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Hydroxide exchange composite membrane based on soluble quaternized polyetherimide for potential applications in fuel cells

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ABSTRACT

A series of soluble quaternized polyetherimides (QAPEIs) have been successfully synthesized by homogeneous quaternization in trimethylamine aqueous solution. ^1H NMR spectra confirm the successful synthesis of QAPEI. The QAPEIs exhibit good solubility in membrane-preparation solvents, making it possible to prepare the QAPEI composite membrane. Novel composite hydroxide exchange membranes have been prepared by incorporating QAPEIs with polytetrafluoroethylene (PTFE) membranes. The SEM images, gas permeation measurements and FTIR spectra show that the QAPEI is successfully filled in PTFE membrane and the resulted composite membrane is dense and smooth. The ion exchange capacity of composite membranes ranges from 0.35 to 0.58 mmol g^{-1} . The composite membranes have appropriate water uptake ($\leq 154\%$) and moderate swelling ratio ($\leq 42\%$) even at 60 °C. The hydroxide conductivity of the composite membrane reaches 11.9 mS cm^{-1} at 20 °C that increases to 35.2 mS cm^{-1} at 60 °C. TGA curve shows that the composite membrane possesses high thermal stability (T_{OD} : 210 °C). All these properties indicate that the QAPEI/PTFE composite membranes are good candidates for use as HEMs in HEM fuel cells.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have shown high power density and high energy efficiency. Unfortunately, high cost and poor durability of platinum-based electrocatalysts in PEMFCs have hindered their commercialization [1,2]. To overcome these problems, hydroxide exchange membrane fuel cells (HEMFCs) have been proposed [3–6]. The catalysts are more stable in HEMFCs than in PEMFCs, and HEMFCs allow the use of non-precious metal catalysts [7–12]. In addition, HEMFCs show relatively lower methanol

permeability and simpler water management compared with PEMFCs [13–15].

Hydroxide exchange membranes (HEMs) are the key components of HEMFCs. They are used to separate the fuels and oxidant and conduct hydroxide ions simultaneously. So far, the research and development of high-performance HEMs is one of the most challenging works in HEMFCs. In general, HEMs have been prepared by chloromethylating polymer materials and then aminating them with quaternization reagents, which is a convenient and effective method to introduce quaternary ammonium functional groups into the

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polymer matrix. In this way, many polymer materials have been used as the matrix to develop HEMs, such as polysulfone [16,17], polyethersulfone cardo (PES-C) [18], polyetherketone cardo (PEK-C) [19], poly (ether ether ketone) (PEEK) [20], poly (phthalazinon ether sulfone ketone) (PPESK) [21], polyetherimide (PEI) [22], polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene (SEBS) [23,24], poly (phthalazinone ether sulfone) (PES) [25], poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) [26], and poly(arylene ether sulfone) (PAES) [27].

Quaternary ammonium is the most frequently used functional group for HEMs. Trimethylamine aqueous solution is usually used as the quaternization reagent to introduce quaternary ammonium into polymers. However, it is noted that quaternization reactions are heterogeneous for most chloromethylated polymers because they are insoluble in trimethylamine aqueous solution. This causes the incomplete quaternization, leading to the lower ion conductivities of HEMs compared with PEMs prepared by homogeneous sulfonating reactions. Moreover, most quaternized polymers are insoluble in ordinary polar membrane-preparation solvents such as N-methyl-2-pyrrolidone (NMP), N,N-dimethylformamide (DMF) and dimethylacetamide (DMAc). Hence, it's very meaningful to find an easy soluble polymer material after chloromethylation and quaternization. To date, there are few reports about such polymers, especially commercially available polymers.

Polyetherimide (PEI) is a commercial high-performance engineering polymer and has been used to prepare quaternized PEI (QAPEI) by the heterogeneous quaternization and the final QAPEI was insoluble [22]. In our study, we found the way to obtain soluble QAPEI by a homogeneous quaternization with trimethylamine aqueous solution. Furthermore, HEM was prepared by compositing QAPEI with PTFE to strengthen the mechanical property. Then, their properties such as ion exchange capacity, water uptake, swelling ratio, hydroxide conductivity, and thermal stability were investigated.

2. Experimental

2.1. Materials

Polyetherimide (PEI Ultem®1000) in pellet form was purchased from General Electric Plastics (USA), and dried in a vacuum oven at 105 °C for 10 h prior to being used. Polytetrafluoroethylene (PTFE) membranes were purchased from Hangzhou Anow Microfiltration Co., Ltd. The average pore size of the PTFE membranes is 0.1 μm, and the average thickness is 54 μm. Chloromethyl octyl ether (CMOE) was synthesized according to Ref. [28]. N,N-dimethylformamide (DMF), dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), 1-methyl-2-pyrrolidone (NMP), 1,2-dichloroethane, zinc chloride, ethanol, potassium hydroxide, and trimethylamine aqueous solution (33%) were obtained commercially and used as received without further purification. All the chemicals used in the experiments are analytical grade. Prior to being used, fresh deionized water was boiled to remove CO₂.

2.2. Preparation of composite hydroxide exchange membranes

2.2.1. Chloromethylation of polyetherimide

Chloromethyl methyl ether (CMME) is commonly used as the chloromethylation reagent, but it is highly toxic and carcinogenic. Therefore, CMOE was used in this study because of its low toxicity and volatility [28]. Specifically, 2.0 g PEI was first dissolved in 50 ml 1,2-dichloroethane in a flask equipped with a reflux condenser and a magnetic stirrer. Then 1.0 g zinc chloride was added dropwise, following by the addition of 4 ml freshly synthesized CMOE. The mixture was stirred at 60 °C for a certain time, typically from 1 h to 6 h. Afterwards, the product was precipitated in ethanol from the reaction mixture, washed with ethanol and deionized water several times and subsequently dried at 60 °C for 12 h. Note that the drying temperature should be low to avoid the crosslinking which would make CMPEI insoluble in trimethylamine aqueous solution. The chemical structures and synthetic process are shown in Fig. 1.

2.2.2. Quaternization of polyetherimide

Different from other reported polymers, CMPEIs were soluble in trimethylamine aqueous solution, so the quaternization reaction was homogeneous and sufficient. Specifically, CMPEI powder was immersed in 33 wt% trimethylamine aqueous solution at 40 °C for 12 h. The CMPEI powder would be gradually dissolved in the solution with the process of reaction. The solution was then poured into an evaporating dish and dried to obtain QAPEI. The process of the quaternization is also shown in Fig. 1.

2.2.3. Preparation of QAPEI/PTFE composite membranes

The dried QAPEI was dissolved in DMSO to make a 25 g L⁻¹ solution. Before used, PTFE membranes were swelled in anhydrous ethanol for 3 h to improve its wettability in DMSO. The QAPEI/PTFE composite membranes were then obtained by immersing PTFE membranes into QAPEI solution and heating at 50 °C to remove all the solvent. After that, the composite membranes were immersed in 1 M KOH solution at room temperature for 24 h to exchange the ion from Cl⁻ to OH⁻. The resulted membranes were washed and immersed with deionized water until neutral.

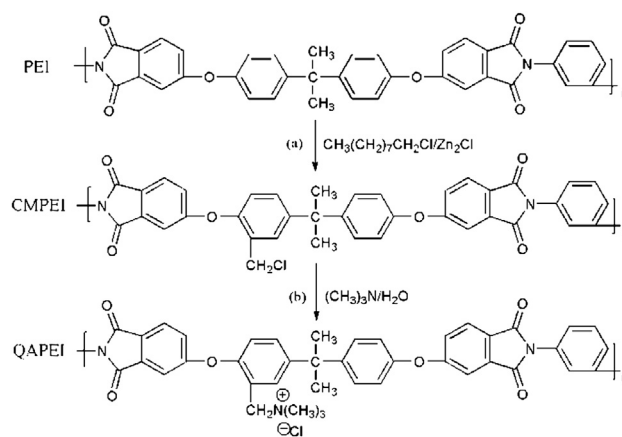


Fig. 1 – Synthesis of the quaternized polyetherimide.

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