



Novel modification method to prepare crosslinked sulfonated poly(ether ether ketone)/silica hybrid membranes for fuel cells

Shaoguang Feng^a, Yuming Shang^{a,**}, Guoshun Liu^a, Wenqi Dong^a,
Xiaofeng Xie^{a,*}, Jingming Xu^a, V.K. Mathur^b

^a Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing 100084, PR China

^b Department of Chemical Engineering, University of New Hampshire, NH 03824, USA

ARTICLE INFO

Article history:

Received 16 December 2009

Received in revised form 22 February 2010

Accepted 23 February 2010

Available online 1 March 2010

Keywords:

Proton exchange membranes

Sulfonated poly(ether ether ketone)

Crosslink

Hybrid membranes

DMFC

ABSTRACT

Crosslinked organic–inorganic hybrid membranes are prepared from hydroxyl-functionalized sulfonated poly(ether ether ketone) (SPEEK) and various amounts of silica with the aims to improve dimensional stability and methanol resistance. The partially hydroxyl-functionalized SPEEK is prepared by the reduction of some benzophenone moieties of SPEEK into the corresponding benzhydrol moieties which is then reacted with (3-isocyanatopropyl)triethoxysilane (ICPTES) to get a side chained polymer bearing triethoxysilyl groups. These groups are subsequently co-hydrolyzed with tetraethoxysilane (TEOS) and allow the membrane to form a crosslinked network via a sol–gel process. The obtained hybrid membranes with covalent bonds between organic and inorganic phases exhibit much lower methanol swelling ratio and water uptake. With the increase of silica content, the methanol permeability coefficient of the hybrid membranes decreases at first and then increased. At silica content of about 6 wt.%, the methanol permeability coefficient reaches a minimum of $7.15 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, a 5-fold decrease compared with that of the pristine SPEEK. Despite the fact that the proton conductivity is decreased to some extent as a result of introduction of the silica, the hybrid membranes with silica content of 4–8 wt.% shows higher selectivity than Nafion117.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Direct methanol fuel cells (DMFCs) have been considered as promising portable power source for their high efficiency, high power density, low noise and the simplicity of system [1–3]. Proton exchange membranes (PEM) are the key components of DMFC systems. Currently, the widely used PEMs are perfluorosulfonic acid membranes, such as DuPont's Nafion. These membranes have exceptional oxidative and chemical stability as well as high protonic conductivity [4]. However, several shortcomings such as the high cost, low conductivity at high temperature and low humidity and high methanol crossover have limited their applicability [5–8]. Therefore, the development of alternative PEMs that will overcome these problems is of great importance. Considerable efforts have been made to synthesize novel membranes, such as sulfonated poly(arylene ether ketone)s (SPAEK) [9–11], sulfonated poly(arylene ether sulfone)s (SPAES) [12–15], sulfonated

polyimide (SPI) [16–18], and acid-doped polybenzimidazole (PBI) [19–21], etc. Among the numerous alternative polymers, sulfonated poly(arylene ether ketone)s are good candidates on account of their low cost, high glass transition temperatures and high proton conductivity, which depend on their degree of sulfonation [22]. Compared to perfluorinated sulfonic acid membranes, sulfonated poly(arylene ether ketone)s are reported to have lower acidity and a smaller characteristic separation length and wider distribution of the proton-conducting channels with more dead-end “pockets” and a larger internal interface between the hydrophobic and hydrophilic domains [23]. Therefore, to achieve high proton conductivity, sulfonated poly(arylene ether ketone) membranes require a high sulfonation level. Unfortunately, such a high sulfonation level usually makes them swell excessively and even soluble in methanol/water solution which may lead to deterioration in mechanical properties and high methanol permeation making them unsuitable for DMFC applications [24]. Therefore, modification of PEMs to improve their dimensional stability and decrease the methanol swelling and crossover could be an effective approach to improve their performance.

Crosslinking could be a simple and powerful method to improve their dimensional stability and avoiding the irreversible swelling. By crosslinking, the synthesized polymers could satisfy the need for high degree of sulfonation and dimensional stability [25–27].

* Corresponding author at: A316, INET, Tsinghua University, Beijing, China. Tel.: +86 10 6278 4827; fax: +86 10 6278 4827.

** Corresponding author. +86 10 8019 4009; fax: +86 10 8019 4009.

E-mail addresses: yshang@mail.tsinghua.edu.cn (Y. Shang), xiexf@mail.tsinghua.edu.cn (X. Xie).

Organic–inorganic hybrid membranes may be another alternative to provide controllable chemical and physical properties by combining the effects of organic polymers and inorganic compounds [28–30]. Several studies have showed that the presence of inorganic particles in the organic polymer matrix can reduce the methanol permeability of the hybrids due to the dispersed silica particles acting as methanol barriers [31–33]. Chang and Lin [33] synthesized a series of organic–inorganic composite materials based on polyethylene glycol (PEG)/SiO₂ through sol–gel processes. Due to the introduction of SiO₂, thermal stability of the hybrid membrane enhanced enormously. Some of the hybrid membranes exhibited low methanol permeability without sacrificing their conductivities significantly. Su et al. [34] developed a series of sulfonated poly(phthalazinone ether ketone) (sPPEK) and sulfonated silica nanoparticles (silica–SO₃H) nanocomposite membranes. The strong –SO₃H/–SO₃H interaction between sPPEK chains and silica–SO₃H particles led to ionic crosslinking in the membrane structure, which increased both the thermal stability and methanol resistance of the membranes. The membrane with 7.5 phr of silica–SO₃H (phr = g of silica–SO₃H/100 g of sPPEK in membranes) exhibited low methanol crossover, high bound water content, and a proton conductivity of 3.6-fold increase to that of the pristine sPPEK membrane. The properties of hybrid materials are in general influenced by particle sizes and interaction between the dispersed and continuous phases [35]. In order to obtain homogeneous and transparent organic–inorganic hybrid membranes, it is necessary to increase the compatibility between organic polymer and inorganic phase. The introduction of covalent bonds between organic polymer and inorganic phases would be effective in increasing the compatibility [35].

In this study, a novel modification method was used to prepare crosslinked organic–inorganic hybrid membranes based on sulfonated poly(ether ether ketone) (SPEEK) and silica with the aims to improve the dimensional stability and methanol resistance. The introduction of covalent bonds between organic polymer and inorganic component effectively avoided the phase separation. Firstly, the partially hydroxyl-functionalized SPEEK was performed by the reduction of some benzophenone moieties of SPEEK into the corresponding benzhydrol moieties. Then SPEEK/silica hybrid composite materials having covalent crosslinking bonds between two phases were prepared through the reaction of hydroxyl-functionalized SPEEK with (3-isocyanatopropyl)triethoxysilane (ICPTES) and tetraethoxysilane (TEOS). The molecular structure and morphology of the prepared SPEEK/silica hybrid membranes were characterized by FT-IR and scanning electron microscopy (SEM).

The water uptake, swelling ratio, proton conductivity and methanol permeability properties of the prepared hybrid membranes were studied and correlated with the molecular structure.

2. Experimental

2.1. Materials

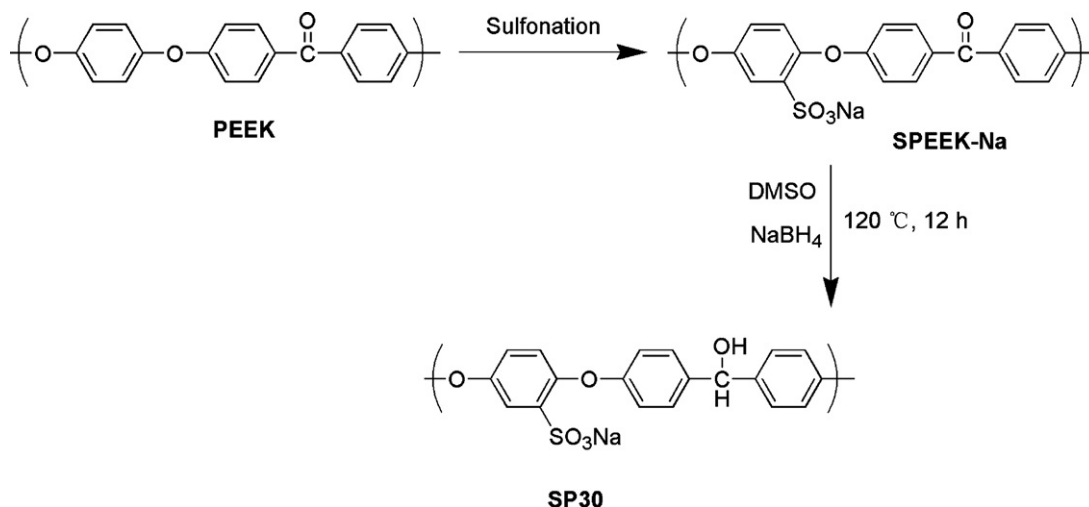
SPEEK was prepared as reported in the literature [36]. The sulfonation degree (SD) and ion exchange capacity (IEC) of SPEEK, used in this study, are 87.6% and 2.37 mequiv. g⁻¹, respectively. Sodium borohydride (NaBH₄), dimethylsulfoxide (DMSO), (3-isocyanatopropyl)triethoxysilane (ICPTES) and tetraethoxysilane (TEOS) were purchased from Beijing Chemical Co. China and used as received.

2.2. Hydroxylation of SPEEK

As shown in Scheme 1, hydroxyl-functionalized SPEEK containing 30 mol% hydroxyl group unit was synthesized as follows: DMSO (45 mL) and NaBH₄ (0.0363 g) were added to a 100 mL round bottomed flask equipped with a reflux condenser and a drying tube. The mixture was heated at 120 °C and 4.5 g SPEEK was then added. After stirring at 120 °C for 12 h, the polymer solution was cooled to room temperature and 3 mL methanol was added while stirring. The abbreviation used for membrane described in this article is as follows: SP30, where 30 refer to carbonyl reduction percentage of SPEEK.

2.3. Preparation of sol–gel precursor solution

The precursor solution was prepared by mixing two solutions, A and B. Solution A containing the triethoxysilyl-functionalized SPEEK was prepared as follows. ICPTES was added slowly into the above-prepared SP30 solution as a bonding agent (molar ratio of hydroxyl group/ICPTES = 1). The mixture was stirred and refluxed at 70 °C for 24 h to complete the reaction. The reaction was carried out under dry nitrogen atmosphere to prevent moisture in the reactor. The triethoxysilyl-functionalized SPEEK was obtained by an addition reaction between isocyanic groups in ICPTES and hydroxyl groups in SP30. Solution B contained TEOS/H₂O with a molar ratio of 1:4. Diluted HCl was used as a catalyst for hydrolysis (pH 4). The mixture of A and B was aged at room temperature for 1 h and then at 30 °C for 3 h.



Scheme 1. Synthesis of SP30.

Download English Version:

<https://daneshyari.com/en/article/1289365>

Download Persian Version:

<https://daneshyari.com/article/1289365>

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