

Ecofriendly and Simplified Synthetic Route for Polysulfone-based Solid-State Alkaline Electrolyte Membrane

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Abstract: Problem statement: Recently the alkaline system for fuel cell enhance their presence because of possibility of no-precious-metal catalyst and low over potential at cathode reaction. The anion exchange membrane for alkaline membrane fuel cell should be a key technology in order to achieve the practical performance as fuel cells. Alkaline anion exchange membranes of high ionic conductivities are made from polysulfone by adding a chloromethyl pendant group to the polysulfone, follow by reacting the chloromethyl group with amine to form quaternary ammonium pendant groups which act as the counter ion for hydroxide anion. Chloromethyl methyl ether, N,N-dimethylformamide and methanol are commonly used as agent for providing excellent conversions, but they are now considered to be carcinogenic. To avoid the use of such hazardous materials, in our work we used paraformaldehyde, chlorotrimethylsilane, N-methylpyrrolidone and ethanol as agent for providing conversion. **Approach:** Polysulfone (PS) was chloromethylated using chlorotrimethylsilane as a chloromethylation reagent, resulting in the formation of Chloromethylated Polysulfone (CMPS). CMPS was converted to a quaternized form using trimethylamine and precipitated into ethanol. The powder was dissolved in N-methylpyrrolidone, followed by aminated with a 25 wt% trimethylamine. **Results:** The resulting solution was cast onto a flat glass plate and dried in an oven. The membrane was immersed in KOH solution for 24 h to replace the Cl⁻ anion in the polymer with OH⁻. **Conclusion:** The swelling behavior of polysulfone-based solid-state alkaline electrolyte membrane was closely related to the degree of water uptake (25 WU%, 7.5 SD%) and the ion-exchange capacity was 1.05 mmol g⁻¹, which is sufficient for electrolyte membranes used in alkaline fuel cells.

Key words: Alkaline electrolyte membrane, solid-state alkaline, polysulfone, simplified synthetic route

INTRODUCTION

Alkaline Fuel Cells (AFCs) are hydrogen-fuelled cells containing a liquid electrolyte (aqueous KOH solution) and show the best performance among all known fuel cells operating below 200°C, mainly owing to facile kinetics at the cathode and anode and the use of cheap non-noble metal catalysts, such as nickel and silver (McLean and Niet, 2002; Varcoe and Slade, 2005). However, their electrolyte is easily poisoned by CO₂, which dramatically reduces their performance (Abuin *et al.*, 2010). Solid-state polymer electrolytes with a less corrosive alkaline medium, such as a hydroxide anion exchange membrane, are alternatives to KOH solution. Anion Exchange Membranes (AEMs) are a key technology for achieving good performance in alkaline membrane fuel cells owing to their lower cost and higher durability as compared to

those of commercial conducting polymers and proton exchange membranes. Currently, there is a growing interest in AEMs (Abuin *et al.*, 2010; Asazawa *et al.*, 2007; Bianchini *et al.*, 2009; Fujiwara *et al.*, 2008; Hou *et al.*, 2008; Li *et al.*, 2009; Lu *et al.*, 2008; Matsumoto *et al.*, 2011; Scott *et al.*, 2008; Sleightholme *et al.*, 2008; Tamain *et al.*, 2007; Yang *et al.*, 2008; Yang, 2007; Varcoe and Slade, 2005; Varcoe *et al.*, 2007a; 2007b; Varcoe, 2007). The development of high-performance AEMs depends on the type of membrane materials, ionomers and synthetic methods used, namely, (a) polymers blended with alkaline media; (b) pyridinium-based polymers; (c) radiation-grafted and quaternized polymers; and (d) chloromethylated, quaternized and alkalinized polymers. Many types of AEMs based on quaternized polymers have been developed, such as polysiloxane containing a quaternary ammonium group (Kang *et al.*, 2004),

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poly(oxyethylene methacrylates) containing an ammonium group (Yi *et al.*, 1999), quaternized polyethersulfone cardo (Li and Wang, 2005), quaternized poly (phthalazinone ethersulfone ketone) (Su *et al.*, 2004) and radiation-grafted poly(vinylidene fluoride) and poly(tetrafluoroethylene-hexafluoropropylene) (Danks *et al.*, 2003). As a frequently used polymer-based engineering material, Polysulfone (PS) possesses excellent high-temperature creep resistance, high chemical and oxidative resistance and excellent electrical and mechanical properties. AEMs prepared via chloromethylated and quaternized routes are the most crucial because of their good physical and relatively high chemical stability. Chloromethylether was commonly used as a chloromethylating agent for providing excellent conversions and high product yields, but it is now considered to be carcinogenic and its use has been restricted since the 1940s (IARC, 1974; Laskin *et al.*, 1971; Taylor and Laughlin, 1976). In our work, we used paraformaldehyde and chlorotrimethylsilane as chloromethylating agents and low toxicity solvents, such as N-Methylpyrrolidone (NMP) and ethanol, instead of N,N-dimethylformamide and methanol, respectively.

MATERIALS AND METHODS

All chemicals were purchased from Sigma-Aldrich and used without further purification. Quaternary Ammonium Polysulfone (QAPS) was synthesized in a two-step sequence (chloromethylation and quaternization), as shown in Fig. 1. The chloromethylation of PS was carried out in a three-neck round-bottom flask with a mechanical stirrer. PS (5 g) was dissolved in chloroform (250 mL). After adding stannic chloride (SnCl_4) (0.27 mL) and paraformaldehyde (6.792 g) to the solution, chlorotrimethylsilane (28.64 mL) was added dropwise. The solution was stirred for 48 h at 55°C. The Chloromethylated Polysulfone (CMPS) thus obtained was precipitated into ethanol, washed several times with deionized water and then dried in a vacuum oven

for 12 h at 80°C. Quaternization was carried out using the dried CMPS (1.88 g). The powder was dissolved in NMP (18.85 mL) and further aminated with a 25 wt% trimethylamine solution (3.15 mL) at 60°C for 15 h to obtain QAPS-Cl. The resulting QAPS-Cl solution was cast onto a clean, flat glass plate and dried in an oven at 70°C for 72 h. The QAPS-Cl membrane was immersed in KOH solution (1 M) for 24 h to replace the Cl^- anion in the polymer with OH^- . This process was repeated four times to ensure complete displacement. Finally, the OH-type QAPS (QAPS-OH) membrane was repeatedly rinsed with deionized water until the pH of the residual water was neutral. ^1H NMR (300 MHz, CDCl_3 (PS and CMPS), DMSO-d_6 (QAPS-Cl and QAPS-OH), 25°C, TMS) and FT-IR spectroscopies were used to confirm the AEM structure at each synthesis step. Because the quaternized polymer forms were not soluble in CDCl_3 , DMSO-d_6 was used as the solvent. Water uptake (WU%) and Swelling Degree (SD%) were estimated to determine the percentage of water uptake by the membrane and the Ion-Exchange Capacity (IEC) was determined by the back titration method.

RESULTS

The ^1H NMR spectra in Fig. 2 confirms the structure of PS, as follows (ppm): 6.9-7.9 (multi Hs on phenyl group) and 1.7 (CH_3). As shown in Fig. 2b, chloromethylation occurred at the activated aryl ring between the isopropyl and ether bonds, according to the integrated intensity of peak 9 ($\delta = 4.6$ ppm) (s, 2H, CH_2). Figure 3a shows peak 2 ($\delta = 3.0$ ppm) (s, 9H, CH_3), which clearly indicates the conversion of a chloromethyl group into a quaternary ammonium group. The intensity ratio of peak 1 ($\delta = 4.6$ ppm) (br, 2H, CH_2) to peak 2 was approximately 2:9, which closely matches the ratio of the number of H atoms on the original chloromethyl group to that on the newly attached quaternary ammonium group. This result also indicates that the conversion of the chloromethyl group into the quaternary ammonium group was nearly completed in the second step.

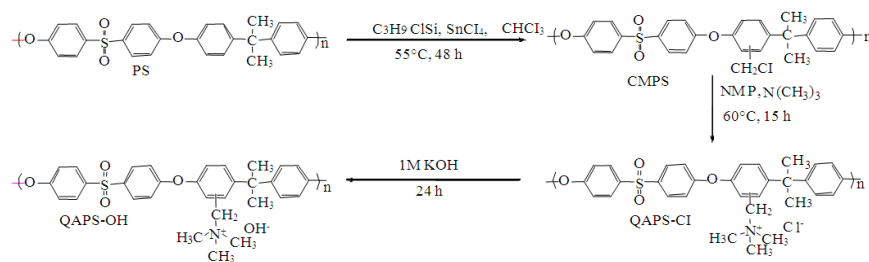


Fig. 1: Preparation of QAPS with OH^- anions via chloromethylated intermediates

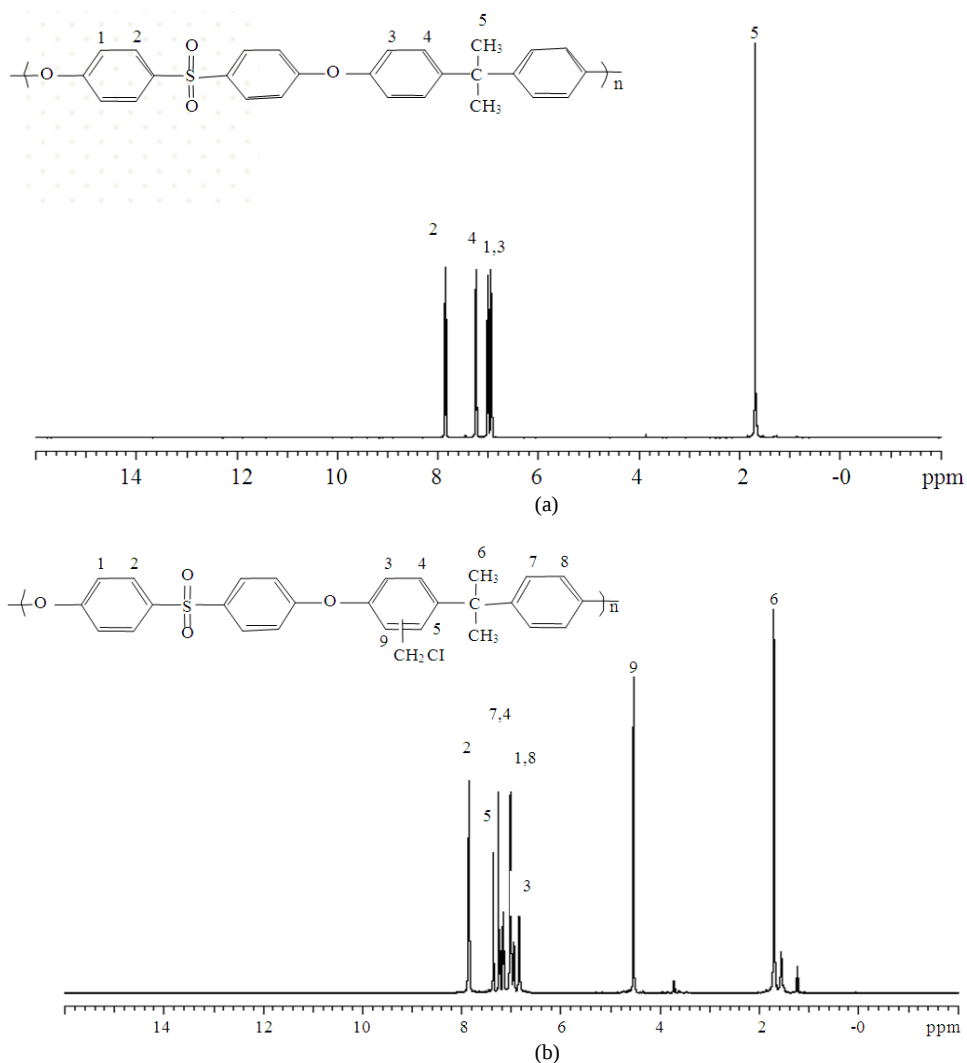


Fig. 2: ^1H NMR spectra of (a) PS and (b) CMPS in CDCl_3

Figure 3b shows the ^1H NMR spectra corresponding to the final product, QAPS-OH. In addition to the well-resolved peaks corresponding to H atoms on the QAPS chain, as shown in Fig. 3a and b, a split peak can be observed at $\delta = 4.6$ ppm (d, $j = 27$ Hz, 2H, CH_2) and a new peak emerges at $\delta = 5.9$ ppm (br, w, 1H, OH), indicating that the Cl^- anion has been successfully substituted by OH^- anion, as shown in Fig. 3b.

The structure of the products was further confirmed by FT-IR analysis. As can be seen in Figure 4, the IR absorption band of PS clearly indicates the presence of the sulfonic group ($\text{O}=\text{S}=\text{O}$) in the polymer back bond at 1149.5 and 1238.2 cm^{-1} . The IR absorption bands at 1485.1 and 1585.4 cm^{-1} are characteristic of the phenyl group. A new characteristic peak with high intensity

was observed at 1683.7 cm^{-1} , corresponding to the aminated aromatic salts.

DISCUSSION

This confirms the successful introduction of ammonium groups into the polymer QAPS-Cl. Therefore, chloromethylation is the most important step in preparing AEMs; the chloromethylated polymer is readily modified further by the high reactivity of the tethered chloromethyl group. The membrane thickness was controlled at 125 μm in the dry state. The membrane swelling behavior was closely related to the degree of water uptake (25 WU%, 7.5 SD%) and the IEC was 1.05 mmol g^{-1} , which is sufficient for electrolyte membranes in AFCs.

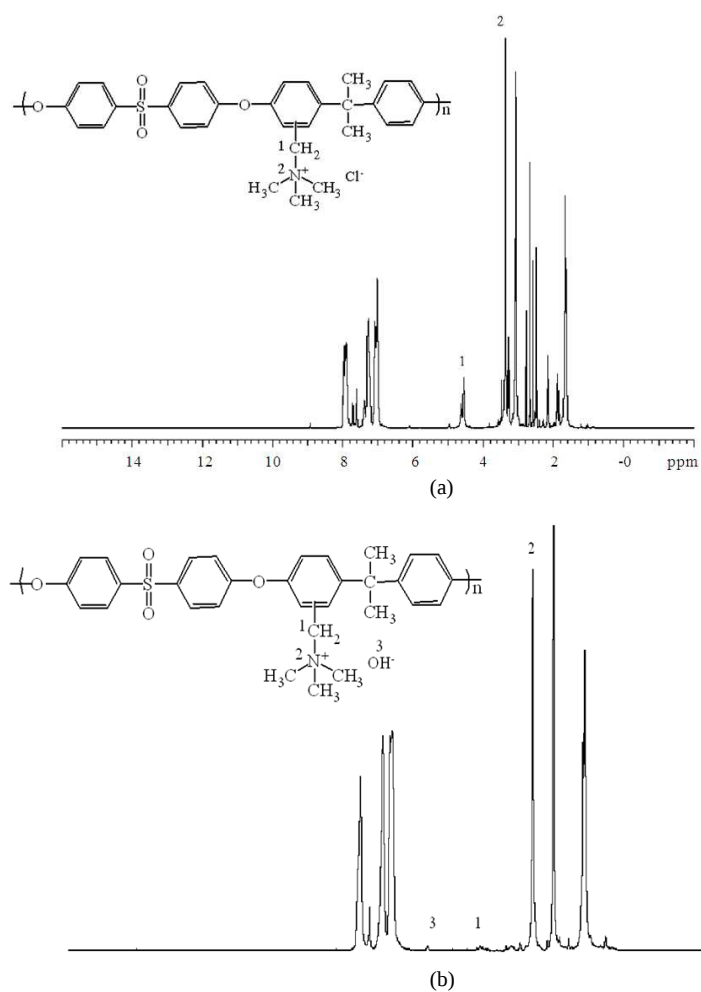


Fig. 3: ^1H NMR spectra of (a) QAPS-Cl and (b) QAPS-OH in DMSO- d_6

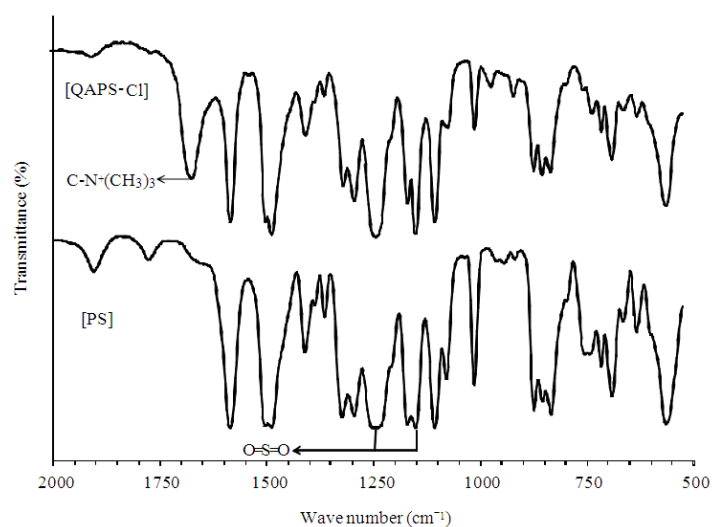


Fig. 4: FT-IR spectra of PS and QAPS-Cl

However, the polymer should be more physically and chemically characterized in terms of ion conductivity, thermal stability, solubility in water and alcohol for further applications as an electrolyte in AFCs.

CONCLUSION

In summary, this is a simplified synthetic route to quaternized PS using reagents of low carcinogenic toxicity. Quaternized PS was prepared by chloromethylation followed by quaternization using trimethylamine as an amination agent. Finally, alkalization was carried out to transform the PS from the Cl⁻ form to the OH⁻ form using 1 M KOH solution.

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