



Enhanced performance of anion exchange membranes *via* crosslinking of ion cluster regions for fuel cells



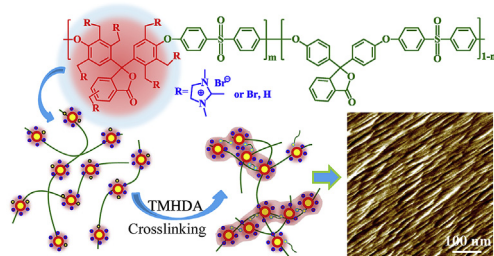
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HIGHLIGHTS

- Crosslinked AEMs was prepared *via* crosslinking of ion cluster regions.
- Effect of crosslinking on AEMs' morphology and properties was studied.
- The AEMs showed high ionic conductivity in the range 52.2–143.4 mS cm⁻¹.
- The AEMs showed superb ratio of relative conductivity to relative swelling.
- The single cell achieved a peak power density of 83.6 mW cm⁻² at 80 °C.

GRAPHICAL ABSTRACT



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ABSTRACT

Development of anion exchange membranes (AEMs) with high hydroxide conductivity, good dimensional and alkaline stabilities is still a challenge for the practical application of AEM fuel cells. In this study, we report a new strategy to prepare high-performance AEMs with crosslinked ionic regions. A series of phenolphthalein-containing poly(arylene ether sulfone)s crosslinked AEMs was synthesized by grafting ion groups selectively and densely on the phenolphthalein units to form ion clusters that are further crosslinked to generate the hydrophilic ionic regions. The crosslinking reaction not only improved the dimensional stability of the AEMs, but also increased the aggregation of the ion clusters leading to the formation of hydrophilic/hydrophobic phase-separated morphology and ion-conducting channels. As a result, enhancements in both ion conductivity and dimensional stability can be achieved. The cross-linked AEMs showed high hydroxide conductivities in the range of 52.2–143.4 mS cm⁻¹ from 30 to 80 °C and a superb ratio of relative conductivity to relative swelling at 80 °C. Furthermore, the crosslinked AEMs also exhibited good mechanical properties, thermal and alkaline stabilities and desirable single cell performance. This work presents a promising strategy for the synthesis of high-performance AEMs for fuel cells.

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1. Introduction

Fuel cells have been widespread recognized as an alternative energy generation technology due to their high efficiency, low

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pollution and operation using renewable fuels [1,2]. The development of fuel cells addresses both energy issues and environmental concerns. Recently, anion exchange membrane fuel cells (AEMFCs) are attracting great interest as an alternative to proton exchange membranes fuel cells (PEMFCs) [1,2]. AEMFCs offer several advantages over PEMFCs including the faster oxygen reduction reaction kinetics in an alkaline environment. This leads to relatively higher cell efficiencies and allows for the use of non-noble metal catalysts (such as Co and Ni), potentially reducing the cost of the fuel cells [3–6]. As a key component of AEMFCs, the ion conductivity and stability of anion exchange membranes (AEMs) control the cell performance and lifetime of AEMFCs [7].

However, the current AEMs showed insufficient conductivity or/and stability which limits their practical use. The ion conductivity is pertinent to the combination of ionic exchange capacity (IEC), the hydration level and microphase-separated structure of the membrane material [8]. A direct approach to improve the ion conductivity is to increase the IEC. However, AEMs with high IEC would suffer from excessive swelling which can lead to a poor dimensional stability and mechanical strength, and lose their practical applications. Crosslinking between polymer chains has shown to be an effective way to restrict swelling [7,9–13]. However, the commonly used crosslinking method usually requires an additional crosslinkable molecule or is based on high-temperature thermal treating, which increases the complexity of the process and can degrade the cation groups more easily during the thermal crosslinking. Furthermore, those crosslinking strategies often have a weak or an opposite effect on improving ion conductivity due to the lower mobility of hydroxyl ions in the crosslinked AEMs with smaller free volume and lower water uptake.

Recent researches show that well-defined microphase-separated structure between the hydrophobic polymer backbones and the hydrophilic ionic domains containing functional groups can facilitate the formation of ion-conducting channels and improve the ion conductivity [14,15]. Based on this strategy, several AEMs bearing anion-conductive functional groups on the hydrophilic segments of the block copolymers (so-called “block-type” AEMs) [16–21] or on the pendent side-chains grafted on the polymer main chains (so-called “side-chain-type” AEMs) [22–26] have been prepared recently. However, these AEMs also suffered from significant swelling when their IEC was increased for higher conductivity. It seems to be a trade-off relationship between ion conductivity and dimensional stability. This creates a need for new methods to enhance ion conductivity without compromising dimensional stability.

Herein, we report a new strategy to prepare high-performance AEMs via crosslinking between ionic regions. A novel phenolphthalein-based monomer bearing heptabenzylmethyl was synthesized and polymerized with other monomers. The as-synthesized polymer was further brominated, followed by imidazolium functionalization with 1,2-dimethylimidazole (DIM) and crosslinking with N,N,N',N'-tetramethyl-1,6-diaminohexane (TMHDA) to prepare crosslinked AEMs. The TMHDA acting as the quaternization reagent could provide ion exchange functional sites after the crosslinking reaction. Moreover, DIM and TMHDA were chosen from various imidazoliums and diamines because they have a better alkaline stability [27–29]. Along these processes, the ion groups (imidazolium and quaternary ammonium groups) were introduced selectively and densely on the phenolphthalein units and tended to form ion clusters as the hydrophilic ionic regions. Furthermore, the crosslinking of the hydrophilic ionic regions would not only improve the dimensional stability of the membrane, but also intend to increase the aggregation of the ion clusters, allowing for the formation of microphase-separated structure and ion-conducting channels. Then the as-prepared membranes

were characterized. The effect of crosslinking on the structure and properties of the membranes was studied by varying the ratio of DIM to TMHDA.

2. Experimental

2.1. Materials

4-Methylphthalic anhydride (98%, Aladdin, China), 2,3,6-trimethylphenol (99%, Aladdin, China), DIM (98%, Sigma-Aldrich, St. Louis, MO), methanesulfonic acid (99%, Aladdin, China), TMHDA (98.0%, TCI, Japan), 4,4'-difluorodiphenyl sulfone (FPS) (99%, TCI, Japan), phenolphthalein (98%, Sigma-Aldrich, St. Louis, MO) and N-bromosuccinimide (NBS) (99%, Aladdin, China) were used as received. Toluene and N,N-dimethylacetamide (DMAC) (99.8%, Aladdin, China) were purified by stirring over 4 Å molecular sieves. Benzoyl peroxide (BPO) (99%, Sinopharm, China) was purified by recrystallizing from chloroform. All other reagents were purchased from Shanghai Sinopharm Chemical Reagent Co., Ltd (China) and used as received.

2.2. Preparation of the AEMs

2.2.1. Synthesis of the monomer heptamethyl phenolphthalein (HMPPH)

HMPPH was synthesized from 2,3,6-trimethylphenol and 4-methylphthalic anhydride, as shown in Scheme S1 (Supporting Information). A typical synthesis procedure is detailed below. Methanesulfonic acid (27 mL, 0.416 mol), 4-methylphthalic anhydride (11.9984 g, 0.074 mol) and 2,3,6-trimethylphenol (18.1133 g, 0.133 mol) were added in a 150 mL three-necked round-bottomed flask equipped with a condenser, a magnetic stirrer, a thermometer and a gas inlet and outlet. The reaction was carried out at 90 °C for 5 h under nitrogen. The reaction mixture was cooled to room temperature (RT) and slowly poured into ice water to yield a precipitate. The precipitate was filtered and washed with hot deionized (DI) water for several times to get a crude product. The product was crystallized from toluene twice and dried at 80 °C under vacuum for 24 h to obtain pure HMPPH (yield: 71%).

2.2.2. Synthesis of heptamethyl phenolphthalein-containing poly(arylene ether sulfone)s (HPPES)

The precursor HPPES was synthesized via condensation polymerization, as shown in Scheme 1. The procedure for the synthesis of HPPES is detailed below. 2.2281 g (7 mmol) of phenolphthalein, 2.5425 g (10 mmol) of FPS, 1.2494 g (3 mmol) of HMPPH, 3.4553 g (25 mmol) of K₂CO₃, 15 mL of DMAC and 7 mL of toluene were introduced into a 100 mL round-bottomed flask equipped with a Dean-Stark apparatus, a magnetic stirrer, a condenser, and a gas inlet and outlet and stirred at 145 °C for 4 h under nitrogen. After removing the toluene, the mixture was heated to 165 °C for another 20 h. The resulting mixture was then cooled to RT and poured into 500 mL of an aqueous methanol solution (methanol/DI water = 1/1, v/v) to give a white solid precipitate. Subsequently, the precipitate was stirred at 85 °C for 5 h in the aqueous methanol solution, collected by filtration and purified by Soxhlet extraction with methanol for 12 h, and finally dried at 80 °C for 24 h in a vacuum oven to yield a product.

2.2.3. Bromination of HPPES

The bromination of the HPPES was conducted using NBS as the bromination agent and BPO as the initiator, as shown in Scheme 1. A typical procedure is as follows. 5.0000 g of HPPES (containing 18.1 mmol of –CH₃) and 35 mL of 1,1,2,2-tetrachloroethane (TCE)

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