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Highly Conductive and Stabilized Side-chain-type Anion Exchange Membranes: Ideal Alternatives For Alkaline Fuel Cells Applications

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1. Characterizations

Structure identification: the chemical compositions of the polymers synthesized in this study were identified by ^1H NMR (Bruker 510 instrument operating at 400 MHz).

Ion exchange capacity (IEC): Experimental IECs was measured using the Mohr approach. Firstly, the membranes were converted into Cl^- form by immersing them into aqueous NaCl (1 mol/L) solution for 24 h. The membranes (in Cl^-) were washed with deionized water for several times and dried at 60 ^oC under vacuum for 24 h and subsequently, their weights were recorded. The membranes were then converted into the SO_4^{2-} form by immersing them in aqueous Na_2SO_4 (0.5 mol/L) solution for 24 h. The Cl^- ions, released from the membranes, were then titrated with aqueous $AgNO_3$ (0.05 mol/L) using K_2CrO_4 as a colorimetric indicator. IEC (expressed as mmol/g), was calculated from the amounts of $AgNO_3$ consumed in the titration process and the mass of the dry membranes in the Cl^- form.

Water uptake (WU): A sample of membrane (1 cm × 4 cm) was immersed in deionized water at a pre-set temperature for 24 h. After this hydration step, the sample was removed from the water, and the surfaces were quickly wiped with tissue paper. The mass and length were immediately measured. The water uptake (WU) of membranes was calculated as follows:

$$WU = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\% \qquad (1)$$

where W_{wet} is the hydrated mass and W_{dry} corresponding to wet weight and dry weight respectively (recorded after the membranes were dried at 60 ^oC until a constant weight was reached).

Linear dimensional swelling (LER): LER was determined by immersing samples (1 cm in width and 4 cm in length) into water at 30 ^oC for 24 h, the changes were calculated from:

$$LER = \frac{L_{wet} - L_{dry}}{L_{dry}} \times 100\% \qquad (2)$$

where L_{dry} and L_{wet} are the length of the membrane at dry state and wet state, respectively.

λ: this parameter is equal to the average number of water molecules per QA group, is employed to evaluate the water absorption of ionic groups, and calculated by

$$\lambda = \frac{WU(\%) \times 10}{18 \times IEC(mmol/g)} \quad (3)$$

Hydroxide conductivity: the measurement of hydroxide conductivity of an anion exchange membrane (AEM) was performed using the four-point probe technique. An Autolab Zahner Zennium E (Germany) under galvanostatic mode with an AC current amplitude of 0.1 mA and a frequency range of 1 MHz -100 Hz was adopted for determining hydroxide conductivity. The as-tested AEM was placed into a Teflon cell where it was compactly in contact with 2 current collecting electrodes and 2 potential sensing electrodes (the distance between the potential sensing electrodes was set to be 1 cm). The cell was completely immersed in deionized water and the impedance spectrum was measured. The testing was done as quickly as possible to minimize the potential error caused by the reaction of the hydroxide ions with dissolved carbon dioxide in the AEMs, which results in the formation of carbonate/bicarbonate anions and a reduced AEM conductivity. The resulting hydroxide conductivity was calculated according to the following equation:

$$\sigma = \frac{L}{RWd} \quad (4)$$

where R is the membrane resistance, L is the distance between potential sensing electrodes, and W and d are the width (1 cm) and thickness of the membrane respectively. At the pre-determined temperatures, the samples were equilibrated for at least half an hour prior to measurements.

Atomic force microscopy (AFM): Tapping mode AFM observations were performed with a veeco diInnova SPM, using micro-fabricated Cantilevers with a force constant of approximately 20 N/m.

Transmission electron microscopy (TEM): the sample was prepared as follows: membranes were stained by soaking in 1 mol/L KI solution for two days, then rinsed with water for several times and dried under vacuum at room temperature. The samples were sectioned to yield slices about 100 nm thick using a LEICA UC6+UC7 ultramicrotome and coated on copper grids. Electron pictures were taken with a JEM-2100 transmission electron microscope using as accelerating voltage of 200 kV.

Thermal stability: Thermal stability of samples was measured using a TGA Q5000 instrument under nitrogen atmosphere at a heating rate of 10 ^{o}C /min.

Mechanical performance: Prior to mechanical stretch, the as-prepared membranes were immersed in water for 4 h for wet measurements. The tensile measurements were carried out using a Q800 dynamic mechanical analyser (DMA, TA Instruments) at a stretch rate of 0.5 N/min.

Alkaline stability evaluation: The as-prepared AEMs were treated by aqueous NaOH (2 mol/L) solutions at 60 ^oC for 30 days or at 80 ^oC for 15 days. They were then thoroughly washed with deionized water (to remove the excess sodium hydroxide) and immersed in deionized water prior to the measurement of the conductivities, IECs and mechanical properties as well as ^1H NMR characterizations. The structure and hydroxide conductivity at 30 ^oC were recorded as a function of aging time in the alkaline solution.

Fuel cell testing: The Pt/C catalysts (60%w/w in metal content) were ultrasonically mixed with the D-SC-paAE100% or L-SC-paAE100% ionomers solution to yield inks containing 20%w/w of ionomers and 80%w/w of catalysts. Then the resulting catalyst inks were used to fabricate gas diffusion electrodes (GDEs) by manually spraying onto a large 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 membrane is quaternary ammonium functionalized brominated poly(phenylene oxide) (QPPO) with an IEC of 1.9 mmol/g, which is prepared referring to the previous report.[1] The prepared GDE and membranes were then converted to OH^- form by immersing in aqueous NaOH (1 mol/L) solution for 12 h followed by thorough washing with water. 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 alkaline fuel cells were tested by using an 890E Multi Range fuel cell test station (Scribner Associates, USA) in a galvanic mode at 60 ^oC and 80 ^oC. H_2 and O_2 were humidified at 60 ^oC and 80 ^oC (100% RH) and fed with a flow rate of 1000 cm^3/min without a backpressure. The cell voltage at each current density was recorded after the power output stabilized. For the duration testing, the power density curves were recorded at intervals of 20 mins, and this testing lasted 1 hour.

2. Computation details

The Martini coarse-grained (CG)[2] model was employed to describe the SC, D-SC, L-SC systems. Four kinds of beads including paAE segments (Backbone), alkyl side chains (SC), quaternary ammonia cations (QA), hydrated hydroxide anions (OH) were involved (Fig. S1). In our simulations, the Backbone and SC were represented by nonpolar (N) and apolar (C) interaction sites, respectively. Both QA and hydrated hydroxide anions OH were represented by charged interaction site (Q) with one positive and one negative charge, respectively. 12 Backbone beads were used to construct the backbone of a unit, and each polymer chain consisted of 10 units. All the simulated systems contained 800 polymer chains, with corresponding number of OH beads added to maintain the whole system electric neutrality. The bonded and non-bonded interaction parameters in the original report were used here.[2] The only change lay in the force constant K_{angle}, which was set to be 50 kJ/(mol·rad^2) to describe the rigid backbone.

Firstly, the polymer chains were scattered randomly in a cubic box; then the reasonable starting configuration of the system was obtained via an annealing protocol in the NVT ensemble for 60.0 ns. Subsequently, a 50.0 ns simulation in the NPT ensemble was performed at P = 1 atm and T = 300 K to equalize the system. The velocity rescale thermostat and Berendsen isotropic barostat were employed to impose constant temperature and pressure, respectively. Finally, a 100.0 ns simulation in the NPT ensemble was carried out at P = 1 atm and T = 300 K for the collection of the product. The velocity rescale thermostat was employed to regulate the temperature, while the Parrinello-Rahman isotropic coupling algorithm was used to maintain constant pressure. The time step of 20.0 fs was chosen for all molecular dynamics (MD) simulations. The periodic boundary conditions were applied in all three directions. The electrostatic interactions were treated by the reaction field approach with a screening constant of 15. A cutoff distance of 1.1 nm was used for both the electrostatic interactions and the van der Waals interactions. All the MD simulations were performed using the GROMACS package,[3] and all the snapshots were collected using VMD.[4]

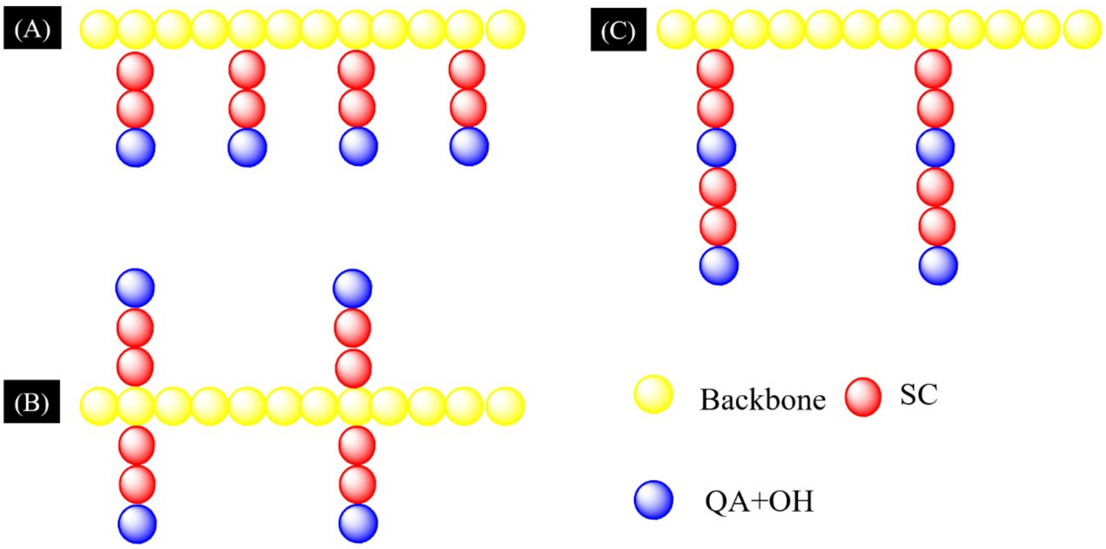


Fig. S1. The models used for the calculated system (A) SC; (B) D-SC; (C) L-SC.

3. Materials and synthesis

Materials: Poly(arylene ether phosphine oxide)s bearing amino moieties was kindly provided by Tianjin Yanjin Technology Co. Ltd. (Tianjin, China) and denoted as paAE by the company. The commercial paAE was purified by firstly dissolving in NMP, precipitating in purified water, and drying at 60 ^{o}C until constant weights were reached. The compositions of paAE were identified by ^{1}H NMR using d-DMSO as solvents (Fig. S2). Brominated poly(phenyleneoxide) (Br-PPO) was kindly given by Tianwei Membrane Corporation Ltd. (Shandong, China). The commercial Br-PPO was purified by firstly dissolving in NMP, precipitating in purified water, and drying at 40 ^{o}C until constant weight was reached. 1,6-dibromohexane, N,N,N',N'-tetramethyl-1,6-diaminohexane, N,N-Diisopropyl-ethylamin (DIPEA) were purchased from Energy Chemical Co., Ltd. Bromoethane (AR), tetrahydrofuran (THF, AR), acetonitrile (AR), diethyl ether (AR), N-methyl-2-pyrrolidolone (NMP, AR), trimethylamine aqueous solution (TMA, AR), dimethyl sulfoxide (DMSO, AR), sodium chloride (NaCl, AR), sodium sulfate (Na_2SO_4, AR), sodium hydroxide (NaOH, AR), silver nitrate ($AgNO_3$, AR), potassium chromate (K_2CrO_4, AR), ethanol (AR) were purchased from Sinopham Chemical Reagent Co., Ltd. All these reagents were used as received without further purification. Deionized water was used throughout the experiments.

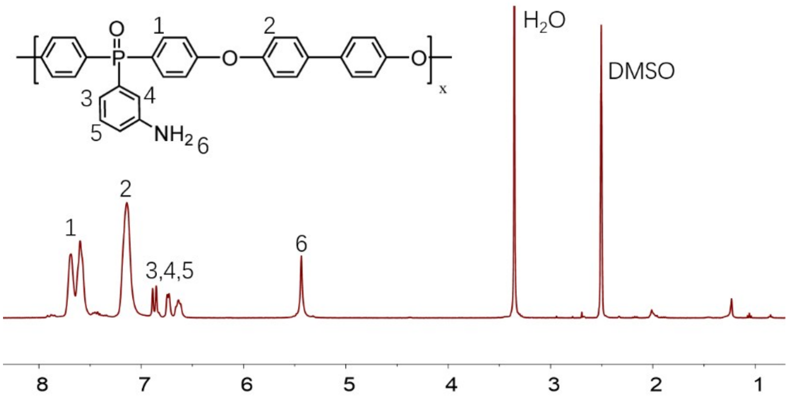


Fig. S2 The ^{1}H NMR spectrum of representative paAE with 100% -NH_2 functionalization (d-DMSO).

Synthesis of 6-bromo-N,N,N-trimethylhexane-1-aminium bromide (BrQA) (Scheme S1): Dry trimethylamine gas was continuously bumbled into a stirred solution of 1,6-dibromohexane (10 mL) in THF (100 mL) 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. The resulting monomers were exchanged with $NaBF_4$ to gain BF_4^- type monomers. The chemical structure of BrQA in the Br^- form was confirmed by the ^{1}H NMR employing D_2O as solvent and depicted in Fig. S3.

Scheme S1. The synthesis route of BrQA.

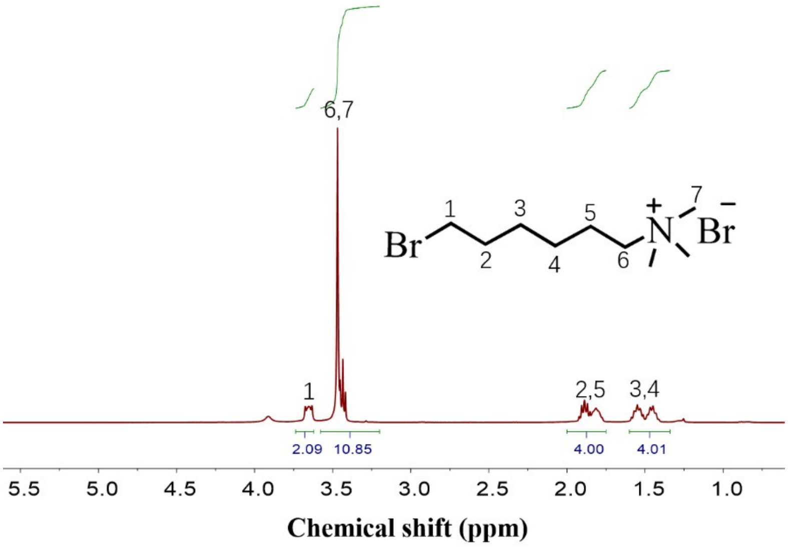
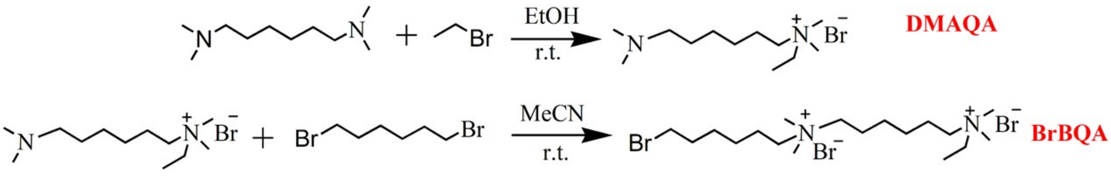


Fig. S3. The ^{1}H NMR spectrum of BrQA (D_2O).

Synthesis of 6-(dimethylamino)-N-ethyl-N,N-dimethylhexan-1-aminium bromide (DMAQA) (Scheme S2): 10 mL bromoethane in 40 mL ethanol was slowly dropwise added into 40 mL N,N,N',N'-tetramethyl-1,6-diaminohexane in 80 mL ethanol. The reaction was carried out for 48 hours at room temperature under continuous stirring. Then the ethanol was removed by rotary evaporation to obtain white solids. Acetone was used to dissolve the products and other impurities cannot dissolve in acetone. By means of filtration, the unreacted monomers were removed. The purified product was gathered by evaporating acetone in vacuum. The chemical composition of DMAQA was characterized by the ^{1}H NMR employing D_2O as the solvent and depicted in Fig. S4.



Scheme S2. The synthesis routes of DMAQA and BrBQA.

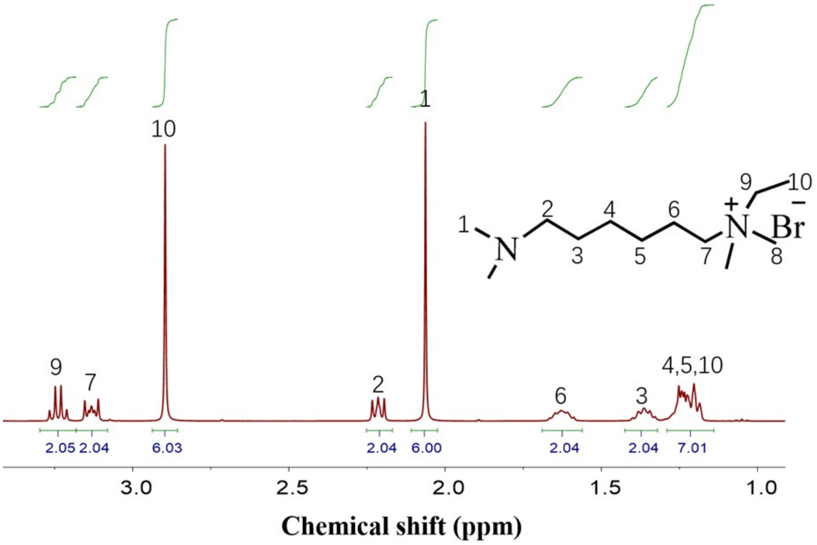


Fig. S4. The ^{1}H NMR spectrum of DMAQA (D_2O).

Synthesis of 12-bromo-N6-ethyl-N1,N1,N6,N6,- tetramethylhexane-1,6-diaminium bromide (BrBQA) (Scheme S2): After obtaining DMAQA, the quaternary ammonium reaction was performed for the second time. 1.807 g in 20 mL acetonitrile was slowly dropwise added into 10 mL 1,6-diaminohexane. This step reaction was carried out for 24 hours at room temperature. Then the solution was poured into excess diethyl ether to gain white solids. The resulting white solids were washed by acetone for several times to get purified products. The chemical composition of DMAQA was characterized by the ^{1}H NMR employing D_2O as the solvent and depicted in Fig. S5.

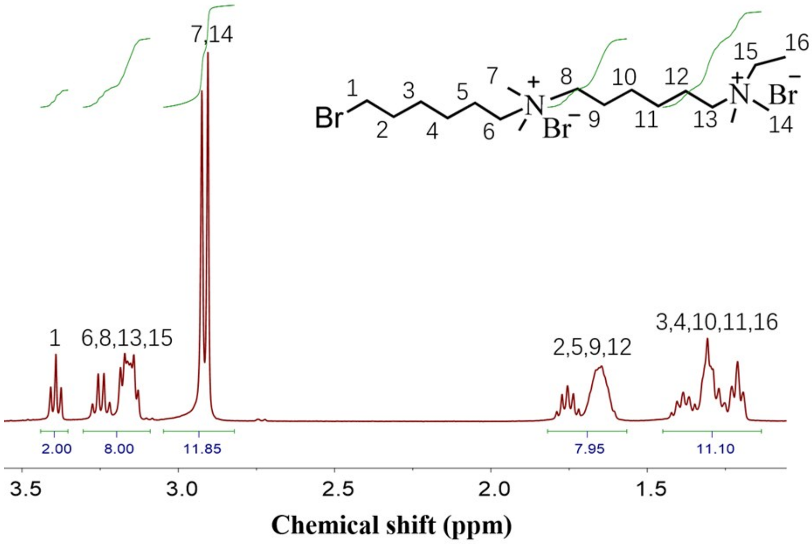


Fig. S5. The ^{1}H NMR spectrum of BrBQA (D_2O).

Synthesis of D-SC-paAE: The reaction process of D-SC-paAE100% was used as an exemplary project to show the synthesis details of D-SC-paAE100%. 0.5 g paAE with 100% $-NH_2$ functionalization degrees and 20 mL NMP were added in a three-neck, round-bottomed flask under N_2 atmosphere. After the polymers completely dissolved, 1390 μL DIPEA were added as acid binding agents. This process lasted for 2 hours at 60 ^{o}C. Then, 2.61 g BrQA (in the form BF_4^-) monomers were added for the ultimate reaction. The reaction was performed for 48 hours at 130 ^{o}C.

Synthesis of L-SC-paAE: The synthesis of L-SC-paAE is completely identical with that of D-SC-paAE. The only difference lies the added DIPEA and BrBQA (in the Br^- form) amounts are 348 μL and 0.36 g, respectively. And the reaction time was shortened to 24 hours to avoid extravagant grafting.

Synthesis of quaternary ammonium functionalized brominated poly(phenylene oxide) (QPPO): Br-PPO was immersed in excess aqueous TMA (1 mol/L) solutions for 20 h at 30 ^{o}C to allow the partial conversion of $-CH_2Br$ to QA groups. The IEC of the gained membranes is 1.90 mmol/g, which will serve as separator membranes for fuel cell measurements.

Membranes preparation: The resulting products were dissolved into DMSO to get 5 wt % solution and then the solution was filtered. The above solution was cast onto a sufficiently levelled glass plate, and dried at 60 °C for 24 h to get the membranes. Then the membrane was converted into OH^- form through treating the membranes in 1 mol/L NaOH at room temperature for 24 h; they were washed thoroughly and immersed in deionized water for 48 h to remove residual NaOH. The OH^- form membranes were characterized immediately.

4. Activation energy

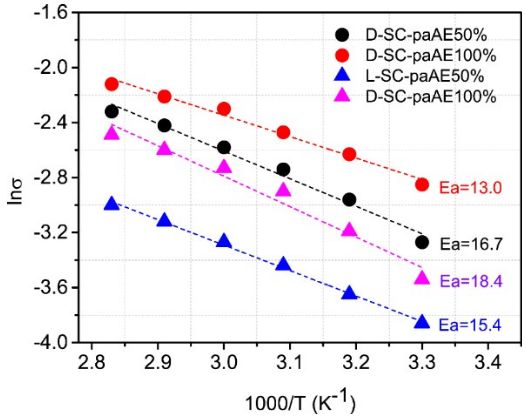


Fig. S6 Hydroxide conductivity of four as-prepared AEMs as a function of temperature for estimation of activation energies.

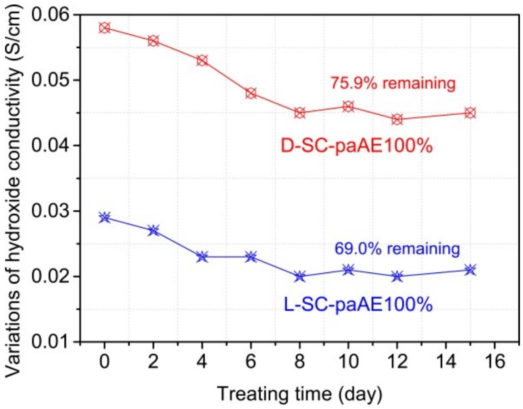


Fig. S7 The variations of hydroxide conductivity at 30 °C as a function of alkaline treating time (2 mol/L NaOH, 80 °C)

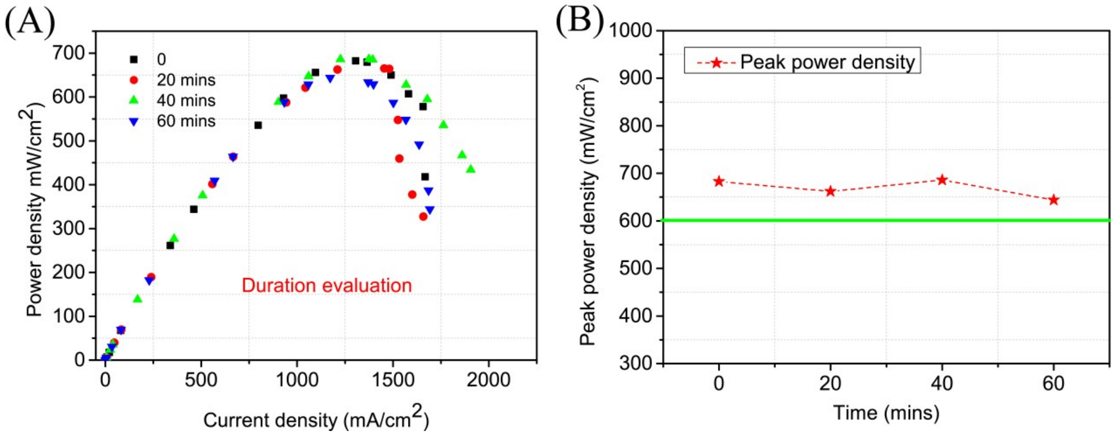


Fig. S8 (A) The power density curves of AEMFCs using D-SC-paAE100% as ionomers in both of cathode and anode at 80 °C. The data was recorded every 20 min after the cell temperature being stable at 80 °C and the process of single cell experiment at 80 °C lasted 60 min. (B) The peak power densities as a function of lasting testing time.

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