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⁻]: ¹H NMR (300 MHz, d⁴-methanol): (CH₃)₂N⁻: δ 2.34 ppm, 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 3.26 ppm, 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 10 wt%, 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: ¹H NMR (300 MHz): ¹H NMR(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\(^\circ\)C for 24 h and weighed to determine the dry mass (in Cl\(^-\) form). The IEC of the membrane is calculated with eq 1:

\[
IEC = \frac{n_i(H^+) - n_f(H^+)}{m_{\text{dry}(H^+)}}
\]  

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 \(m_{\text{dry}(Cl)}\) 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\(^\circ\)C using AC impedance spectroscopy (IviumStat, The Netherlands). A membrane in OH\(^-\) form was cut into 2×2 cm\(^2\) 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:

\[
\sigma = \frac{l}{R_{\text{mem}} \times A}
\]

where \(l\) is the membrane thickness in cm, \(A\) is the electrode area in cm\(^2\), and \(R_{\text{mem}}\) is the high-frequency resistance in \(\Omega\).

**Swelling degree:** In order to obtain the swelling degree (denoted as s.d.%), the dimension of the dry membranes (in Cl\(^-\) form, denoted as \(x_{\text{dry}(Cl)}\)) 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 \(x_{\text{dry}(OH)}\) can be determined after wiping the excess water from the surface. Accordingly, the s.d.% was calculated via eq 3:

\[
s.d. \% = \frac{x_{\text{hyd}(OH)} - x_{\text{hyd}(Cl)}}{x_{\text{hyd}(Cl)}}
\]
**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 \(^1\)HNMR.

**Glass-transition temperature \((T_g)\):** \(T_g\) was determined on a differential scanning calorimeter (DSC Q200, TA Instruments) at a heating rate of 20\(^\circ\)C/min under nitrogen atmosphere. The samples were heated from -30\(^\circ\)C to 260\(^\circ\)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/cm\(^2\), and the area of the electrodes was 9 cm\(^2\). 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\(_2\)-O\(_2\) 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

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

<table>
<thead>
<tr>
<th></th>
<th>QAPS</th>
<th>DQAPS</th>
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</thead>
<tbody>
<tr>
<td>IEC (mmol/g)</td>
<td>1.05</td>
<td>1.91</td>
</tr>
<tr>
<td>Mechanical strength (MPa)</td>
<td>9.6</td>
<td>16.5</td>
</tr>
<tr>
<td>Glass transition temperature (°C)</td>
<td>217.5</td>
<td>236.2</td>
</tr>
</tbody>
</table>

† 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.