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Constructing a rigid crosslinked structure for enhanced conductivity of imidazolium functionalized polysulfone hydroxide exchange membrane

Jian Dai ^a, Gaohong He ^{a,b}, Xuehua Ruan ^a, Wenji Zheng ^a, Yu Pan ^a, Xiaoming Yan ^{a,b,*}

^a State Key Laboratory of Fine Chemicals, School of Petroleum and Chemical Engineering, Dalian University of Technology, 2 Dagong Road, Panjin, LN 124221, China

^b State Key Laboratory of Fine Chemicals, Research and Development Center of Membrane Science and Technology, School of Chemical Engineering, Dalian University of Technology, 2 Linggong Road, Dalian, 116024, China

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ABSTRACT

A series of novel bis-imidazolium crosslinked polysulfone membranes (CL-PSf-ImOHs) membranes were prepared through simultaneous quaternization and crosslinking reactions of 4,4'-bis(2-methylimidazole-1-ylmethyl)diphenyl (bis-Im-diPh) and chloromethyl groups on the polymer during the membrane formation. The novel bis-Im-diPh crosslinker possesses a rigid bis-phenyl structure, which creates large free volume and leads to the formation of continuous hydroxide conducting channels in the membrane as demonstrated by TEM. The properties of the crosslinked membrane were controlled by varying the molar ratio ($R_{d/c}$) of bis-Im-diPh and chloromethyl groups from 0.18 to 0.33. With increasing $R_{d/c}$, the swelling ratio decreases, and the hydroxide conductivity increases. The CL-PSf-ImOH membrane with $R_{d/c}$ of 0.33 exhibits the conductivity of 112 mS cm^{-1} at 60°C , much higher than that of non-crosslinked membrane (83 mS cm^{-1} , losing its morphology at 60°C) and those of other crosslinked membranes ($17\text{--}68 \text{ mS cm}^{-1}$) prepared with the similar methods. In addition, the CL-PSf-ImOH membranes show good dimensional stability at elevated temperatures.

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Introduction

As a promising technology to provide a sustainable future for human, fuel cells attract wide attention in the world [1].

Among those cells, polymer electrolyte fuel cells, including proton exchange membrane fuel cells (PEMFCs) and hydroxide exchange membrane fuel cells (HEMFCs), have been widely developed in last decades [1,2]. Comparing to PEMFCs, HEMFCs allow the use of low-cost metal catalysts which is

* Corresponding author. State Key Laboratory of Fine Chemicals, School of Petroleum and Chemical Engineering, Dalian University of Technology, 2 Dagong Road, Panjin, LN 124221, China. Tel.: +86 427 2631803.

E-mail address: yanxiaoming@dlut.edu.cn (X. Yan).

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attributed to the kinetics enhancing of the oxygen reduction in the base environment [3]. In addition, HEMFCs also have the advantages of lower alcohol permeability and easier water management [4].

Hydroxide exchange membrane (HEM) is one key component of HEMFCs, serving as hydroxide conductor and fuel/oxidant separator [1,4–6]. The HEMs are required to possess high ionic conductivity and excellent stability (e.g. chemical, thermal, and dimensional stabilities) [5–10]. HEMs usually have lower conductivity compared with proton exchange membranes (PEMs), which results from lower mobility of hydroxide ions than protons' in aqueous phase [4,6,8,9]. To enhance the conductivity of HEMs, increasing ion exchange capacity (IEC) is a preferred and effective way [7,9]. Generally, there is an uncontrollable dimensional swelling as a high IEC is achieved [7,9,11–16]. Meanwhile, there is a trade-off between high conductivity and desirable membrane stability [7,9,11–16].

Covalent cross-linking is an efficient way to resolve this trade-off problem [17–44]. To date, there are three covalent crosslinking methods used in the HEM field. The first is the Friedel–Crafts alkylation conducted by thermal initiation [17–21]. Yan et al. prepared membranes with high dimensional stability and excellent solvent-resistance by the reaction between chloromethyl group of CMPSf and trimethoxyl benzene rings in the quaternary phosphonium group [17]. Jasti et al. reported the membranes by introducing bromine atoms onto allyl bisphenol, which reacted with each other at high temperature about 170 °C [18]. The groups with high Friedel–Crafts alkylation activity are required, such as electron-rich benzene ring or benzyl bromine. The second is the olefin metathesis (thermal initiation, photo initiation, catalyst) [22–27]. Coates et al. prepared the membranes by the use of expensive Grubbs second generation catalyst to copolymerize a bis-ammonium-functionalized para-methylbenzene with cyclooctene [22]. Besides, the membranes could be prepared via UV irradiation between quaternized poly-(vinylbenzyl) ammonium salt and N,N'-bis(acryloyl)piperazine [23]. These crosslinking reactions have to be conducted under the existence of special reactant-structure (electron-rich base, olefinic bond), or strict reaction-condition (fine high-temperature control, UV, catalyst), which limits the extensive application. A more universal crosslinking method is the simultaneous quaternization and cross-linking of functional groups-containing cross-linkers [28–44,53]. He et al. reported the membranes crosslinked by 1,4-diazabicyclo [2,2,2] octane (diamine) [29]. The introduction of diamine promises to gain many more conductive groups that is favorable for obtaining higher hydroxide conductivity. F. Zhang et al. reported cross-linked membranes by introducing diamine with different spacer lengths. The membranes with spacer propane diamine have much better performance of hydroxide conductivity and mechanical stability than the membranes with ethane diamine [30]. The possible reason is that the longer spacer structure of crosslinker enhances the microphase separation between two neighboring main chains, which allows the membrane absorb much more water uptake to form continuous hydroxide conducting channels.

In the present work, a series of bis-imidazolium cross-linked polysulfone membranes (CL-PSf-ImOHs) were prepared

by first chloromethylation of Polysulfone (PSf), then quaternization of the obtained chloromethylated PSf by 4,4'-bis(2-methylimidazole-1-ylmethyl)biphenyl (bis-Im-diPh) and 1,2-dimethylimidazole. The bis-Im-diPh works as simultaneous quaternization and crosslinking reactants. Comparing to the reported crosslinkers, the bis-imidazole synthesized here has a long and rigid bis-benzene structure as the spacer which could provide a chance for achieving continuous hydroxide conducting channels. A systematic study about the effects of crosslinking on properties of the HEMs (water uptake, swelling ratio, ionic conductivity, chemical and thermal stabilities) were investigated in details. And, a new concept about ion exchange capacity of wet membrane was introduced to give an insight of the relationship between ion exchange capacity (IEC) and hydroxide conductivity.

Experimental

Materials

Udel P3500 PSf was supplied by Amoco Performance Products Inc. 2-methylimidazole (AR), 4,4'-bis(chloromethyl)-1,1'-biphenyl (AR), SnCl₄ (AR), and 1,2-dimethylimidazole (AR) were purchased from Aladdin Industrial Inc.. The synthesis of chloromethyl octyl ether (CMOE) was followed by the method referred to Ref. [39]. Anhydrous calcium chloride (CaCl₂), sodium hydroxide (NaOH), sodium chloride (NaCl), phenolphthalein, anhydrous magnesium sulfate (MgSO₄), anhydrous sodium sulfate (Na₂SO₄), potassium hydroxide (KOH), and paraformaldehyde (PFA) were used as received. Hydrochloric acid (36%), sulfuric acid (98%), tetrahydrofuran (THF), acetonitrile, 1-methyl-2-pyrrolidone (NMP), ethyl acetate, anhydrous ethanol, octanol, and methylene dichloride were used without further treatment and purification. In all tests, CO₂-free deionized water was used.

Synthesis of 4,4'-bis(2-methylimidazole-1-ylmethyl)diphenyl (bis-Im-diPh)

4,4'-bis(2-methylimidazole-1-ylmethyl)diphenyl was synthesized referring to the literature [47]. 1.44 g 2-methylimidazole, 6.30 g potassium carbonate and 60 ml acetonitrile were added first in 150 ml flask. Then 1.76 g 4,4'-bis(chloromethyl)-1,1'-biphenyl was gradually added. The mixture were stirred violently under reflux for 15 h. The liquid with product was orange, and beige precipitate was formed at the bottom. Then the reaction mixture was treated by filtration and concentration to produce crude brown oil. The brown oil was redissolved in chloroform, washed by deionized water, dried by MgSO₄, filtered and concentrated under vacuum. For facilitating the solidification of brown oil, the diethyl-ether was added. At last, the off-white solid product was gained by drying.

Synthesis of the chloromethylated PSf (CMPSf)

The CMPSf was synthesized according to the Ref. [46]. 4 g PSf was dissolved in 120 ml methylene dichloride at room temperature. Then, 20 ml CMOE was added step-wise. Then

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