



In-situ photocrosslinked hydroxide conductive membranes based on photosensitive poly(arylene ether sulfone) block copolymers for anion exchange membrane fuel cells

Rui He^{a,b}, Pushan Wen^{b,c}, Hai-Ning Zhang^d, Shumeng Guan^d, Guangyong Xie^a, Li-Zhong Li^e, Myong-Hoon Lee^{b,*}, Xiang-Dan Li^{a,**}

^a Key Laboratory of Catalysis and Materials Science of the State Ethnic Affairs Commission & Ministry of Education, South-Central University for Nationalities, Wuhan, Hubei 430074, China

^b Graduate School of Flexible and Printable Electronics, Chonbuk National University, Jeonju, Jeonbuk 54896, South Korea

^c Department of Chemistry and Chemical Engineering, Zunyi Normal College, Zunyi, Guizhou, 563006, China

^d State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan, Hubei 430074, China

^e College of Resources and Environmental Science, South-Central University for Nationalities, Wuhan, Hubei 430074, China



ARTICLE INFO

Keywords:

Photocrosslinking
Multi-block copolymer
Poly(arylene ether sulfone)
Anion exchange membrane
Fuel cell

ABSTRACT

A series of photocrosslinkable multi-block poly(arylene ether sulfone) copolymers containing various block lengths of hydrophilic segments were synthesized. For comparison, a series of random poly(arylene ether) copolymers were also synthesized. The anion exchange membranes (AEMs) were fabricated and in-situ photocrosslinking was carried out by UV irradiation in a swollen state. The microphase-separated morphologies of the multi-block membranes were characterized by SAXS and TEM experiments, and the membrane properties were investigated by measuring ion exchange capacity (IEC), water uptake, water swelling ratio, ionic conductivity, methanol permeability and alkaline stability. IECs and water uptakes of the crosslinked multi-block membranes were in the range of 1.11–1.42 meq g⁻¹ and 14.36–31.01% at 20 °C, respectively. The hydroxide conductivity was in the range of 11.38–25.00 mS cm⁻¹ at 20 °C, and showed a maximum value of 178.77 mS cm⁻¹ at 100 °C. The multi-block membranes exhibited low methanol permeability (2.75×10^{-7} cm² s⁻¹) at room temperature, which is one order of magnitude lower than that of Nafion[®] 117 (23.8×10^{-7} cm² s⁻¹). The crosslinked membranes showed excellent dimensional stability and alkaline stability with only a slight decrease in ionic conductivity. All the multi-block membranes showed superior properties compared to their corresponding random copolymers.

1. Introduction

Fuel cells are recognized as one of the most promising energy conversion devices in aerospace, vehicles, and portable equipment due to their environment-friendly and high energy conversion efficiency [1]. Among the fuel cell technologies, the proton exchange membrane fuel cells (PEMFCs) have been extensively investigated due to their advantages such as pollution-free, low working temperature, ease of operation, high efficiency and so on [2]. However, the PEMFCs have a strong dependence on noble metals such as platinum group as a catalyst, thus increasing the cost and seriously hindering the commercialization of PEMFCs. High fuel permeability is also a limitation to the further development of PEMFC [3,4]. Under such circumstances, a new

type of fuel cell with low fuel permeability was required. Anion exchange membrane fuel cells (AEMFCs) have emerged rapidly as one of the promising substitutes for PEMFCs. AEMFCs possess numerous advantages over PEMFCs. On one hand, less expensive electro-catalysts can be chosen from non-noble metals such as Ag, Co and Ni, and the kinetics of oxygen reduction reaction is enhanced obviously under the alkaline operating environment. On the other hand, AEMFCs retain low fuel permeability because the hydroxide ions migrate from cathode to anode hindering the permeation of fuel. Furthermore, the water management in AEMFCs is relatively simple [5,6]. In the AEMFC, anion exchange membrane (AEM) acts as one of the most important components, and have been extensively explored. Although lots of efforts have been devoted to developing high performance of AEMs by using various

* Correspondence to: Chonbuk National University, 567 Baekje-daero, Jeonju, Jeonbuk 54896, South Korea.

** Correspondence to: South-Central University for Nationalities, No.182, Minzu Road, Wuhan, Hubei 430074, China.

E-mail addresses: mhlee2@jbnu.ac.kr (M.-H. Lee), lixiangdan@mail.scuec.edu.cn (X.-D. Li).

polymer backbone, most of the developed AEMs are not viable compared to the proton exchange membranes, mainly because of the relatively low ionic conductivity and a poor stability in the alkaline environment as well as the loss of mechanical property caused by high water uptake and excessive swelling. Attempts to increase ion exchange capacity (IEC) and ionic conductivity of the AEMs frequently accompanied with a dramatic increase of water uptake and swelling, which could subsequently deteriorate membrane properties such as dimensional stability, durability, mechanical property and methanol permeability [7]. Thus, AEMs with high ionic conductivity and good alkaline stability are still a challenge for researchers [4].

In order to address the issues discussed above, a number of chemical modification methods have been introduced in recent years. On one hand, the synthesis of multi-block copolymer has been regarded as one of the most practical methods to enhance the ionic conductivity. Hydrophobic/hydrophilic block copolymers provide a phase-separated structure to form a continuous ion transport channel, which is beneficial to the increase of ionic conductivity [8–11]. Watanabe et al. synthesized a series of anion conductive multi-block poly(arylene ether)s containing ammonium-functionalized fluorene groups. The resulting AEMs showed IEC values up to 1.93 meq g⁻¹ and the highest hydroxide ion conductivity of 144 mS/cm at 80 °C [12]. Kim et al. reported a series of modified anion conductive poly(arylene ether sulfone) block copolymer with ionic conductivity of 21.37 mS cm⁻¹, which was higher than that of the corresponding random copolymer (17.91 mS cm⁻¹). In addition, the hydrophobic/hydrophilic block copolymer membranes appeared to be more stable than the random copolymer membranes, probably due to their different microphase morphologies [13]. While the concept of block copolymer clearly improved anion conductivity of the membranes by forming an ion transport channel via well-defined phase separation of hydrophilic/hydrophobic domains, the mechanical stability of high IEC membranes was not as good as expected mainly due to high water absorption and excessive swelling. Because the mechanical and chemical stabilities are also critical issues in the application of AEMs, many efforts have been made to improve the stabilities of the AEMs [14,15]. Meanwhile, covalent crosslinking of membranes has been considered as a practical method to enhance the performance of the AEMs [16–20]. Typically, in-situ crosslinked AEMs have been prepared via Friedel-Crafts electrophilic substitutions [21,22] or olefin metathesis techniques [23–25], which induce crosslinking during solution casting to yield AEMs with homogeneous morphologies. Liao et al. synthesized a series of novel cross-linked AEMs, and the three-dimensional aggregated structures of the cross-linked AEMs greatly improved their properties such as dimensional stability, mechanical properties, and chemical stabilities [26]. The biggest tensile strength boost range of 79.8% is given by the crosslinked membranes. Additionally, the crosslinked membranes show excellent chemical stability with 94% of the ionic conductivity of the original membrane retained after being treated in 1 M NaOH solution at 60 °C for 28 days. Xu et al. reported a self-crosslinked AEMs which employed a thermal crosslinking of pendant methacrylate groups at > 60 °C [27]. Recently, we also have reported a novel photocrosslinking method for PEMFCs, which utilizes a photo-induced crosslinking of chalcone moieties in the polymer main-chain [28–30]. In these works, the membrane was immersed in water, and UV light was irradiated on the membrane in a hydrated (water-swollen) state at room temperature to induce a [2 + 2] cycloaddition reaction between two chalcone units in the main-chain yielding a crosslinked structure, as schematically represented in Fig. 1. This method could preserve the percolated ion transfer channel during the photocrosslinking, which improved the mechanical properties, and chemical and thermal stabilities with a minimum loss of proton conductivity.

In this work, to combine the advantages of multi-block copolymers and photocrosslinking in a swelling state, we designed and synthesized a series of photosensitive poly(arylene ether sulfone) multi-block copolymers containing chalcone moiety in the hydrophobic block as

shown in Scheme 1. The hydrophilic blocks with density-distributed quaternary ammonium groups are expected to form a continuous ion transfer channel by microphase-separated morphology. At the same time, the phase-separated hydrophobic blocks containing chalcone moiety not only provide a structural support for improved mechanical properties but also act as crosslinking sites under UV irradiation. The structure of photocrosslinkable poly(arylene ether sulfone) multi-block copolymers were characterized by ¹H NMR, FT-IR, UV-Vis spectroscopy and thermogravimetric analysis. AEMs were prepared after quaternization and subsequent alkalization in NaOH solution. Properties of AEMs before and after photocrosslinking were investigated by measuring water uptake, swelling ratio, ion exchange capacity, ionic conductivity and methanol permeability, and the results were compared with those of AEMs prepared from the random copolymer. The SAXS and TEM were used to characterize the microphase-separated morphology.

2. Experimental

2.1. Materials

4,4'-Dihydroxydiphenyl ether was purchased from Beijing Baishun Chem. Co. Bis(4-fluorophenyl)sulfone (DFDPS) and decafluorobiphenyl (DFBP) were obtained from Sigma Aldrich Chem. Co. Potassium carbonate (K₂CO₃) was purchased from Showa Chemical Co., and dried at 180 °C for 10 h prior to use. 4,4'-Dihydroxy chalcone (4-DHC) was synthesized according to the previous work [31]. 4,4'-Oxybis-[[dimethylamino)methyl]phenol (ODMAMP) was synthesized according to the reported procedures [32]. DFDPS, DFBP and 4-DHC were dried under vacuum at 60 °C for 24 h prior to use. N,N-Dimethylacetamide (DMAc) was obtained from Sinopharm Chemical Reagent Co., and purified by distillation at reduced pressure after stirring with calcium hydride for 24 h.

2.2. Syntheses of copolymers and preparation of AEMs

2.2.1. Synthesis of hydrophobic oligomer block (y = 11)

The hydrophobic oligomer block containing chalcone moiety with a polymerization degree 11 (y = 11) was synthesized by the procedures shown in Scheme 1. DFDPS (1.119 g, 4.4 mmol), 4-DHC (1.154 g, 4.8 mmol) and potassium carbonate (1.327 g, 9.6 mmol) were dissolved using a mixed solvent of DMAc (16.0 mL) and toluene (8.0 mL) in a 100 mL two-neck round-bottomed flask equipped with a Dean-Stark trap. The mixture was heated at 120 °C for 2 h, and refluxed at 135 °C for 8 h under a nitrogen atmosphere. The reaction mixture was cooled down to room temperature, and the slightly viscous solution was diluted with DMAc. Then, the reaction mixture was precipitated in deionized water. After filtration, the solid was dried at 50 °C for 48 h under vacuum, dissolved again in DMAc, and reprecipitated in methanol. Finally, the solid product was dried at 50 °C for 48 h under vacuum.

2.2.2. Syntheses of hydrophilic oligomer blocks (x = 8, 11, 15)

The hydrophilic oligomer blocks with various contents of quaternary ammonium moiety were synthesized through the procedures shown in Scheme 1. A typical polymerization procedure for the hydrophilic oligomer is as follows (e.g. x = 11, where x denotes the expected numbers of repeating units in the hydrophilic oligomer): ODMAMP (1.392 g, 4.4 mmol), DFBP (1.604 g, 4.8 mmol) and potassium carbonate (1.216 g, 8.8 mmol) were dissolved in DMAc (20 mL) in a 100 mL two-neck round-bottomed flask equipped with a Dean-Stark trap and a nitrogen inlet. The reaction mixture was kept at 90 °C for 4 h and cooled down to room temperature. The slightly viscous solution was diluted with DMAc and precipitated in deionized water. After filtration, the solid was dried at 50 °C for 48 h under vacuum. The polymer was dissolved in DMAc and reprecipitated into deionized

Download English Version:

<https://daneshyari.com/en/article/7019858>

Download Persian Version:

<https://daneshyari.com/article/7019858>

[Daneshyari.com](https://daneshyari.com)