Supplementary Information

Improved ion clustering and conductivity of di-quaternized poly (arylene ether ketone sulfone) based alkaline fuel cell membrane

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Section S1

Instrumental analysis

The ¹H NMR spectra was done by NMR spectrometer (Bruker, 500 MHz for ¹H NMR) in CDCl₃ or DMSO-d₆ and chemical shifts were recorded in parts per million (ppm) with reference to tetramethylsilane (TMS).

The FTIR spectra of dried membrane samples were obtained from Spectrum GX series 49387 spectrometer in the range of 4000-500 cm⁻¹ by the KBr pellet method.

The Molecular weight of formed PAEKS were measured by gel permeation chromatography (GPC, Waters 2695, Waters HPLC Alliance model) equipped with Styragel HR 5, HR 4E and HR 0.5 columns coupled with Water 2996 DAD detector (Empower 2 Software) with DMF as eluent after the calibration with standard polystyrene samples.

Thermo gravimetric analyzer (NETZSCH TG 209F1 Libra TGA209F1D-0105-L) were used for the analysis of membranes thermal stability under a nitrogen atmosphere with a heating rate of 10 °C/min from 30 to 800 °C and mechanical stability of membranes were analyzed by heating the sample from 25 to 400 °C under nitrogen atmosphere with 10 °C/min heating rates using NETZSCH DMA 242 instrument.

Scanning electron microscopy (SEM) was recorded by Leo microscope (Kowloon, Hong Kong) after gold sputter coatings on dried membrane samples. Transmission electronic microscopy (TEM) images of the prepared membranes were recorded using a JEOL JEM 2100 microscope. The membrane sample was strained with tungstate ions and sectioned to yield slices 50-100 nm thick using a cryomicrotome, and placed on copper grid. Atomic force microscopy (AFM) images of dried membranes were obtained by NTEGRA AURA1 (NTMDT) in tapping mode.

Mechanical strength of membrane was analysed through the tensile stress-strain performance of hydrated membrane in OH⁻ (3.2 cm long, 1 cm width) at room temperature by the ISO 527 S2 method using a Zwick Roell Z2.5 tester with a constant crosshead speed of 20 mm/min. The test Xpert II-V3.5 software was used for data analysis.

Optical images of different membranes were taken by Nikon digital camera (D5100 AF-S DX NIKKOR 18-55mm f/3.5-5.6G VR).

Section S2.

Methanol Permeability

Methanol permeability across the membrane was determined in a two-compartment diffusion cell (50 cm³) separated by an equilibrated membrane (20 cm²). Each compartment was well stirred. Initially, one compartment (A) contained methanol-water mixture, while the other compartment (B) contained double distilled water. Methanol flux was estimated by recording its concentration in compartment (B) with time, using a digital refractometer (Mettler Toledo RE40D refractometer). The methanol permeability (*P*) was finally obtained by the eq. (1).

$$P = \frac{1}{A} \frac{C_{B(t)}}{C_A(t-t_0)} V_B l$$
 (1)

where A is the effective membrane area, l the membrane thickness, $C_{B(t)}$ the methanol concentration in compartment B at time t, $C_A(t - t_0)$ the change in the methanol concentration in compartment A between time 0 and t, and V_B the volume of compartment B. All experiments were carried out at room temperature, and the uncertainty of the measurements was less than 2%.

Methanol permeability for di-DQP-OH (68 %) membrane is $1.28 \times 10^{-7} \text{ cm}^2/\text{sec}$ and selective parameter is found around $3.65 \times 10^5 \text{ S s}/\text{cm}^3$.

DB (%)	mono-DQP-OH					di-DQP-OH			
	$WU^{1}(\%)$		SR (%)		_	WU^{1} (%)		SR (%)	
	30 °C	65 °C	30 °C	65 °C		30 °C	65 °C	30 °C	65 °C
56	28.86	33.42	11.46	12.46		36.26	44.65	14.42	19.86
62	34.15	40.76	14.24	16.28		44.18	54.68	15.26	22.64
68	39.48	48.18	15.36	19.62		49.47	63.44	18.52	24.84

Table S1. WU and SR values for mono-DQP-OH and di-DQP-OH membranes at different temperature (30 °C & and 65 °C).



Fig. S1 Variation of DB values with time/temperature.



Fig. S2 XRD spectra for (a) mono-DQP-OH (DB: 68%) and (b) di-DQP-OH (DB: 68%) AMs.



Fig. S3 TGA spectra for (a) mono-DQP-OH (DB: 68%) and (b) di-DQP-OH (DB: 68%) AMs.



Fig. S4 FT-IR spectra of mono-DQP-OH membrane (A) before and (B) after alkaline treatment.



Fig. S5 FT-IR spectra of di-DQP-OH membrane (A) before and (B) after alkaline treatment.



Fig. S6 Arrhenius plots for different AMs.