



Short communication

# High-performance alkaline ionomer for alkaline exchange membrane fuel cells



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## ABSTRACT

An alkaline ionomer synthesized with a cross-linker, featured with long aliphatic chains of alkyl groups and inherent diamine structures, not only exhibits a high ionic conductivity ( $60.5 \text{ mS cm}^{-1}$ ), but also significantly boosts the peak power density of  $\text{H}_2/\text{O}_2$  alkaline exchange membrane fuel cells to  $342 \text{ mW cm}^{-2}$ .

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## 1. Introduction

Anion exchange membrane fuel cells (AEMFCs) that utilize alkaline anion exchange membranes (AAEMs) have recently been attracting increasing attention not only because of the enhanced reaction kinetics for both the fuel oxidation and oxygen reductions, but also due to the improved stability and durability of the catalysts in alkaline media [1–4]. As a key component of AEMFCs, an alkaline ionomer is needed to form the ion transport pathways between the reaction sites in the catalyst layer and the membrane. Polysulfone (PSFs), possessing the excellent thermal and chemical stability, has been widely used as the base polymer to synthesize the alkaline ionomer over the past decades [5,6].

Typically, to improve the ionic conductivity, PSFs are often designed with a high ionic exchange capacity (IEC), responding to the number of the conductive groups in the polymer. An increase in the IEC, however, will lead to an increase in the water uptake, resulting in the dissolution of the alkaline ionomer in the solvents at elevated temperatures [3]. To address this issue, different types of cross-linker were proposed to cross-link the functional groups, which help to strengthen the interactions in the polymer matrix, disfavor chain mobility, and reduce void volumes which contain the water molecules in the polymer matrix [7]. When the water uptake is suppressed with the cross-linking process, the alkaline ionomer with high IEC becomes more stable in the solvents even at elevated temperatures.

The hydroxide ionic conductivity can be theoretically improved by increasing the IEC during the cross-linking process, but it can also be sacrificed during the cross-linking process to certain extent due to improper selection of cross-linkers. The reduction in the ionic conductivity

as a result of cross-linking is attributed, in part, to that of the reduced hydroxide ion mobility by the short chain of cross-linkage, and in part, to the fact that chloromethyl groups will be changed to tertiary amine groups, instead of forming the bi-quaternization structure [8]. Hence, it is critically important to select a suitable cross-linker that can not only increase the IEC to enhance the ionic conductivity, but can also simultaneously minimize the aforementioned negative effect on the ion mobility. In this work, we present an alkaline ionomer obtained through cross-linking chloromethylated PSFs (CMPSFs) by N,N,N',N'-tetramethyl-1,6-hexanediamine (TMHDA) and simultaneously quaternizing by trimethylamine (TMA). TMHDA takes the role of both the cross-linker and amination reagent. The long aliphatic chain of the alkyl groups ( $-(\text{CH}_2)_6-$ ) enables the influence of the cross-linking process on the hydroxide ion mobility to be significantly reduced. It is demonstrated that the ionomer will not dissolve in the mixture until the IEC exceeds  $1.62 \text{ mmol g}^{-1}$  after the cross-linking process. As a result, the synthesized ionomer exhibits not only a high ionic conductivity, but also a low swelling degree.

## 2. Experimental

### 2.1. Synthesis of CMPSFs and diamine cross-linked quaternized polysulfone (DAPSF)

The DAPSF was synthesized through three steps: chloromethylation, quaternization and alkalization as reported elsewhere [3]. The CMPSFs were synthesized using chloromethyl methyl ether as the chloromethylation reagent. The obtained CMPSFs were dissolved into N, N-Dimethylformamide (DMF) to form 5 wt.% solutions. The quaternization process was performed by adding TMHDA and TMA in a molar ratio of  $1(-\text{CH}_2\text{Cl}):3(\text{TMHDA}):5(\text{TMA})$  in sequence. The

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excess of amination agents were added to guarantee the complete amination process. The mixed solutions were stirred at 40 °C for 10 h and precipitated in methanol and dried under vacuum at 60 °C. For comparison, the ionomer only aminated by TMA was also prepared without the cross-linking reagent, denoted by TAPSF.

## 2.2. Characterization and fuel cell performance

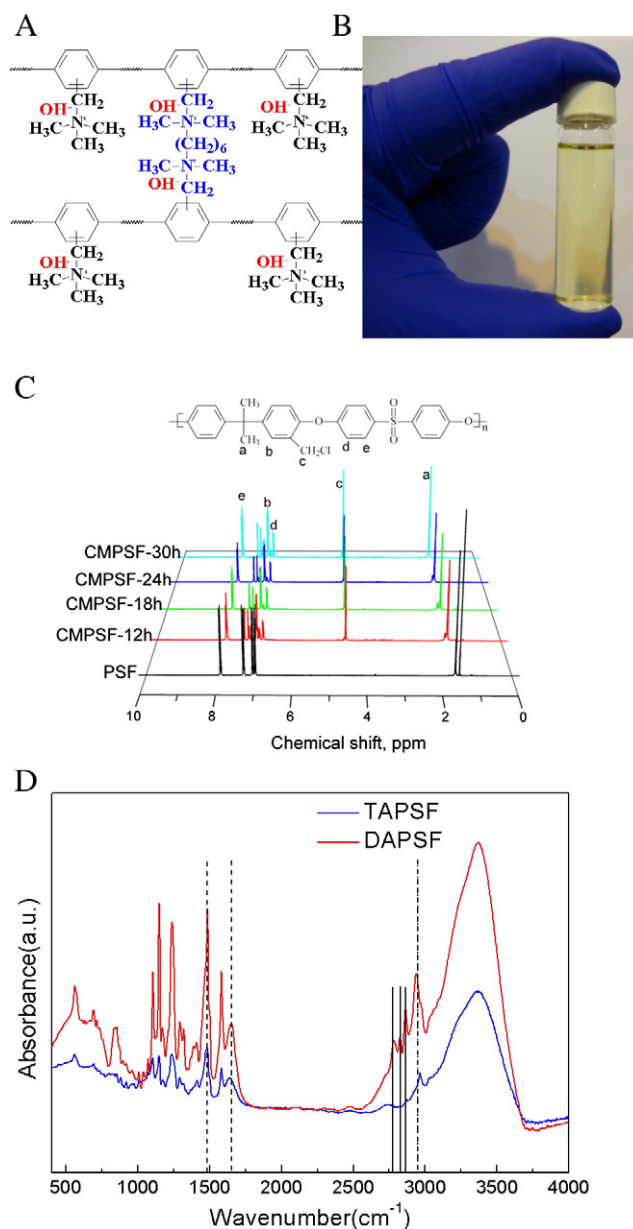
CMPSFs were characterized by  $^1\text{H}$  NMR analysis performed on a Bruker AV 400 spectrometer. FTIR absorption spectra of TAPSF and DAPSF were recorded on FTS 6000 (Bio-Rad) with a resolution of  $4\text{ cm}^{-1}$  and a spectral range of  $400\text{--}4000\text{ cm}^{-1}$ . The IEC of the ionomers was determined by the back titration method. The ionic conductivities of the ionomers were measured with a four electrode conductivity clamp using an AC impedance method. The swelling degree was measured in home-made device as reported elsewhere [3]. Fuel cell performance was performed in a single cell hardware (Fuel Cell Technologies) installed on a Fuel Cell Testing Equipment (Arbin). The catalyst ink composed of Pt/C and DAPSF was spray-coated on both sides of TAPSF, making the catalyst-coated membrane (CCM). The CCM was sandwiched between the gas-diffusion layers (SIGRACET GDL 25BC) to form membrane electrode assemblies (MEAs). MEAs were activated by cycling between OCV and 100 mV with a decrement step of 100 mV every 5 min, until stable performance between two cycles was obtained.

## 3. Results and discussion

The chemical structure of DAPSF is shown in Fig. 1A. A transparent yellow solution was obtained after dissolving DAPSF into DMF (Fig. 1B). The chloromethylation of PSFs was confirmed by  $^1\text{H}$  NMR spectra (Fig. 1C). The appearance of new peak at 4.58 ppm (designated as 'c') is assigned to the hydrogen proton of attached chloromethyl groups ( $-\text{CH}_2\text{Cl}$ ), indicating the chloromethylated polysulfone formed. The infrared spectra were employed to confirm the amination/crosslink reaction process (Fig. 1D). The peaks at  $2964\text{ cm}^{-1}$ ,  $1635\text{ cm}^{-1}$  and a sharp peak at  $1485\text{ cm}^{-1}$  are attributed to the stretching vibration of quaternary ammonium groups, suggesting the successful preparation of TAPSF and DAPSF. While the new peaks appearing at  $2864\text{ cm}^{-1}$ ,  $2825\text{ cm}^{-1}$  and  $2781\text{ cm}^{-1}$  is attributed to the stretching vibration of  $-\text{CH}_2-$ , coming from the cross-linked structure.

The IEC of the ionomers is 0.91, 1.21, 1.45, 1.62 and  $1.86\text{ mmol g}^{-1}$ , corresponding to the chloromethylation time of 8, 12, 18, 24 and 30 h. The result shows IEC increases with the chloromethylation time, indicating that the number of chloromethyl group tethering on the skeleton of PSFs increases with the prolonged reaction time. The solubility behaviour of the ionomer before and after the cross-linking process was determined in water at 80 °C. TAPSF with a low IEC did not dissolve in the solvent, but it became unstable when the IEC was larger than  $1.21\text{ mmol g}^{-1}$ . After the cross-linking process, DAPSF did not dissolve in the solvents until the IEC exceeded  $1.62\text{ mmol g}^{-1}$ . The above results suggest that the cross-linking process stabilizes the alkaline ionomer with an increased IEC, resulting from the formation of inherent network structures which strengthen the interchain interaction according to the high density of cross-linkage ( $-(\text{CH}_2)_6-$ ).

The hydroxide conductivities of TAPSF and DAPSF were measured in deionized water by varying temperatures (Fig. 2A). All the ionomers exhibit an increase in the hydroxide conductivities with increasing temperature, implying that the effect of possible degradation of the functional groups at elevated temperatures is small. Comparing the hydroxide conductivity at the same IEC indicates that the cross-linking process did affect the conductivity, but the influence is insignificant. At the same IEC, the ionic conductivity of DAPSF is slightly lower than that of TAPSF; for example at  $1.21\text{ mmol g}^{-1}$  and 80 °C, the conductivity of DAPSF and TAPSF is  $42.6$  and  $40.8\text{ mS cm}^{-1}$ , respectively. The slight decrease in the ionic conductivity can be attributed to the fact



**Fig. 1.** (A) Chemical structure of cross-linked quaternized polysulfone; (B) a photograph of DAPSF with IEC  $1.62\text{ mmol g}^{-1}$ ; (C)  $^1\text{H}$  NMR spectra of PSF and CMPSF; (D) FTIR spectra of TAPSF and DAPSF.

that the inherent network structures created during the cross-linking process restricted the mobility of the hydroxide anion, but the cross-linked part of chloromethyl functional groups have not been consumed during the cross-linking process and it still contributes to the hydroxide conductivity.

More interestingly, it is found that the cross-linking process makes the ionomer with a high IEC stable and the IEC is as high as  $1.62\text{ mmol g}^{-1}$ . The increased density of ionic clusters helps to enhance the hydroxide ion transportation, resulting in a significant increase in the ionic conductivity. The DAPSF with an IEC of  $1.62\text{ mmol g}^{-1}$  shows an ionic conductivity as high as  $60.5\text{ mS cm}^{-1}$ , which is 1.4 times higher than that of TAPSF with an IEC of  $1.21\text{ mmol g}^{-1}$  at 80 °C. It is also found that the ionic conductivity ( $30.3\text{ mS cm}^{-1}$ ) of DAPSF at 30 °C is higher than that of the commercial ionomer, including AS-4 ( $13\text{ mS cm}^{-1}$ ) [9] and FAA HEM ( $17\text{ mS cm}^{-1}$ ) [10].

The variation in the swelling degree of the ionomer with IEC and temperature is presented in Fig. 2B, from which it can be seen that TAPSF with an IEC of  $1.21\text{ mmol g}^{-1}$  swells over 30% at 30 °C and

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