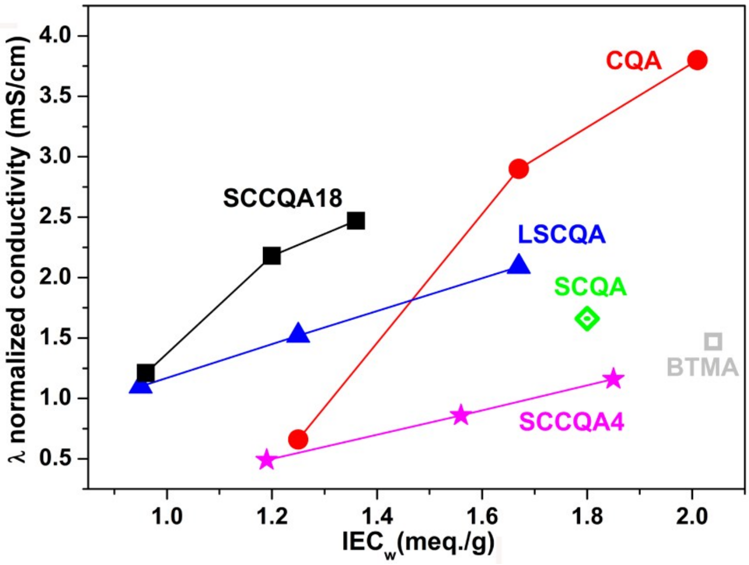


Fig. S3 Hydration number (λ)-normalized hydroxide conductivity at 20 °C in water as a function of IEC_w values.

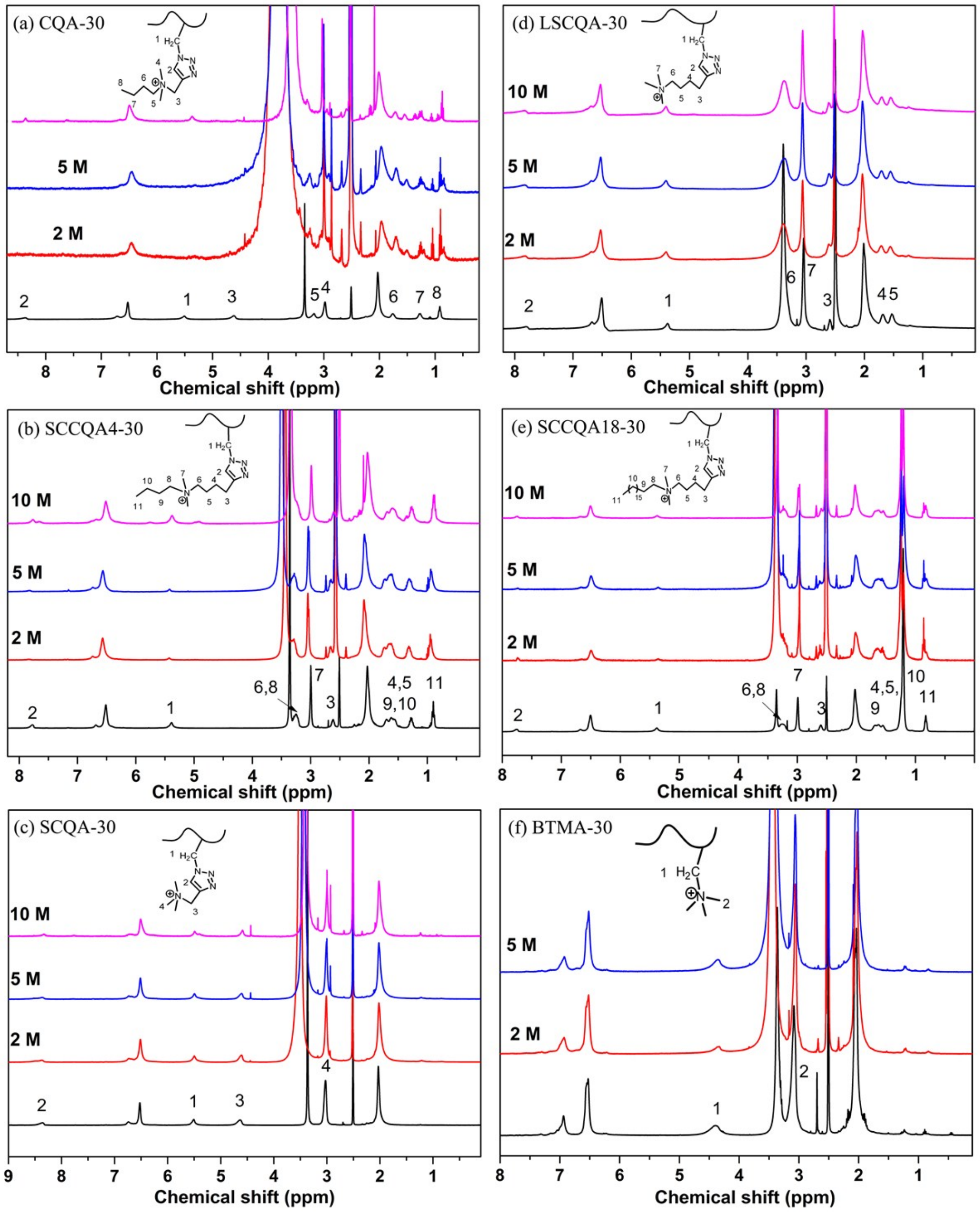


Fig. S4 ^{1}H NMR spectra of PPO AEMs in DMSO-d_6 before and after alkaline stability testing in 2M, 5M and 10 M NaOH at 80 °C for 200 h.

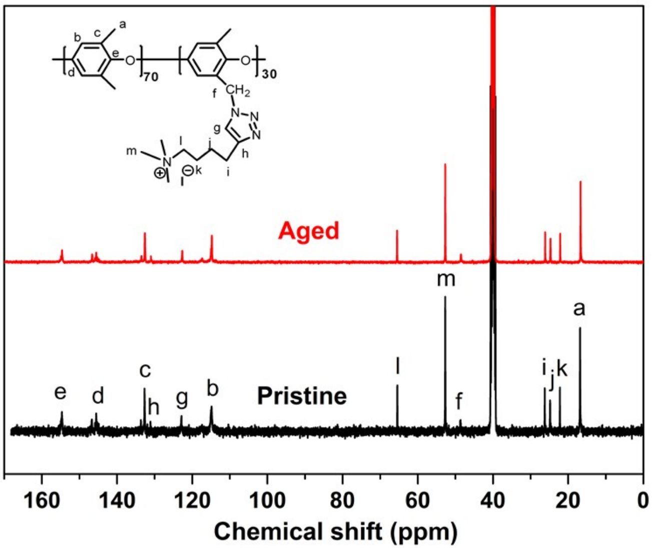


Fig. S5 ^{13}C NMR spectra of LSCQA-30 membrane in DMSO-d_6 before and afteralkaline stability at 80 °C in 10 M NaOH for 200 h.

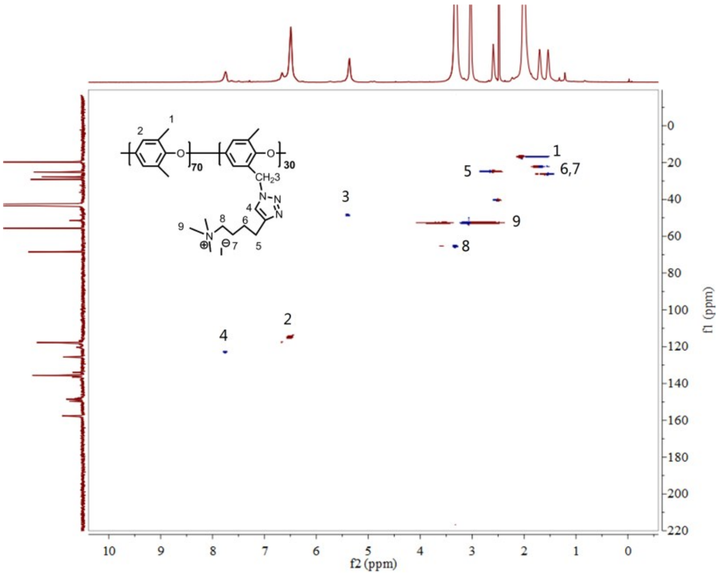


Fig. S6 ^{1}H-^{13}C HSQC NMR spectra of LSCQA-30 membrane in DMSO-d_6 after exposure to 10 M NaOH at 80 °C for 200 h.

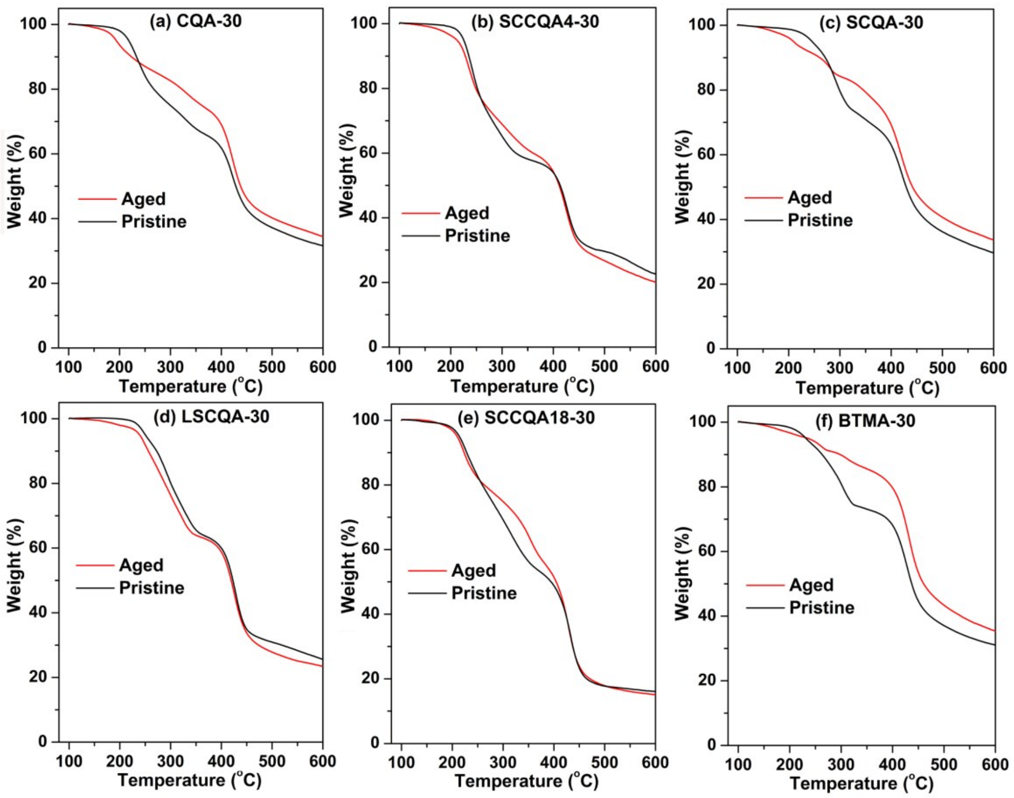


Fig. S7 TGA curves of PPO AEMs before and after storage in 10 M NaOH at 80 °C for 200 h.

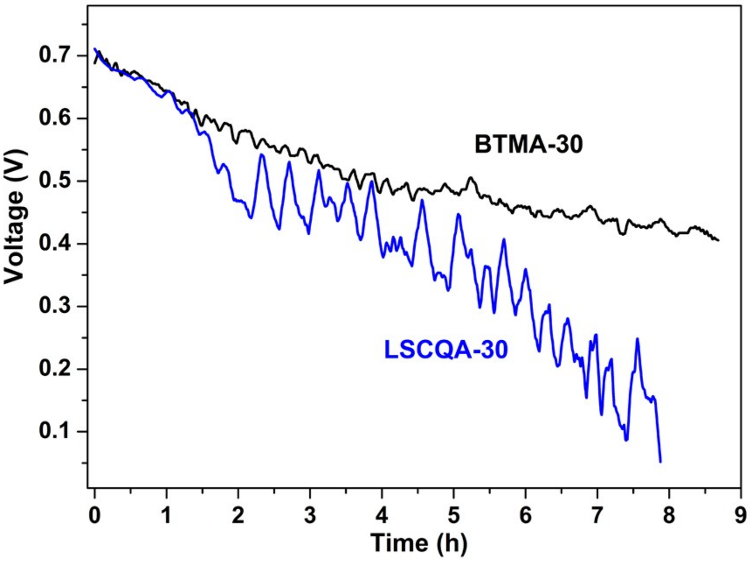


Fig. S8 Lifetime tests of AEMFCs with LSCQA-30 and BTMA-30 membranes at 50 mA/cm^2. Test conditions: catalyst loadings of ～0.5 mg Pt/cm^2 and ～0.2 mg AS-4/cm^2 for both anode and cathode, H_2/O_2 flow rate of 200/200 sccm (no backpressure).

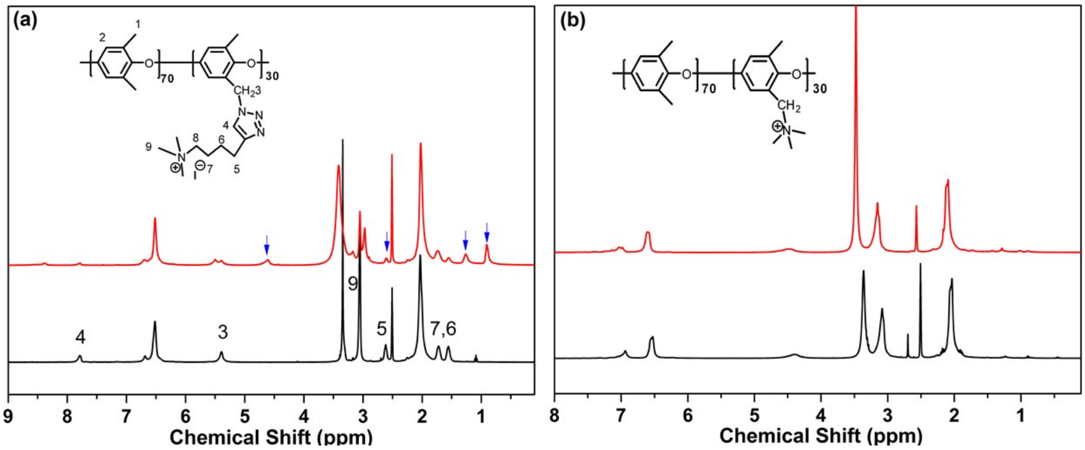


Fig.S9 ^{1}H NMR spectra of (a) LSCQA-30 and (b) BTMA-30 membranes before (black) and after (red) fuel cell durability test at 50 mA/cm^2

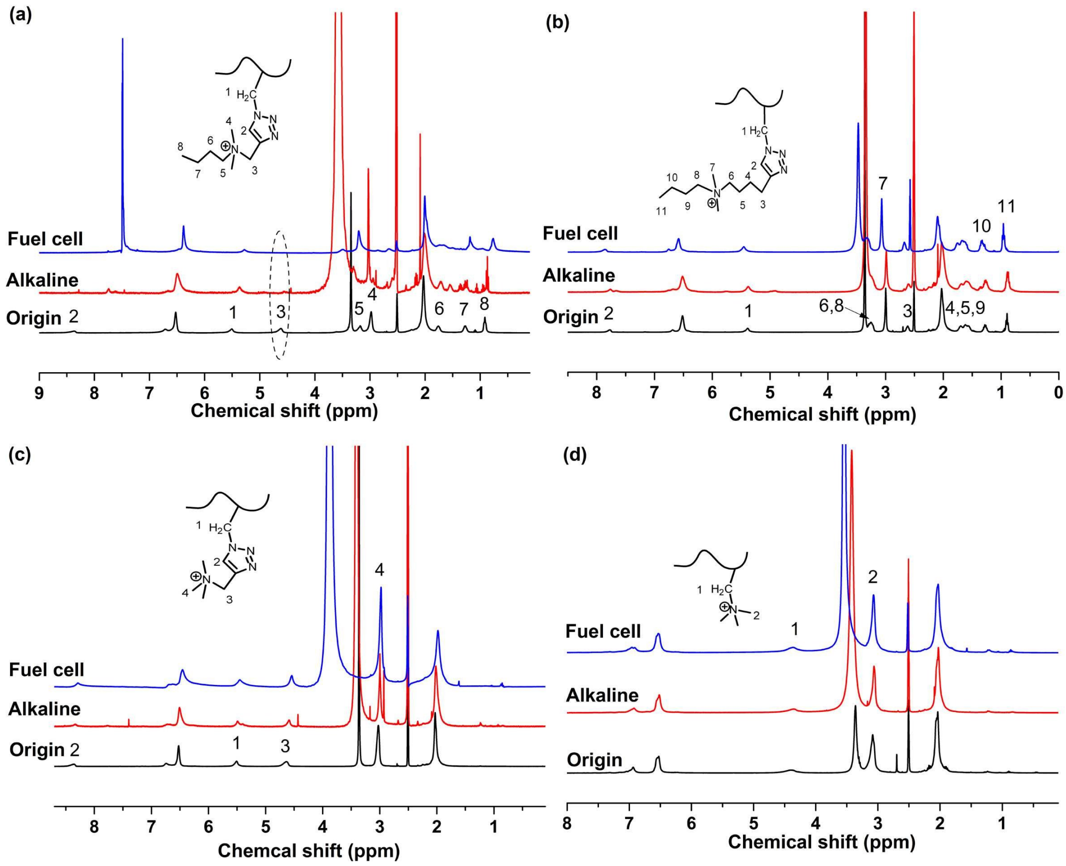


Fig. S10 ^{1}H NMR spectra of (a) CQA-30, (b) SCCQA4-30, (c) SCQA-30, and (d) BTMA-30 membrane before and after fuel cell durability test at 100 mA/cm^2 and after alkaline stability testing in 10 M NaOH (5 M for BTMA-30)

Table S1. Solubility of membranes before and after fuel cell durability test.

Membrane	Before		@100 mA/cm^2 [a]			@ 50 mA/cm^2 [a]	
	DMSO	$CHCl_3$	DMSO	$CHCl_3$	co-solvent[b]	DMSO	$CHCl_3$
CQA-30	+	—	—	—	+	+	—
LSCQA-30	+	—	—	—	+	+	—
SCCQA-30	+	—	+	—	NT[c]	+	—
BTMA-30	+	—	+	—	NT[c]	+	—

[a] after fuel cell durability test at galvanostatic mode; [b] the mixture of DMSO and $CHCl_3$; [c] not tested; +, soluble; —, not soluble.

Table S2. Mechanical Properties of PPO AEMs before and after alkaline stability testing[a]

Membranes	Tensile strength (MPa)		Elongation at break (%)	
	pristine	aged[b]	pristine	aged[b]
BTMA-30	39.4	43.3	10.2	5.0
SCQA-30	40.5	44.8	8.0	6.9
CQA-30	25.6	31.0	5.3	9.0
LSCQA-30	39.0	39.5	21.0	9.1
SCCQA4-30	26.5	30.8	3.1	3.7
SCCQA18-30	25.1	30.7	11.6	5.4

[a] Dry membranes were tested at 20 °C, 50 % RH. [b] The AEMs immersed in 10 M NaOH solution at 80 °C for 200 h.