Journal of Membrane Science 492 (2015) 505–517

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Direct polymerization of a novel sulfonated poly(arylene ether ketone sulfone)/sulfonated poly(vinylalcohol) crosslinked membrane for direct methanol fuel cell applications

Jingmei Xu [a], Hongzhe Ni [a], Shuang Wang [b], Zhe Wang [a,b,*], Huixuan Zhang [a,**]

[a] College of Chemical Engineering, Changchun University of Technology, Changchun 130012, People's Republic of China
[b] Advanced Institute of Materials Science, Changchun University of Technology, Changchun 130012, People's Republic of China

ARTICLE INFO

Article history:
Received 21 April 2015
Received in revised form
7 June 2015
Accepted 21 June 2015
Available online 25 June 2015

Keywords:
Sulfonated poly(vinyl alcohol)
Crosslinked membranes
Methanol permeability
Selectivity
Direct methanol fuel cells

ABSTRACT

Sulfonated poly(arylene ether ketone sulfone) copolymers containing carboxylic acid groups (C-SPAEKS) were prepared by direct aromatic nucleophilic substitution polymerization. Novel C-SPAEKS-based crosslinked membranes containing different amounts of sulfonated poly(vinyl alcohol) (SPVA) were fabricated. The Fourier transform infrared and ^{1}H NMR analyses showed the presence of carboxylic acid and sulfonic acid groups, as well as ester bonds in the crosslinked membranes. As expected, the crosslinked membranes exhibited enhanced thermal stability relative to the uncrosslinked membranes. Both the atomic force microscopy (AFM) and transmission electron microscopy (TEM) images clearly show the hydrophilic domains and hydrophobic polymer backbone. The methanol permeability coefficients of the crosslinked membranes with the SPVA content from 10% to 90% ranged from 10.67×10^{-7} cm^2 s^{-1} to 1.05×10^{-7} cm^2 s^{-1} at 25 °C, and from 22.24×10^{-7} cm^2 s^{-1} to 2.41×10^{-7} cm^2 s^{-1} at 60 °C, which are much lower than those of C-SPAEKS membrane (12.79×10^{-7} cm^2 s^{-1} at 25 °C and 26.85×10^{-7} cm^2 s^{-1} at 60 °C). The proton conductivities of all the crosslinked membranes were above 10^{-2} S cm^{-1}, satisfying the requirement of fuel cells. Furthermore, the crosslinked membranes exhibited a high selectivity, further confirming that this series of crosslinked membranes are potential candidates as new polymeric electrolyte materials for direct methanol fuel cells.

1. Introduction

Direct methanol fuel cells (DMFCs) have attracted much interest, due to their advantages of inexpensive raw materials, high energy conversion efficiency, and low operating temperature [1,2]. The transportation of methanol fuel is more convenient than that of hydrogen fuel. This is because methanol is liquid at room temperature and atmospheric pressure. Furthermore, it has a simple molecular structure, and its electrochemical activity is relatively high [3–7]. Thus, DMFCs are more promising for proton exchange membrane fuel cells (PEMFCs) applications.

Currently, two technical difficulties directly affect the commercialization of DMFCs. One difficulty is that CO is generated during the electrochemical oxidation in anode, thus poisoning the catalyst, Pt, and severely reducing the rate of methanol electrochemical oxidation [8]. The other difficulty is that methanol may permeate through the membranes from the anode to the cathode. Methanol crossover not only decreases the fuel efficiency, but also reduces the open circuit voltage of cathode, thus decreasing fuel cell performance [9–11]. Therefore, it is still important in fuel cell research to develop a suitable catalyst and a methanol-hindered proton exchange membrane (PEM) material.

There are numerous kinds of PEM materials. Nowadays, the most widely used membrane is Nafion (DuPont), which serves as a benchmark PEM. Nafion has a special structure consisting of a polytetrafluoroethylene hydrophobic main chain responsible for its good chemical stability. The pendant side chains of Nafion with hydrophilic sulfonic groups provide the desired proton conductivity [12–15]. Nafion has several advantages such as good mechanical properties, excellent chemical stability, a long service life, and outstanding proton conductivity at 100% relative humidity. However, Nafion still has many disadvantages [16]. For example, (i) when the temperature is higher than 100 °C or the

* Corresponding author at: Advanced Institute of Materials Science, Changchun University of Technology, Changchun 130012, People's Republic of China. Fax: +86 431 85716155.
** Corresponding author. Fax: +86 431 85716465.
E-mail addresses: wzccut@126.com (Z. Wang), Zhanghx@mail.ccut.edu.cn (H. Zhang).

http://dx.doi.org/10.1016/j.memsci.2015.06.031
0376-7388/

humidity is low, the proton conductivity of Nafion decreases significantly, (ii) the methanol permeability of Nafion is high and increases with increasing methanol concentration [17], and (iii) Nafion is expensive and its synthesis is difficult. Several methods have been developed to modify Nafion® membranes, such as doping inorganic particles, small organic molecules, and polymers. However, these methods could not solve the technological problems of Nafion essentially. In order to obtain good performance and inexpensive PEM materials, the host polymer chain should be changed.

Nowadays, sulfonated poly(arylene ether ketone sulfone) (SPAEKS) membranes is one of the most promising alternative PEM materials due to their low cost, excellent thermal and mechanical properties, good chemical stability, and suitable methanol permeability resistance [18,19]. However, this series of membranes face a common problem. When the degree of sulfonation (DS) is too high, although the proton conductivity can reach a higher level, the membranes may excessively swell, causing a sharp increase in methanol crossover. Therefore, it is necessary to modify the SPAEKS materials. Crosslinking is a feasible and effective method to suppress methanol crossover and enhance the dimensional stability of highly sulfonated polymers [20,21]. As crosslinker, PVA possesses excellent methanol resistance, good hydrophilic property and a high density of reactive functional groups favorable for crosslinking by irradiation, chemical, or thermal treatments [22]. Higa et al. reported the preparation of PVA-based crosslinked membranes [23]. The membranes exhibited low water uptake and excellent methanol barrier properties because the crosslinking structure. However, the proton conductivities decreased drastically after crosslinking. The lowest proton conductivity was only 6.29×10^{-3} S cm^{-1}. That is because that PVA is a non-conductive crosslinker, and it would dilute the density of sulfonic acid groups, leading to lower proton conductivity [21,24]. Lee et al. reported the application of crosslinked PVA membranes containing sulfonic acid groups. The membranes exhibited good thermal stabilities and solubility. The membranes showed low methanol permeability and high proton conductivities. The introduced sulfonic acid groups enhanced the proton conductivities of the membranes dramatically. This series of crosslinked membranes were evaluated as a potential PEM in fuel cell applications [25]. Yang reported the application of SPEEK-based composite membranes containing sulfonated poly(vinyl alcohol) (SPVA) [26]. The synthetic process of SPVA is simple and the raw material is accessible. The SPVA exhibited good solubility and film-forming properties. He proved that the methanol permeability of such composite membranes decreased with increasing SPVA content. That is due to the excellent methanol diffusion resistance properties of SPVA. Methanol is poor solvent for SPVA and SPVA is not soluble in methanol. The proton conductivities of the composite membranes maintained at 5×10^{-2} S cm^{-1} at 80 °C. That is because SPVA contains conductive sulfonic acid groups, which can promote the conduction of protons and improve the proton conductivity [25,27].

In this study, direct copolymerization method was used. This method has many advantages, such as controllable DS, accurate number of sulfonic acid groups in each repeating unit of the polymer [28–31], and avoidable crosslinking and degradation reactions [32,33]. Novel C-SPAEKS-based crosslinked membranes with different contents of SPVA were fabricated. Moreover, carboxylic acid groups were introduced to participate in the crosslinking reaction, reduce the number of dissipative sulfonic acid groups and the extent of proton conductivity decreased. This study aims to improve the dimensional stabilities and mechanical properties of the C-SPAEKS/SPVA crosslinked membranes, thus increasing their resistance to methanol crossover. The properties of the C-SPAEKS/SPVA crosslinked membranes were studied in detail and compared to those of uncrosslinked C-SPAEKS/SPVA membrane, pure C-SPAEKS (DS=80%) membrane and C-SPAEKS/PVA membrane. Moreover, the relationship between their performance and different SPVA contents was also investigated.

2. Experimental

2.1. Materials

3,3′-Disulfonated 4,4′-dichlorodiphenyl sulfone (SDCDPS) and 4-carboxylphenyl hydroquinone (4C-PH) were synthesized in-house [34,35] 4,4′-Difluorobenzophenone (99% purity) was purchased from Yanbian Longjing Chemical Company. 2,2-Bis(4-hydroxyphenyl)propane (bisphenol A) (AR grade) was purchased from Tianjin Guangfu Chemical Reagent Company. *N*-methyl-2-pyrrolidinone (NMP) (99% purity), dimethyl sulfoxide (DMSO) (AR grade), toluene, HCl, H_2SO_4, PVA, and anhydrous K_2CO_3 (AR grade) were purchased from Beijing Chemical Reagent Company. All these chemicals were dried under vacuum at 60 °C for 24 h prior to their use.

2.2. Synthesis of C-SPAEKS copolymers and sulfonated-PVA

The C-SPAEKS copolymers were synthesized by nucleophilic aromatic substitution reactions (Scheme 1). The molar ratio of bisphenol A to 4C-PH was 7:3, and the DS (80%), i.e., the number of sulfonic acid groups per repeating unit of the polymer was kept constant. The polycondensation reaction for synthesizing the C-SPAEKS copolymers was carried out as follows:

First, 4,4′-difluorobenzophenone (4.140 g, 18 mmol), SDCDPS (5.892 g, 12 mmol), 4C-PH (2.070 g, 9 mmol), and bisphenol A (4.788 g, 21 mmol) were added to a 250 mL three-necked flask equipped with a mechanical stirrer, reflux condenser, and N_2 inlet. Next, K_2CO_3 (4.140 g, 30 mmol) and NMP (40.14 mL) were added. Toluene (30 mL) was used as the azeotropic agent. The reaction mixture was refluxed for 4 h at 130 °C to remove all the water from the reaction mixture. Next, the toluene was distilled out completely, and the temperature of the reaction mixture was raised slowly and kept at 190 °C for 20 h. After the completion of the polymerization reaction, the reaction mixture was cooled to room temperature, and the resulting viscous solution was poured into 500 mL 1.0 M HCl solution to precipitate the copolymers. The obtained copolymers were ground to fine powders using a blender. The copolymer powders were washed with deionized water for several times to remove the water-soluble salts and residual solvents. Finally, the copolymer powders were dried at 80 °C for 24 h.

SPVA was synthesized by the following process. First, 2 g PVA was dissolved in 20 mL deionized water and stirred while heating to obtain a homogeneous solution. Excessive H_2SO_4 was added to the PVA solution dropwise at 0 °C. Then, the mixture was heated at 40 °C for 3 h. The reaction is shown in Scheme 2. The mixture was then precipitated by adding anhydrous ethanol, and the precipitate was washed with anhydrous ethanol until pH 6.0. The resulting SPVA was dried in a vacuum oven at 40 °C for 48 h. The DS of SPVA was 2.38%.

2.3. Membrane preparation

The C-SPAEKS/SPVA uncrosslinked membranes were denoted as Un-C/S-*xx*, where *xx* refers to the weight ratio of SPVA to the total weight of C-SPAEKS and SPVA. For example, Un-C/S-20 was fabricated by dissolving C-SPAEKS (0.80 g) and SPVA (0.20 g) in 8 mL and 2 mL of DMSO, respectively, and stirred to form a homogeneous solution. Then, the solution was blended, cast onto a