Anion Exchange Membranes with Branched Ionic Cluster for Fuel Cells

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1. Characterizations

^{1}H NMR spectra was performed with an AV III 400 NMR spectrometer (^{1}H resonance at 400 MHz, Bruker). Tapping mode atomic force microscopy (AFM) was recorded by a Veeco diinnova SPM. Tensile strength and elongation at break of the membranes were measured using a Q800 dynamic mechanical analyser (DMA, TA Instruments) at a stretch rate of 0.5 N min^{-1} under air atmosphere. Thermal stability of the membrane was characterized by a Q5000 thermo gravimetric analyser (TGA, TA Instruments) with a temperature increase rate of 10 °C per minute and depicted in Figure S1.

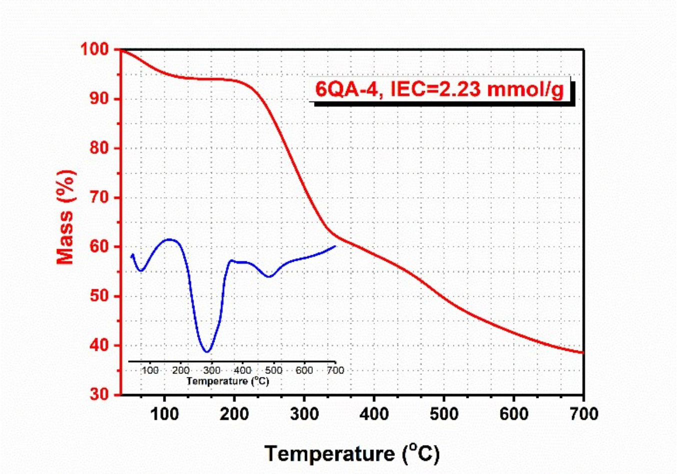

Figure S1. TGA curve of prepared 6QA-4 membrane.

1.1 Water uptake, swelling ratio and ion exchange capacity

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One piece of membrane (4 cm×4 cm) was firstly immersed in distilled water for 24 hours at room temperature. After wiping the excess water on the membrane surface with tissue paper, weight, and length of the membrane were quickly measured. Afterwards, this sample of membrane was dried at 60 ^{o}C for 24 hours. Weight, and length of the dried membrane were again measured and recorded. Liner expansion ratio (LER) of the membrane was calculated as follows:

$$\mathrm{LER} = \frac{\mathrm{L_w} - \mathrm{L_d}}{\mathrm{L_d}} \times 100\% \quad (1)$$

L_w and L_d were defined as the length of the membrane in hydrated and dehydrated conditions respectively. Similarly, water uptake (WU) of the membrane was calculated by the following equation:

$$WU = \frac{W_w - W_d}{W_d} \times 100\% \quad (2)$$

Where W_w and W_d were defined as the mass of the membrane in hydrated and dehydrated conditions respectively.

Ion exchange capacity (IEC) of the prepared membrane was measured as previously reported by our group [1]. One sample of the synthesized AEM was firstly immersed in 1 mol/L NaCl aqueous solution at room temperature for 24 hours, then dried at 80 ^{o}C in vacuum for 24 hours. After the mass of the membrane was recorded, it was immersed in 0.5 mol/L Na_2SO_4 aqueous solution for another 24 hours to release Cl^- from the membrane. Lastly, the solution was titrated with 0.1 mol/L $AgNO_3$ aqueous solution with K_2CrO_4 as indicator. IEC was calculated as follows:

$$IEC\ (mmol/g) = \frac{V_{Ag^+}(ml) \times 0.1\ mol/L}{W_{Cl^-}\ (g)} \quad (3)$$

V_{Ag^+} was the amount of $AgNO_3$ solution consumed while titration and W_{Cl^-} was the mass of the sample in Cl^- form.

1.2 Ionic Conductivity

Ionic conductivity of synthesized AEMs was measured as previously reported by our group[1]. The ionic conductivity (κ) was calculated according to the following equation:

$$\kappa = \frac{L}{RWd} \qquad (4)$$

Where L is the distance between potential sensing electrodes, R is the membrane resistance, d and W are the thickness and width of the sample respectively.

1.3 Estimation of the alkaline stability

One sample of synthesized AEM was soaked in 2 mol/L aqueous KOH solution at 60 ^{o}C for increasing lengths of time. Afterwards, the membranes were immersed in deionized water and washed frequently for 24 h to remove the residual KOH. Afterwards, hydroxide conductivities of the samples were again measured and compared with its initial values.

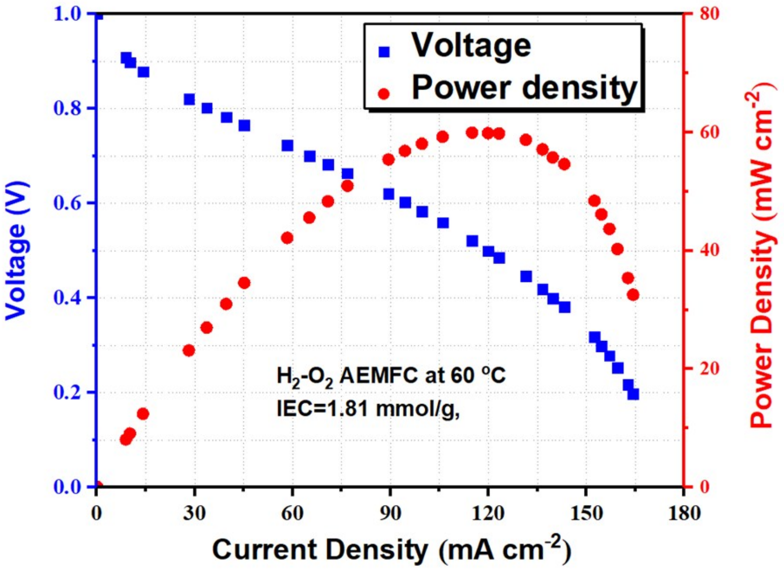
1.4 Fuel cell testing

Pt/C or PtRu/C catalysts (60% w/w in metal content) were ultrasonically mixed with the QPPO ionomer solution to yield inks containing 20% w/w of ionomer and 80% w/w of catalyst. Then the resulting catalyst inks were used to fabricate gas diffusion electrodes (GDEs) by hand spraying onto a larger area gas diffusion layer (GDL, Toray TGP-H-060). The metal loading in both anode and cathode was controlled to be 0.5 mg/cm^{-2}, and the electrode area was 12.25 cm^{2}. The prepared GDE and membranes were then converted to OH^{-} form by immersing in aqueous NaOH (1 mol dm^{-3}) solution for 12 h followed by thorough washing with UPW. The resulting GDE was correctly placed on both sides of the membrane to make the membrane electrode assembly (MEA) in situ: no hot pressing was used. Single cell APEFCs were tested using an 890E Multi Range fuel cell test station (Scribner Associates, USA) in a galvanic mode at 60 ^{o}C. H_2 and O_2 were humidified at 60 ^{o}C (100 % RH) and fed with a flow rate 1000 cm^{3} min^{-1} with a backpressure of 0 MPa symmetrically on both sides. The cell voltage at each current density was recorded after the power output stabilized.

Table S1: Further enhancing the IEC led to excess swelling ratio and decreased hydroxide conductivity.

Membrane	IEC (mmol/g)	WU (%)	Swelling (%)	OH^{-} Conductivity (mS/cm)
6QA-4	2.23	58.5	14.4	31.0
6QA-5	2.34	82.7	17.6	33.0
6QA-6	2.57	120.2	28.4	25.2

Figure S2 Fuel cell performance of prepared AEM at lower IEC value of 1.81 mmol/g.



2. Materials

Perfluorobiphenyl, bi-phenol A, dibromohexane, Cs_2CO_3 and 2,4,6-tris-(dimethylaminomethyl)-phenol was purchased from Energy Chemical Co. Ltd. (Shanghai, P.R. China) and used as received. N,N-Dimethylformamide (DMF, AR), tetrahydrofuran (THF), ether, ethanol, chloroform, trimethylamine aqueous solution (33 %), Hydrochloric acid (HCl) aqueous solution (37% AR), sodium chloride (AR), sodium hydroxide (AR) and sodium sulfate (Na_2SO_4, AR) were purchased from Sinopham Chemical Reagent Co. Ltd. Deionized water was used throughout.

2.1 Synthesis of Fluorinated Poly Arylene Ether (FPAE)

Perfluorobiphenyl (7.3179 g), bi-phenol A (5 g) and K_2CO_3 (10 g) were reacted in 40 mL DMF at 40 ^{o}C under N_2 atmosphere. 24 hours later, 1 g of perfluorobiphenyl was added and the solution was stirred at 60 ^{o}C for another 24 h. Afterwards, the resulting solution was poured into excess water and filtrated. After dried at 60 ^{o}C for 24 h, the polymer was redissolved by $CHCl_3$ and precipitated in methanol. After filtration and dried at 60 ^{o}C, white polymer product were obtained and named as FPAE. NMR spectrum of FPAE was recorded using $CDCl_3$ as the solvent and depicted in Figure S3 (Below).

2.2 Synthesis of 6-bromo-N,N,N-trimethylhexan-1-aminium Bromide (BrC6QA)

To a stirred solution of dibromohexane (10 mL) in THF (100 mL) was continuously bumbled dry trimethylamine gas at ambient temperature and pressure for 3 hours. Afterwards, the reaction mixture was stirred at room temperature for 48 hours. The white precipitate was collected and washed with ether followed by dried in vacuum for 48 hours (Yield=92 %). NMR spectrum of BrC6QA was obtained employing D_2O as solvent and depicted in Figure S3 (Upper).

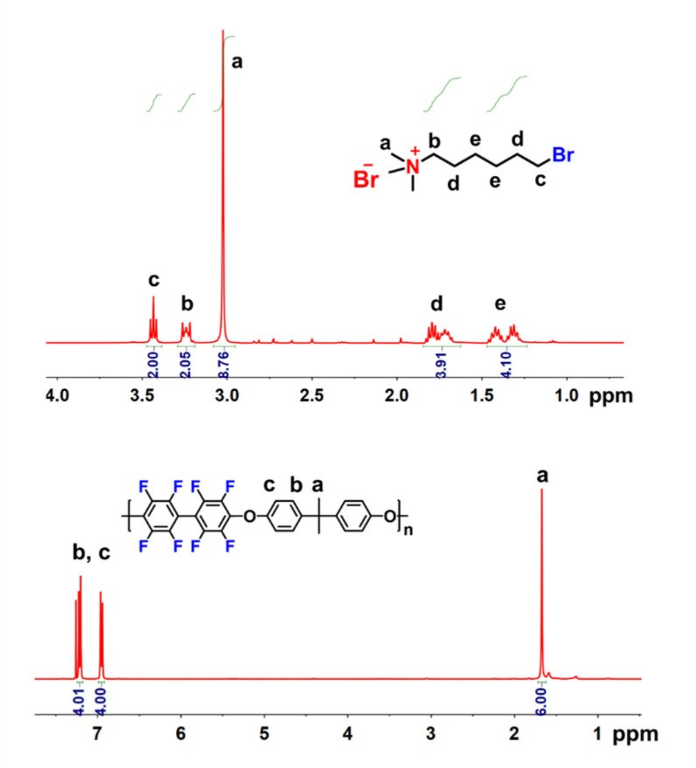


Figure S3. ^{1}H NMR spectra of BrC6QA (upper) and FPAE (Below).

2.3 *Synthesis of Tertiary Amine Functionalized FPAE (3TA-FPAE)*

The grafting ratio of tertiary amine was controlled by the added amount of tris(dimethylaminomethyl) phenol (3TA-OH). The synthetic procedure of 3TA-FPAE-4 is described here: FPAE (0.5 g), 3TA-OH (0.15 g) and Cs_2CO_3 (1 g) was added to 20 mL DMF. The reaction mixture was heated to 100 ^oC and stirred under N_2 atmosphere for 24 h. The 3TA-FPAE-4 was obtained by precipitating into ether and washed with water. NMR spectrum of 3TA-FPAE-4 was recorded using $CDCl_3$ as the deuterated solvent.

2.4 Synthesis of the AEMs with Branched Ionic Cluster (6QA-x)

3TA-FPAE (0.5 g), BrC6QA (1.25 equiv) were dissolved in 10 mL DMF. The reaction mixture was heated to 60 ^oC and stirred for 24 hours. The resulting solution was precipitated in ether and washed with $CHCl_3$. After dried in vacuum at room temperature for 24 h, 6QA-x was obtained and characterized by NMR using DMSO-d_6 as the deuterated solvent. Anion exchange membrane of 6QA-x can be obtained by casting onto a glass plate and dried at 80 ^oC for 4 hours.

Reference

[1] J. Ran, L. Wu, T. Xu, Enhancement of hydroxide conduction by self-assembly in anion conductive comb-shaped copolymers, Polymer Chemistry, 4 (2013) 4612.