Supplementary Information

A Strategy for Disentangling the Conductivity-Stability Dilemma in Alkaline Polymer Electrolytes

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I. Experimental details

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%), glycidyltrimethylammonium chloride (GTMAC), dimethylamine (Shanghai Chemical Reagent Co. Ltd, 33wt% aqueous solution), N,N-dimethylformamide (DMF, Shanghai Chemical Reagent Co. Ltd, 99%), potassium hydroxide (Sinopharm Chemical Reagent Co. Ltd, 85%), hydrochloric acid (Sinopharm Chemical Reagent Co. Ltd, 37%) were used as received.

1-dimethylamino-2-hydroxy-3-trimethylammoniumpropane chloride (DHTC): GTMAC (10 g) was dissolved in water (50 mL) to form a solution and added into a 33wt% aqueous solution of dimethylamine (20 mL) at room temperature. Then the reaction mixture was

stirred for 5 h at 60°C. After the reaction, the solvent and excess dimethylamine was removed on a rotary vacuum evaporator at 50°C to yield the DHTC.

DHTC ([(CH₃)₂NCH₂CH(OH)CH₂N(CH₃)₃]⁺ Cl⁻): ¹HNMR (300MHz, d⁴-methanol): (CH₃)₂N-: δ 2.34ppm, s, 6H; (CH₃)₂NCH₂-: δ 2.37-2.42 ppm, d, 2H; -CH(OH)-: δ 4.24-4.31 ppm, m, 1H; -CH₂N⁺(CH₃)₃: δ 3.36-3.39 ppm, d, 2H; -N⁺(CH₃)₃: δ 3.26ppm, s, 9H. ESI-MS (m/z; found): 161.1 (100%, M⁺).

Chloromethylation of polysulfone (CMPS): CMPS used in this study was synthesized following procedures reported in our early works. The chloromethylation process of PS was carried out in a three-neck round-bottom flask with a mechanical stirrer. PS (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) were precipitated into methanol, washed several times with deionized water, and then dried in a vacuum oven for 24 h at 60°C.

Dual-cation quaternary ammonium polysulfone (DQAPS): Dried CMPS powders were dissolved in DMF to form a solution of 10wt%, into which DHTC was added and stirred for 5 h at 40°C to produce DQAPS (the grafting degree of cations was determined by the amount of DHTC added). The resulting DQAPS solution was cast onto a clean, flat glass plate and dried in oven at 55°C for 20 h and then further dried in a vacuum oven at 80°C for 10 h. To replace the Cl⁻ anion in DQAPS for OH⁻, the DQAPS membrane was immersed in 1 mol/L KOH solution for 10 h. This process was repeated for four times to ensure a complete displacement. Finally, DQAPS membrane with OH⁻ anion was repeatedly rinsed with deionized water until the pH of residual water was neutral.

Measurements: ¹*HNMR* (300 *MHz*): 1HNMR(300 MHz) analysis was performed on a Varian Mercury VX-300 spectrometer using deuterated dimethyl sulfoxide ([D₆]DMSO) as the solvent and tetramethylsilane (TMS) as the internal reference.

Fourier-transform infrared (FT-IR) characterization: Fourier infrared (FT-IR) spectra of membranes were obtained on a Nicolet 6700 FT-IR spectrometer with a wave number resolution of 4 cm⁻¹ and range of 400~4000 cm⁻¹.

Ion exchange capacity (IEC): The IEC of APE was determined by titration. A membrane

(in OH⁻ form) was immersed in a standard hydrochloric acid solution (0.1 mol/L, 30 mL) for 48 h. The solution was then titrated with a standard solution of potassium hydroxide (0.1 mol/L) to pH = 7. The membrane was washed and immersed in deionized water for 24 h to remove any residual 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 with eq 1:

$$IEC = \frac{n_{i(H^+)} - n_{f(H^+)}}{m_{dry(H^+)}}$$
(1)

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

Ionic conductivity: The OH⁻ conductivity of fully hydrated membranes with different IEC was measured at 60°C using AC impedance spectroscopy (IviumStat, The Netherlands). A membrane in OH⁻ form was cut into 2×2 cm² and sandwiched between two electrodes made of Teflon-bounded carbon film. The membrane resistance was measured under the open-circuit mode over a frequency range of 1Hz to 1MHz with oscillating amplitude of 5 mV. The ionic conductivity was calculated as:

$$\sigma = \frac{l}{R_{\rm mem} \times A} \tag{2}$$

where *l* is the membrane thickness in cm, *A* is the electrode area in cm², and R_{mem} is the high-frequency resistance in Ω .

Swelling degree: In order to obtain the swelling degree (denoted as *s.d.*%), the dimension of the dry membranes (in Cl⁻ form, denoted as $x_{hyd(Cl)}$) was recorded first. The membrane was then immersed in 1 mol/L KOH solution for 48 h to convert Cl⁻ into OH⁻, and washed with deionized water for several times to remove the remaining KOH. The dimension of the membranes $x_{hyd(OH)}$ can be determined after wiping the excess water from the surface. Accordingly, the *s.d.*% was calculated via eq 3:

$$s.d. \% = \frac{x_{hyd(OH)} - x_{hyd(CI)}}{x_{hyd(CI)}}$$
(3)

Mechanical strength: A tensile tester (CMT6503, Shengzhen SANS Test Machine Co. Ltd, China) was employed to analyze the tensile stress–strain behavior of fully hydrated membranes in OH⁻ form at room temperature. A constant crosshead speed of 5 mm/min was used for samples of 1 cm in width and 3 cm in length.

Grafting degree (*GD*): GD is defined as the portion of those structural units in APE that were grafted with functional groups. The actual level of GD can be characterized by ¹HNMR.

Glass-transition temperature (T_g): T_g was determined on a differential scanning calorimeter (DSC Q200, TA Instruments) at a heating rate of 20°C/min under nitrogen atmosphere. The samples were heated from -30°C to 260°C, and T_g was reported as the temperature at the middle of the thermal transition from the second heating scan.

Fuel Cell Tests: Pt/C (60%, Johnson Matthey Co.) was mixed with DQAPS ionomer solution and sprayed on each side of the DQAPS membrane (50 ± 2 µm in thickness) to produce the catalyst-coated membrane (CCM). The Pt loading in both anode and cathode was 0.3 mg/cm², and the area of the electrodes was 9 cm². The weight percentage of DQAPS in both the anode and the cathode was 15 wt%. The resulted CCM was pressed between two pieces of Teflon-treated carbon paper (Toray-250) to make a membrane electrode assembly (MEA).

 H_2 -O₂ fuel cell tests were conducted (850e Multi Range, Scribner Associates Co.) using fully humidified (RH=100%) H_2 and O_2 flowing at 50 mL/min. The *I-V* curves were measured point by point galvanostatically and the voltage was not taken after 10 min of polarization.

II. Supplementary table and figure

	QAPS	DQAPS
IEC (mmol/g)	1.05	1.91
Mechanical strength (MPa)	9.6	16.5
Glass transition temperature (°C)	217.5	236.2

Table S1. Physicochemical properties of QAPS and DQAPS membranes[†].

† The membrane was pretreated in water at 30°C for 1 hour, and the mechanical strength was measured at room temperature. The glass transition temperature was measured via DSC.



Figure S1. FTIR spectra of QAPS and DQAPS membranes.



Figure S2. Performance of H₂-O₂ APEFC using DQAPS membrane (50±2 μm thick, IEC=1.91mmol/g) and ionomer. Pt/C (60%, Johnson Matthey Co.) was employed as the catalysts in both anode and cathode, each with a loading of 0.3 mg/cm². The weight percentage of DQAPS ionomer in the catalyst layers was 15 wt%. Testing conditions: 60°C, RH=100%, pure H₂ and O₂ gases were flowing at a rate of 50 mL/min, no back pressure.