

Supplementary Information

Constructing Ionic Highway in Alkaline Polymer Electrolytes

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I. Supplementary figures and tables

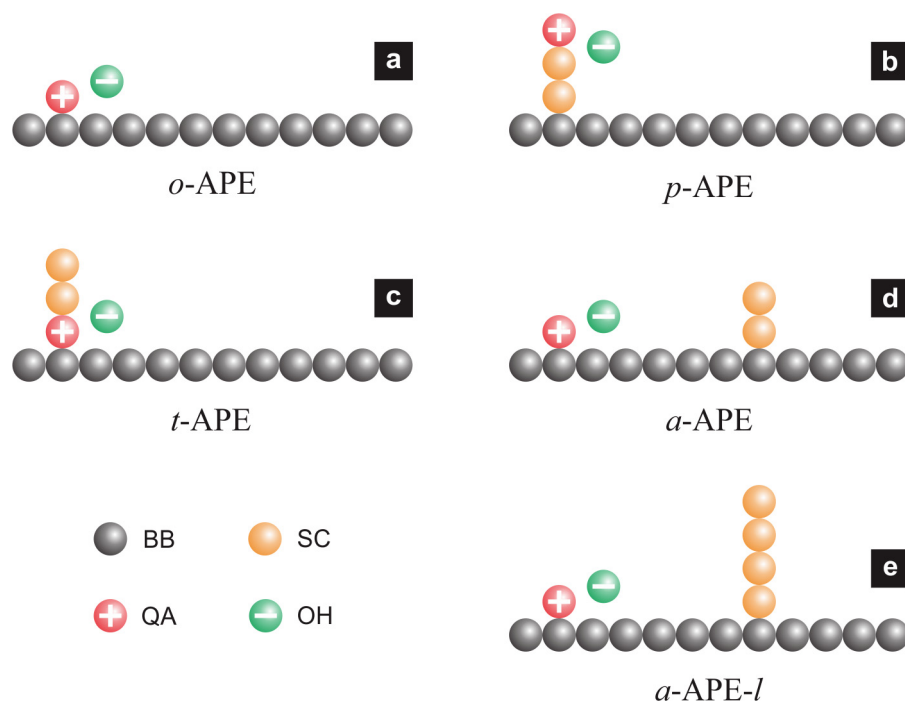


Fig. S1. The monomer models for the simulated APEs: **(a)** *o*-APE, **(b)** *p*-APE, **(c)** *t*-APE, **(d)** *a*-APE, and **(e)** *a*-APE-*l* (where *l* denotes a longer side chain). Four types of beads, backbone segment (BB), side chain segment (SC), quaternary ammonia ion (QA), and hydrated hydroxide ion (OH), are used as the building blocks to construct the APE systems. Note when mapping the above APE models to the quaternary ammonia polysulfone (QAPS) system, one monomer corresponds to two sulfone units (see Methods for detail).

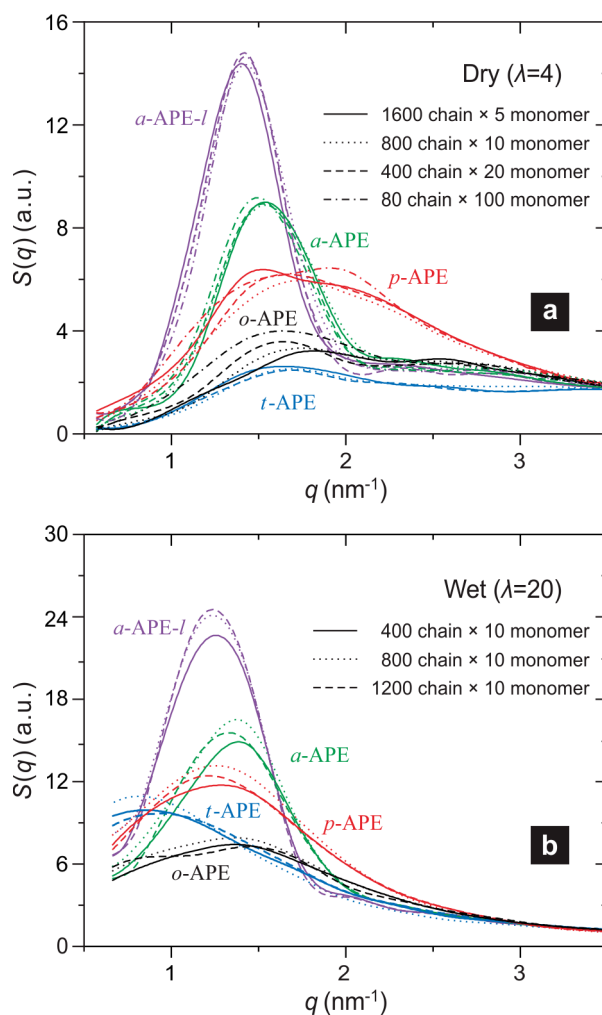


Fig. S2. Representative results for the effects of polymer length (a) and system size (b) on the structure factor for the simulated APEs in dry (a) and wet (b) states, showing that the simulation parameters employed in the present work (800 polymer chains with each consisting of 10 monomers) are reasonable, and the structure factors thus obtained are reliable. (See Methods for computational detail.)

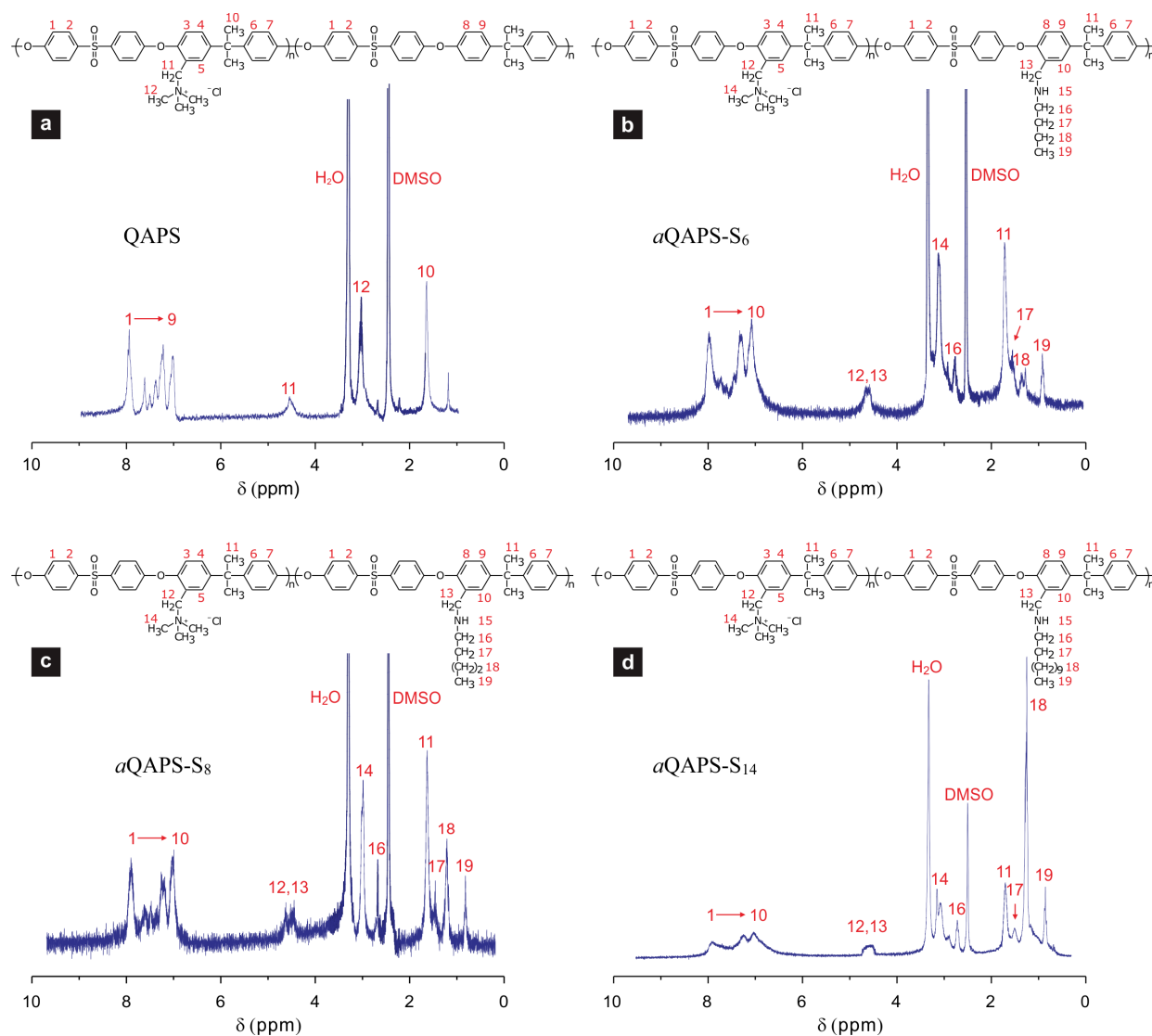


Fig. S3. ^1H NMR results of QAPS (a), $a\text{QAPS-S}_6$ (b), $a\text{QAPS-S}_8$ (c), and $a\text{QAPS-S}_{14}$ (d).

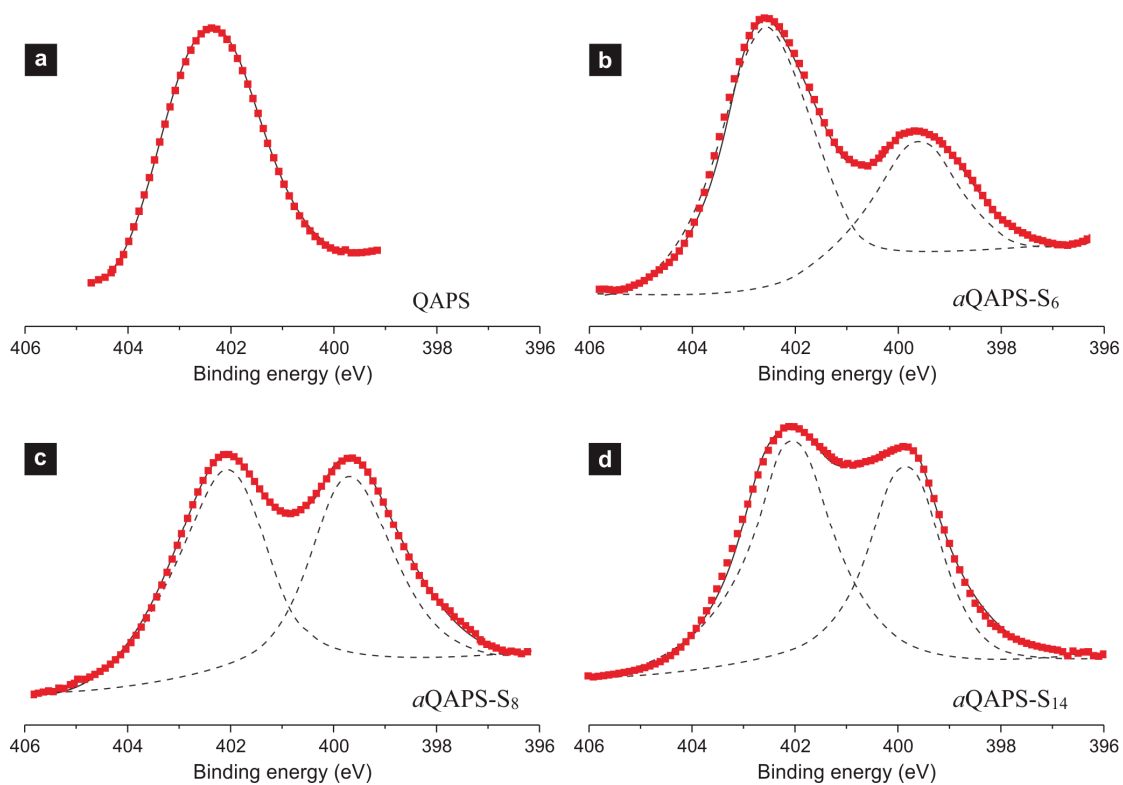


Fig. S4. N(1s) XPS signals of QAPS (a), *a*QAPS-S₆ (b), *a*QAPS-S₈ (c), and *a*QAPS-S₁₄ (d). The binding energies (BE) of 399.8 and 402.3 eV correspond to the secondary amine in the side chain and the quaternary ammonium group at the backbone, respectively^{S1}.

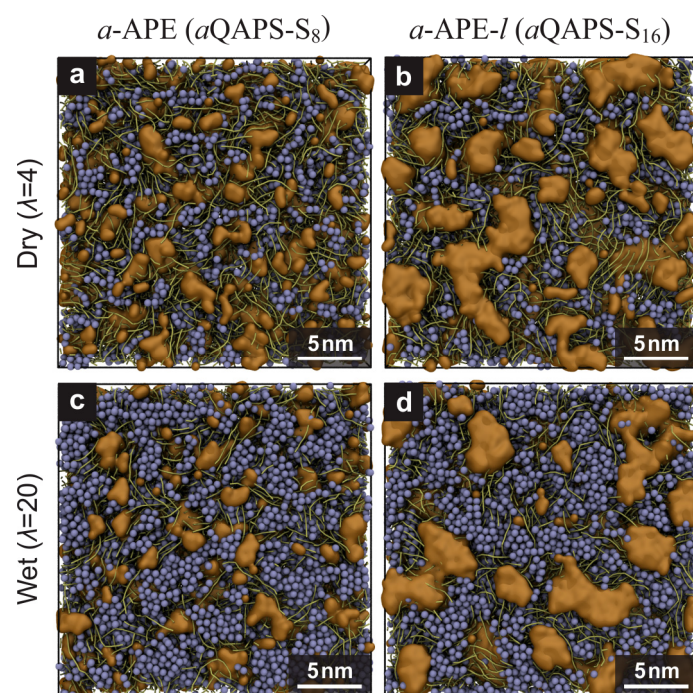


Fig. S5. CGMD simulation results for *a*-APE and *a*-APE-*I*, corresponding to *a*QAPS-S₈ and *a*QAPS-S₁₆, in dry and wet states.

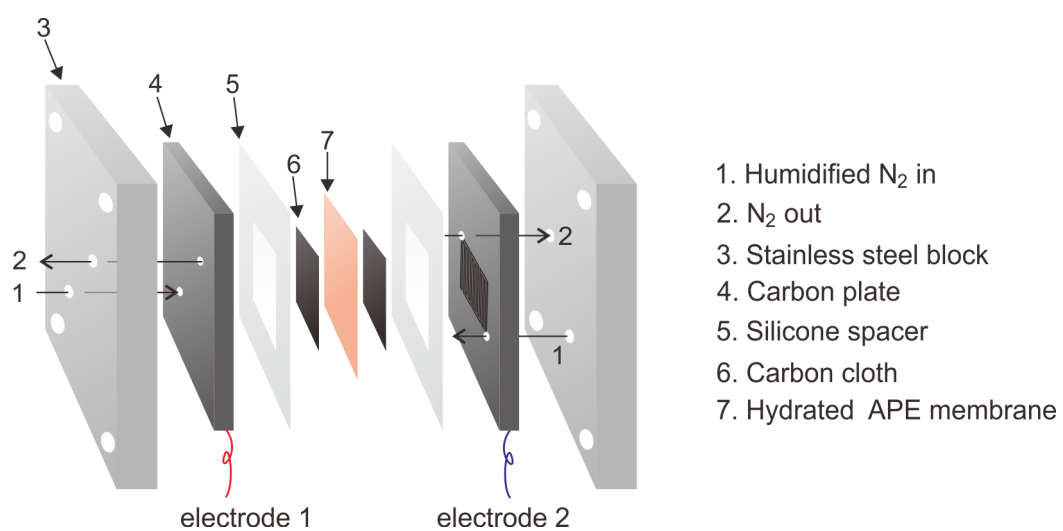


Fig. S6. Schematic illustration of the device used for the two-probe AC-impedance measurement. (See Methods for operation detail.)

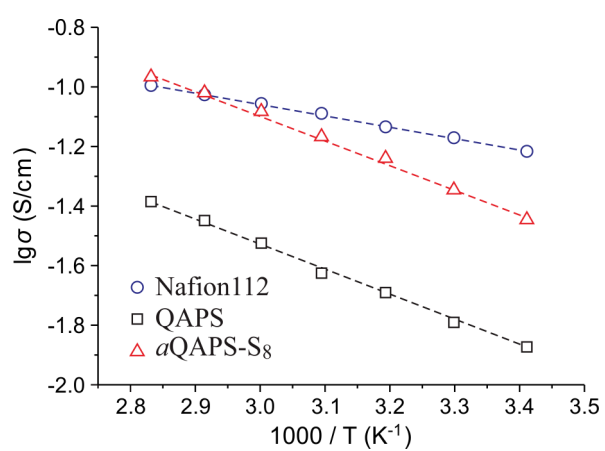


Fig. S7. The Arrhenius plot of Fig. 4b. The thus-calculated apparent activation energy of ionic transportation is ca. 7 kJ/mol for Nafion and ca. 17 kJ/mol for QAPS and *a*QAPS-S₈.

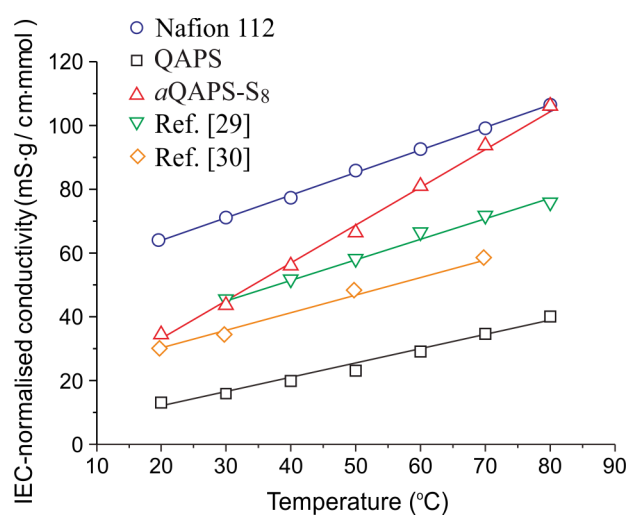


Fig. S8. It is the IEC-normalised conductivity, rather than the apparent ionic conductivity, that describes the ionic conduction efficiency. Although APE membranes reported in Ref. [29] (IEC=1.93 mmol/g) & [30] (IEC=2.3 mmol/g) exhibited apparent ionic conductivities comparable to that of Nafion 112 (IEC=0.95 mmol/g), their ionic conduction efficiency are still not high. For the first time, we find that the OH^- conduction in APE (α QAPS-S₈ in this case) can be made as efficient as the H^+ conduction in Nafion at 80°C.

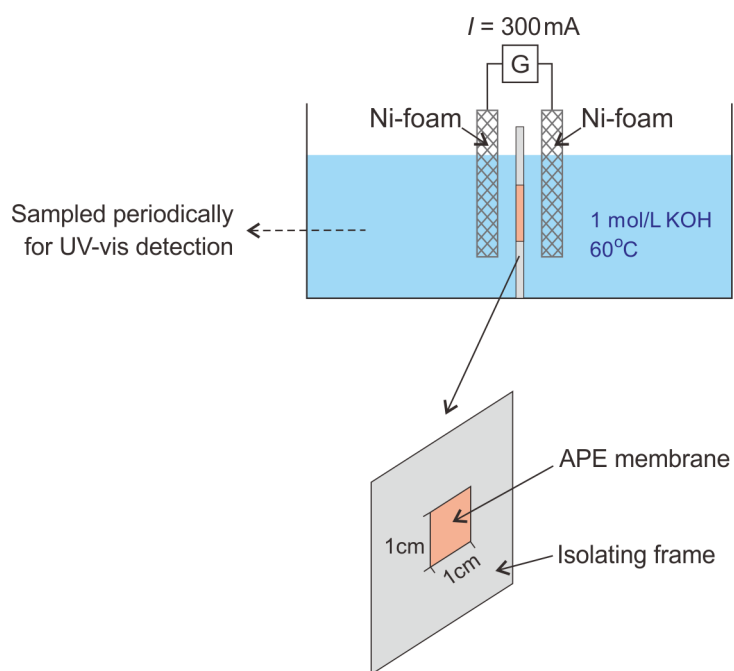


Fig. S9. The experimental setup for the electrolysis test of APE membranes. Water was periodically added into the cell to maintain the solution volume. The whole cell was immersed in a thermostatic bath. (See Methods for operation detail.)

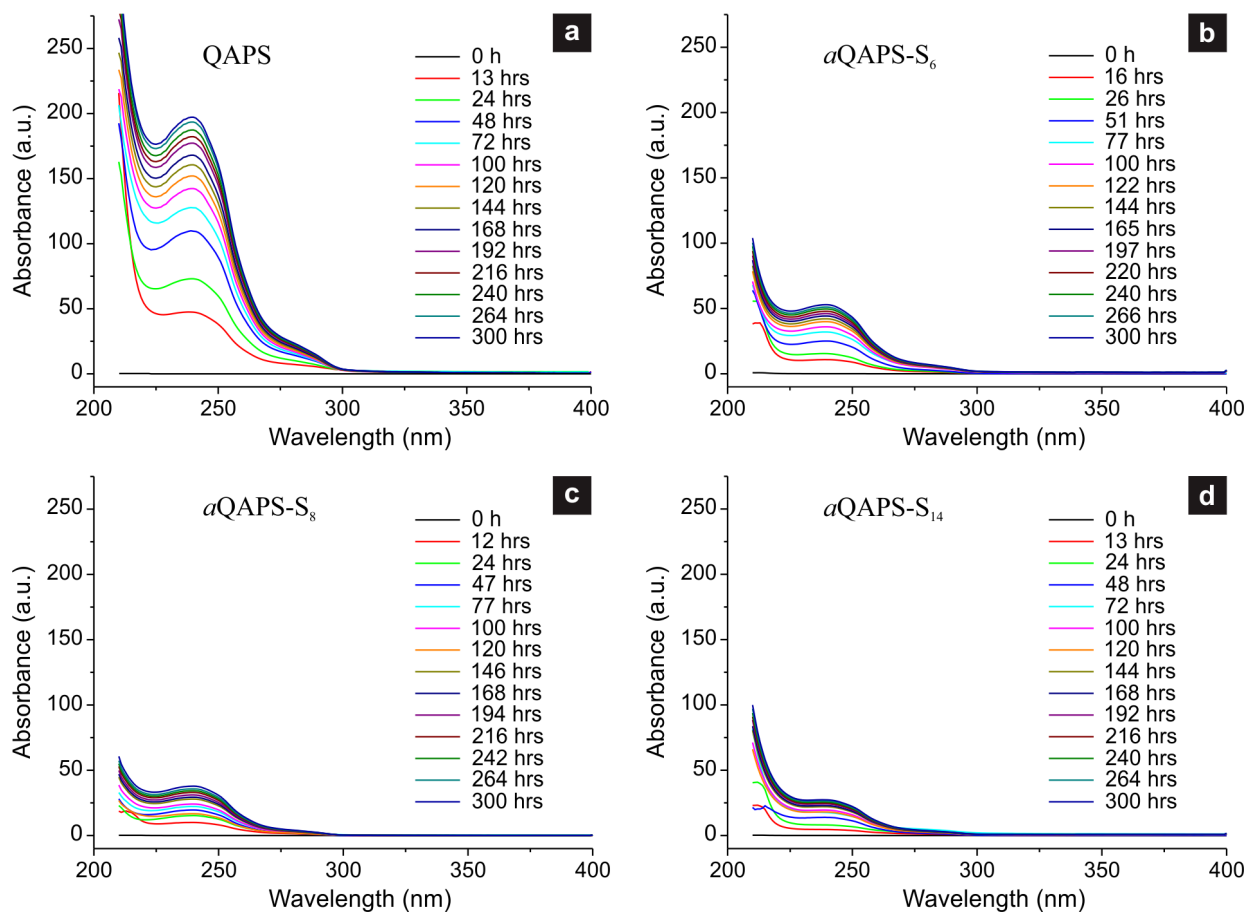


Fig. S10. UV-vis signals recorded during the electrolysis test of the studied APE membranes.

A clean 1 mol/L KOH solution was used as the reference. The signal peaked at around 240 nm is due to the absorption of the phenyl group in degraded APE fragments.

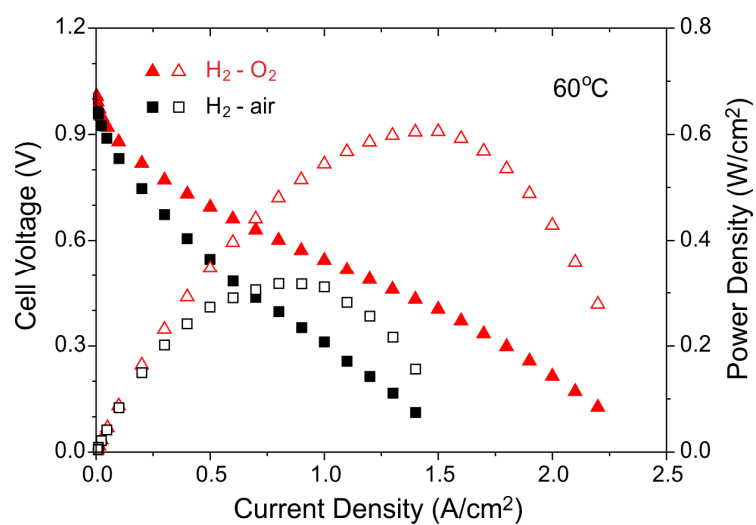


Fig. S11. Fuel-cell tests of the *a*QAPS-S₈ in form of both membrane (50 μm thick) and ionomer in the electrodes. Pt/C (60%, Johnson Matthey Co.) was employed as the catalysts in both anode and cathode with the Pt loading of 0.4 mg/cm², and the weight percentage of *a*QAPS ionomer in the catalyst layers was 20 wt%. Gases were fully humidified and fed at a rate of 120 mL/min with a back pressure of 0.1 MPa. The cells were operated at 60°C.

Table S1. Mechanical strength and hydration level of the studied SPEs.

	Mechanical strength (MPa) [†]		Hydration level (λ)	
	25°C	80°C	25°C	80°C
QAPS	11.8±3.8	3.4±2.7	21±2	57±5
<i>a</i> QAPS-S ₆	20.9±2.4	11.9±1.9	20±3	40±3
<i>a</i> QAPS-S ₈	22.5±3.5	12.1±2.3	20±3	38±2
<i>a</i> QAPS-S ₁₄	23.1±4.1	12.5±1.1	20±1	40±4
Nafion-112	25.1±4.4	23.3±3.4	21±3	22±2

[†] The membrane was pretreated in water at a specific temperature for 1 hour, and then the mechanical strength was measured at room temperature.

Table S2. The IEC of the studied APEs before and after various stability tests.

Sample	Condition [†]	Duration (hours)	IEC by NMR (mmol/g)	IEC by titration (mmol/g)
QAPS	none	-	1.05±0.06	1.02±0.04
	electrolysis	300	0.75±0.02	0.72±0.03
	hydrolysis	300	0.78±0.02	0.74±0.01
	water	500	0.74±0.03	0.77±0.07
<i>a</i> QAPS-S ₆	none	-	1.06±0.05	1.02±0.07
	electrolysis	300	0.94±0.07	0.90±0.04
	hydrolysis	300	0.93±0.05	0.90±0.04
	water	500	0.95±0.04	0.91±0.04
<i>a</i> QAPS-S ₈	none	-	1.04±0.04	1.01±0.02
	electrolysis	300	0.94±0.03	0.91±0.03
	hydrolysis	300	0.93±0.04	0.91±0.02
	water	500	0.96±0.05	0.94±0.04
<i>a</i> QAPS-S ₁₄	none	-	1.03±0.07	1.01±0.03
	electrolysis	300	0.92±0.03	0.90±0.07
	hydrolysis	300	0.93±0.07	0.90±0.04
	water	500	0.98±0.02	0.92±0.05

[†] The APE membranes were treated under different conditions. “none” represents as-prepared membranes; “electrolysis” indicates that the membranes were tested under electrolysis condition ($j = 300 \text{ mA/cm}^2$ in 1 mol/L KOH at 60°C); “hydrolysis” and “water” mean that the membranes were treated in 1 mol/L KOH at 60°C or in deionized water under N₂ atmosphere at 80°C, respectively.

II. Methods

1. Computational section

Model description. A coarse-grained model²³ was employed to describe the APE system at different hydration levels. In this system, there are five types of beads: backbone segment (BB), side chain segment (SC), quaternary ammonia ion (QA), hydrated hydroxide ion (OH), and water cluster (WT). As shown in Fig. S1, an APE monomer is consisting of 12 BB beads, one QA bead, one OH bead, and certain amount of SC beads. The system size, including the length of a polymer chain and the amount of polymer chains in a periodic box, was adjusted and optimised (following the protocol reported in the literature²²), such that simulation results were well reproducible and structure factors thus obtained were in consistency (as representatively shown in Fig. S2). Finally, we chose a moderate system containing 800 polymer chains (with each consisting of 10 monomers). In case of wet system, additional 32000 WT beads were incorporated. Such a configuration is adequate to generate reliable structural information (vide infra), while also avoids the entanglement trouble caused by using long polymer chains^{S2}.

When mapping the simulated APE model (Fig. S1) to the QAPS system (Fig. 3a & 3b), a coarse bead usually contains 4 non-hydrogen atoms. For instance, a QA bead stands for a $-\text{NMe}_3^+$ group, an OH bead represents one hydroxide ion and three water molecules ($\text{OH}^- \cdot 3\text{H}_2\text{O}$), a WT bead acts as four water molecules ($4\text{H}_2\text{O}$), and an SC bead corresponds to a segment of linear chain such as $-\text{CH}_2\text{NHCH}_2\text{CH}_2-$, $-(\text{CH}_2)_4-$, or $-(\text{CH}_2)_3\text{CH}_3$. The backbone modelling is a little special, to sufficiently blur the atomistic detail, we use a homogeneous string of BB beads to describe each sulfone monomer, and 6 BB beads are found to be a justified length to give proper density. The molecular weight (MW) of the simulated APEs is thus up to 86400 g/mol (200 sulfone units), comparable to that of the experimental polysulfone (Udel P-3500, MW = 80000~86000 g/mol). The density of the simulated APEs (dry: 1.25 g/cm³ & wet: 1.13 g/cm³) is in good agreement with the experimental value (dry: 1.4 g/cm³ & wet: 1.1 g/cm³).

Force field. In the CGMD model²³, beads are classified into four major types: polar (P), nonpolar (N), apolar (C), and charged (Q); and N and Q types are further divided into four subtypes according to their capability to form H-bond: “0” for no H-bond, “d” for H-bond donor, “a” for H-bond acceptor, and “da” for both H-bond donor and acceptor. In our system, WT bead was set as “P”, OH bead “Qda”, QA bead “Q0”, SC bead “C”, and BB bead “Na”. Interactions between two beads include bonding, bending, non-bonded, and electrostatic interactions, which are briefly described in the following.

The bonding interaction is described using Eq. 1. The force constant of the harmonic oscillator potential is $K_{\text{bond}} = 1250 \text{ kJ/mol}\cdot\text{nm}^2$, with an equilibrium distance $R_{\text{bond}} = 0.47 \text{ nm}$.

$$V_{\text{bond}}(R) = \frac{1}{2} K_{\text{bond}} (R - R_{\text{bond}})^2 \quad (1)$$

The bending interaction is described using Eq. 2. The basic equilibrium bond angle is $\theta_0 = 180^\circ$, and the force constant is set to $K_{\text{angle}} = 50 \text{ kJ/mol}\cdot\text{rad}^2$ for the rigid polysulfone backbone.

$$V_{\text{angle}}(\theta) = \frac{1}{2} K_{\text{angle}} \{\cos(\theta) - \cos(\theta_0)\}^2 \quad (2)$$

Non-bonded interactions between two beads (i and j) are described by a 12-6 Lennard-Jones (LJ) potential U_{LJ}

$$U_{\text{LJ}}(r) = 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r} \right)^{12} - \left(\frac{\sigma_{ij}}{r} \right)^6 \right] \quad (3)$$

where r is the distance between i and j , and σ_{ij} is the finite distance where the potential curve goes across the x axis at $U_{\text{LJ}} = 0$. For all LJ interactions the same $\sigma_{ij} = 0.47 \text{ nm}$ is used, and a cutoff distance $r_c = 1.2 \text{ nm}$ is chosen, corresponding to ca. 2.5σ . The LJ potential are smoothly shifted to zero between a distance $r_{\text{shift}} = 0.9 \text{ nm}$ and r_c in order to reduce the cutoff noise. Most of the interaction parameters (ε_{ij}) are set to the original value²³, as tabulated below, except the BB-WT interaction being modified from the original value so as to mimic the hydrophilicity of QAPS. The hydrophilicity of QAPS can be characterized by the contact angle, whose experimental value is $55.1^\circ \pm 2.3^\circ$. If ε is set to 3.4 kJ/mol , the simulated contact

angle is $70.7^\circ \pm 1.7^\circ$. Upon correcting the ε of BB-WT interaction to 3.9 kJ/mol, the simulation value is $55.4^\circ \pm 2.8^\circ$, which justifies such a modification in ε .

Table S3. Interaction parameter ε_{ij} (kJ/mol) used in the CGMD simulation.

Bead type	BB	SC	QA	OH	WT
BB	4.2				
SC	2.6	3.4			
QA	3.4	1.8	3.4		
OH	4.2	1.8	4.2	5.0	
WT	3.9 [†]	1.8	5.0	5.0	5.0

[†] Modified from the original value (3.4 kJ/mol).

For electrostatic interaction, the original force field used a relative dielectric constant $\varepsilon_r=20$ in Eq. 4²³, which is applied in the simulation of wet systems. However, for the dry system where water molecules are present only in OH beads ($\text{OH}^- \cdot 3\text{H}_2\text{O}$), the ε_r should be reduced. We've carried out a series of simulations by tuning the ε_r from 1 to 20, and found that $\varepsilon_r=5$ gave a structure factor most resembling to the experimental result of QAPS.

$$U_{\text{el}}(r) = \frac{q_i q_j}{4\pi\varepsilon_0\varepsilon_r r} \quad (4)$$

Simulation process. In an NPT ensemble, the system was first heated from 300 K under 1 atm to 1000 K under 300 atm within 10 ns, and then annealed to 300 K under 1 atm for 50 ns. Such a high-temperature pretreatment is necessary to fully disentangle the polymer chains, and the high pressure is also needed to confine the system in condensed state. After annealing, the system was further equilibrated at 300 K under 1 atm for 10 ns, followed by a data production for 100 ns, during which a group of structural configurations were consecutively collected. In all simulations, a time step of 20 fs was chosen. The above simulation cycle was repeated for 9 times.

Radial distribution function (RDF). The RDF of hydrophilic particles (i.e., OH, QA, and WT beads) in the system, $g(r)$, was calculated based on the structural configurations produced by each simulation process^{S3}, which describes the averaged relative probability of finding one particle at the position r spherically away from another particle. RDFs of 9 simulation cycles were compared to ensure the reproducibility and then averaged to produce

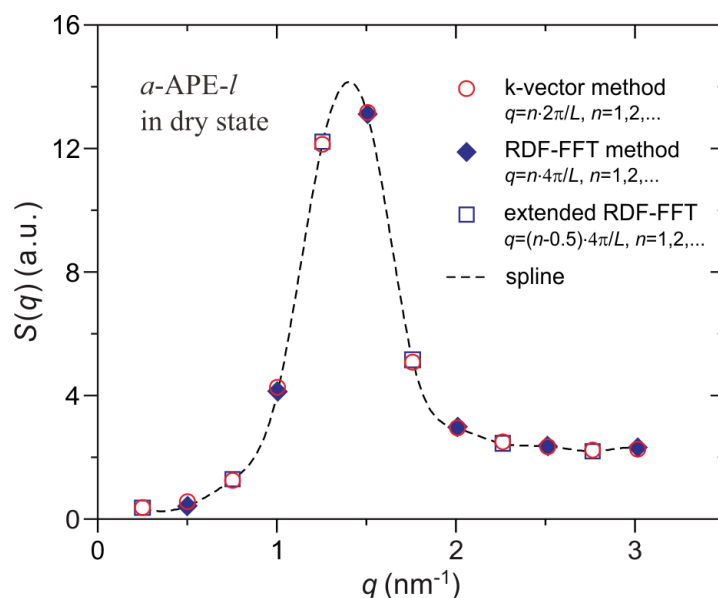
the final result. Generally, the cutoff in RDF calculation was set to 11.0 nm, a bit less than a half of the length of the simulation unit cell, and the bin width chosen for RDF calculation is 0.01 nm.

Structure factor (SF). The SF of hydrophilic particles in the system, $S(q)$, was calculated using either k-vector method or RDF-FFT method. The k-vector method directly calculates $S(q)$ from particles' coordinates (r) through Eq. 5,

$$S(q) = 1 + \frac{1}{N} \left\langle \sum_{a \neq b} \cos[\vec{k} \cdot (\vec{r}_a - \vec{r}_b)] \right\rangle \quad (5)$$

where q is the magnitude of the k vector, r_a and r_b are the coordinate vectors of any two particles among the total N particles in the box. For a periodic cubic system in length L , q must take discrete values $n \cdot 2\pi/L$ ($n=1,2,\dots$). For calculation details, please refer to Ref. [S4].

Demonstrated below is a thus-calculated SF with the sharpest peak. The peak position appears at around 1.4 nm^{-1} , well above the lower limit of q , and the peak width at half height is ca. 0.6 nm^{-1} , greater than twice of the q resolution (ca. 0.25 nm^{-1}), indicating that the system size in our simulations is adequate to capture the structural feature of the studied APEs.



While the k-vector method for $S(q)$ calculation is rather time-consuming, the RDF-FFT method is a much quicker approach^{S4}, in which the SF is calculated through a Fourier transformation (FT) of the above-obtained RDF data $g(r)$,

$$S(q) = 1 + \frac{4\pi}{q} \frac{N}{V} \int_0^\infty r [g(r) - 1] \sin(qr) dr \quad (6)$$

where V is the volume of the simulation box, and r is the radial distance ranging from 0 to $L/2$. Hence the q resolution in this method is thought to be $4\pi/L$, 2x coarser than that of the k-vector method. However we found that the ‘lost’ resolution can be taken back, at least to an excellent approximation, by an extended RDF-FFT approach. Specifically, taking the $g(r)$ as a continuous signal, its FT spectrum is actually also continuous. We took the average spectrum strength in the range from $(n-0.75) \cdot 4\pi/L$ to $(n-0.25) \cdot 4\pi/L$ as the $S(q)$ at $q = (n-0.5) \cdot 4\pi/L$, the result turned out to match very well the corresponding value calculated by k-vector method, as clearly demonstrated in the above figure. Thus the full $S(q)$ can be established by the (extended) RDF-FFT method at a resolution of $2\pi/L$, as good as that of the k-vector method.

In the present work, we usually applied the (extended) RDF-FFT method for routine SF calculations, while employed the k-vector method only for verification of key results.

Software. All simulations were carried out using the LAMMPS code^{S5} and the system snapshots were produced using VMD^{S6}.

2. Experimental section

Materials. Polysulfone (Udel P-3500, Solvay Advanced Polymers, L.L.C., USA), chloromethylmethylether (Shanghai Quhua Chemical Reagent Co. Ltd., 99%), trifluoroacetic acid (Sinopharm Chemical Reagent Co. Ltd., 99%), zinc powder (Shanghai Chemical Reagent Co. Ltd., 95%), 1,2-dichloroethane (Shanghai Chemical Reagent Co. Ltd., 99%), n-butylamine (Sinopharm Chemical Reagent Co. Ltd., 99%), n-hexylamine (Aladdin Chemistry Co. Ltd., 99%), n-octylamine (Aladdin Chemistry Co. Ltd., 99%), n-dodecylamine (Aladdin Chemistry Co. Ltd., 99%), trimethylamine (Shanghai Chemical Reagent Co. Ltd., 33% alcohol solution), N,N-dimethylformamide (DMF, Shanghai Chemical Reagent Co. Ltd., 99.5%), potassium hydroxide (Sinopharm Chemical Reagent Co. Ltd., 85%), hydrochloric acid (Sinopharm Chemical Reagent Co. Ltd., 37%) are used as received from the companies

indicated.

Chloromethylation of polysulfone (PSF). The chloromethylation process of PSF was carried out in a three-neck round-bottom flask with a mechanical stirrer. PSF (10 g) was dissolved in 1,2-dichloroethane (70 mL). After adding zinc powder (1 g) and trifluoroacetic acid (4 mL) into the solution, chloromethylmethylether (20 mL) was added dropwise. The solution was stirred for 5 h at 30°C. The thus-obtained chloromethylated polysulfone (CMPS) was precipitated into methanol, washed several times with deionized water, and then dried in a vacuum oven for 24 h at 60°C.

Synthesis of quaternary ammonium polysulfone (QAPS). CMPS was dissolved in N,N-dimethylformamide (DMF) to form a solution of 15 wt%, into which trimethylamine (50 mol% of the repeat unit of PSF) was added dropwise, followed by stirring the solution at 40°C for 1 h.

Synthesis of *a*QAPS. CMPS was dissolved in N,N-dimethylformamide (DMF) to form a solution of 15 wt%, into which n-alkylamine (50 mol% of the repeat unit of PSF) was added dropwise, followed by stirring the solution at 40°C for 2.5 h. After that, trimethylamine (50 mol% of the repeat unit of PSF) was added, followed by stirring the solution at 40°C for 1 h to prepare the *a*QAPS solution.

Preparation of APE membrane. The QAPS (or *a*QAPS) solution was cast onto a clean, flat glass plate, and dried in oven at 60°C for 16 h and then further dried in a vacuum oven at 80°C for 10 h. To replace the Cl⁻ anion in the polymer with OH⁻, the QAPS (or *a*QAPS) membrane was immersed in KOH solution (1 mol/L) for 10 h. This process was repeated 4 times to ensure a complete displacement. Finally, the OH type QAPS (or *a*QAPS) membrane was repeatedly rinsed with deionized water until the pH of residual water was neutral.

¹H NMR analysis. ¹H NMR (300 MHz) analysis was performed on a Varian Mercury VX-300 spectrometer using deuterated dimethyl sulfoxide (DMSO-d₆) as the solvent and tetramethylsilane (TMS) as the internal reference.

X-ray photoelectron spectroscopy (XPS) measurement. XPS measurements were carried out using a Kratos XSAM-800 spectrometer with an Mg K_α radiator. The N(1s) signal

was collected and analyzed using the software XPSPeak.

UV-vis spectroscopy measurement. UV-vis measurements were conducted on a Mapada UV-6100PC spectrometer. A clean KOH solution was used as the reference for the detection of degraded APE backbone fragments in KOH solution.

Mechanical strength measurement. A tensile tester (CMT6503, Shengzhen SANS Test Machine Co. Ltd., China) was employed to analyze the tensile stress–strain behavior of fully hydrated QAPS and *a*QAPS membranes in OH[−] form at room temperature.

Transmission electron microscopy (TEM) observation. *a*QAPS and QAPS solutions were cast to form thin films on a Cu grid, respectively, followed by exchanging the anions for Γ[−], and then subjected to TEM observations. Images were taken on an ultrahigh-resolution transmission electron microscope (JEOL JEM-2010FEF) using an accelerating voltage of 200 kV.

Small-angle X-ray scattering (SAXS) measurement. SAXS experiments were performed using a NanoSTAR-U (Bruker AXS Inc.) with Cu K_α radiation (wavelength, λ=0.154nm). The generator was operated at 40 kV and 650 μA. Two-dimensional SAXS patterns were obtained using a HI-STAR detector. The effective scattering vector *q* is given by:

$$q = \left(\frac{4\pi}{\lambda}\right) \sin \theta \quad (7)$$

where λ is the wavelength and 2θ is the scattering angle. The Bragg distance *d* is related to *q* by:

$$d = \frac{2\pi}{q} \quad (8)$$

Contact angle measurement. The contact angle of water on QAPS or *a*QAPS surface was measured by drop shape analysis using the DSA100 instrument (German, Krüss). The instrument captured the shapes of water drops formed on the surface in 2 seconds.

Ion exchange capacity (IEC) determination. The IEC of APE can be calculated from the NMR signal (Fig. S3), or determined by titration. For the NMR approach, the relative signal strength of the H atoms on quaternary ammonia group was used to evaluate the grafting degree, which was then converted to IEC defined in the following. For the titration approach,

the membranes (in OH⁻ form) were immersed in a standard hydrochloric acid solution (0.1 mol/L, 30 mL) for 48 h. The solution was then titrated with a standard KOH solution (0.1 mol/L) to pH 7. The membrane was washed and immersed in deionized water for 24 h to remove any remaining HCl, and then dried under vacuum at 45°C for 24 h and weighed to determine the dry mass (in Cl⁻ form). The IEC of the membrane is calculated by:

$$IEC = \frac{n_{i(H^+)} - n_{f(H^+)}}{m_{dry(Cl)}} \quad (9)$$

where $n_{i(H^+)}$ is the amount of proton in the initial HCl solution, $n_{f(H^+)}$ is the amount of proton in the final HCl solution determined by titration, and $m_{dry(Cl)}$ is the mass of the dried membrane in Cl⁻ form.

Water uptake and swelling degree measurement. In order to get the water uptake (WU) and swelling degree (SD), both the weight and the dimension of dry membranes (in Cl⁻ form, denoted as $m_{dry(Cl)}$ and $X_{dry(Cl)}$) were measured first, and then the membrane was immersed in 1 mol/L KOH solution for 48 h to convert Cl⁻ to OH⁻, and washed with deionized water several times to remove residual KOH. The wet mass $m_{hyd(OH)}$ and the dimension $X_{hyd(OH)}$ of the membranes were measured after wiping the excess water from the surface. The WU and the SD are calculated by:

$$WU(\%) = \frac{m_{hyd(OH)} - m_{dry(Cl)}}{m_{dry(Cl)}} \times 100 \quad (10)$$

$$SD(\%) = \frac{X_{hyd(OH)} - X_{dry(Cl)}}{X_{dry(Cl)}} \times 100 \quad (11)$$

Hydration level measurement. The hydration level (λ) represents the ratio between the amount of water molecules and hydroxide ions in the APE, and is defined as follows:

$$\lambda = \frac{n_{OH^-} + n_{H_2O}}{n_{OH^-}} \quad (12)$$

In practice, λ can be calculated based on the IEC and the WU .

Ionic conductivity measurement. A piece of APE membrane (2 cm² in area and 50±3

μm in thickness) were assembled in the device depicted in Fig. S6 for the measurement of OH⁻ conductivity. The measurements were conducted at temperature ranging from 20 to 80°C using a two-probe AC-impedance method under fully humidified N₂ atmosphere, which excludes the influence of CO₂. The membrane resistance was measured under the open-circuit mode over a frequency range of 1 Hz to 1 MHz with oscillating amplitude of 5 mV. The ionic conductivity is calculated by:

$$\sigma = \frac{L}{R_{\text{mem}} \times A} \quad (13)$$

where L is the membrane thickness in cm, A is the electrode area in cm², and R_{mem} is the membrane resistance in Ω. The activation energy of conduction, E_a is calculated from the linear Arrhenius relationship between $\ln \sigma$ and $1/T$:

$$E_a = -b \times R \quad (14)$$

where b is the slope of the regressed linear $\ln \sigma - 1/T$ relationship, and R is the gas constant.

Stability test under electrolysis condition. A piece of APE membrane (50±3 μm in thickness) was framed and assembled in an electrolysis cell as depicted in Fig. S9. The cell, containing 1 mol/L KOH solution, was immersed in a thermostatic bath and the temperature of the KOH solution was maintained at 60°C. A DC current of 300 mA was applied by a galvanostat through two electrodes made of Ni-foam. The current density going through the membrane was thus 300 mA/cm² since the exposed area of the tested membrane was 1 cm². Deionized water was added dropwisely into the cell during the test so as to compensate the consumption of water and to maintain the solution volume.

During the electrolysis test, the KOH solution was sampled periodically for UV-vis detection, after which the solution sample was put back to the electrolysis cell. The signal peaked at around 240 nm in the UV-vis spectra (Fig. S10) was due to the absorption of the phenyl group in degraded APE fragments. After the 100-h test, the APE membrane was rinsed repeatedly with deionized water until the pH of residual water was neutral, and the dried membrane was then weighted. The weight loss of the tested membrane was normalised by the

signal strength of the final UV-vis spectrum, and then every UV-vis signal recorded during the electrolysis test can be converted to a value of weight loss, resulting in the stability curve illustrated in Fig. 4d.

The IECs of the APE membranes after the electrolysis test were determined by both ^1H NMR and titration, results are shown in Table S2.

Fuel cell test. Pt/C catalyst (60 wt% in Pt content, Johnson Matthey) was mixed with certain amount of *a*QAPS- S_8 ionomer solution and sprayed onto each side of an *a*QAPS- S_8 membrane (30 ± 2 μm in thickness) to produce the catalyst-coated membrane (CCM). The Pt loading in both anode and cathode was $0.3 \text{ mg}/\text{cm}^2$, and the electrode area was 4 cm^2 . The resulting CCM was pressed between two pieces of Teflon-treated carbon paper (Toray-250) to make the membrane electrode assembly (MEA). H_2 - O_2 fuel cell tests were conducted at 60°C with fully humidified H_2 and O_2 gases at a flow rate of $120 \text{ mL}/\text{min}$ under 0.05 MPa . The I - V curves and high-frequency impedance were measured using a fuel-cell test station (Scribner 850e).

Supplementary references

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