



Sulfonated polyimides with flexible aliphatic side chains for polymer electrolyte fuel cells

Yan Yin^a, Qing Du^{a,*}, Yanzhou Qin^a, Yibo Zhou^a, Ken-ichi Okamoto^b

^a State Key Laboratory of Engines, Tianjin University, Weijin Road 92, Nankai District, Tianjin 300072, China

^b Faculty of Engineering, Yamaguchi University, Ube, Yamaguchi 755-8611, Japan

ARTICLE INFO

Article history:

Received 28 June 2010

Received in revised form 22 October 2010

Accepted 28 October 2010

Available online 3 November 2010

Keywords:

Fuel cell

Sulfonated polyimide

Polymer electrolyte membrane

Proton conductivity

Methanol permeability

ABSTRACT

A series of sulfonated polyimides (SPIs) were synthesized from a new side group sulfonated diamine, 2,2'-bis(4-sulfobutoxy) benzidine monomer (2,2'-BSBB), 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA), and common nonsulfonated diamine monomers by polycondensation reaction. Membranes were prepared by casting their *m*-cresol solutions. The SPI membranes displayed proton conductivity σ values of 0.2–0.4 S cm⁻¹ at 140 °C in liquid water and showed stronger relative humidity (RH) dependence of proton conductivity compared to that of Nafion 112. Most of the SPI membranes were both tough and flexible and thermally stable up to 230–250 °C. XRD spectra suggested the presence of crystalline structure in the membranes. TEM analysis indicated clear microphase separation structure between hydrophobic main chain and hydrophilic side chain. The fully humidified SPI membranes exhibited obvious anisotropic dimensional changes with much larger expansion in thickness than in plane. The long term proton conductivity stability (ca. 500 h) was confirmed at 140 °C. The methanol permeabilities (P_M) of the SPI membranes were in the range of 4.0×10^{-7} – 1.2×10^{-6} cm²/s with a 50 wt% methanol in feed at 30 °C, which were one order of magnitude smaller than that of Nafion 112. As a result, the membranes displayed much larger selectivity towards both high proton conductance and low methanol permeation, compared to Nafion 112, suggesting high potential application for direct methanol fuel cells (DMFCs).

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

In the past decades, fuel cell has been developed as a promising alternative for energy conversion. Polymer electrolyte membrane (PEM) fuel cells convert the chemical energy directly and efficiently into electrical energy and are widely employed as an alternative power source for stationary co-generation units, automotive and portable applications such as power devices of computers and mobile phones [1]. Hydrogen would be a very convenient fuel for PEM fuel cell due to its high electrochemical reactivity and practically zero pollution level. However, storage and delivery still provide complex problems. An alternative is the use of reformers to generate hydrogen from liquid fuels such as methanol. For the breakthrough of the direct methanol fuel cell (DMFC) technology, suitable membranes with high proton conductivity and low methanol permeability are strongly desired. Hydrated perfluorosulfonic acid membranes, such as DuPont's Nafion membrane, are typically used as the polymer electrolytes in PEM fuel cells because of their high proton conductivity, excellent chemical and mechanical stability, as well as long lifetime. However, these

preferable properties are deteriorated above their glass transition temperature ($T_g = 110$ °C). Furthermore, high cost, high methanol permeability, and environmental inadaptability of the fluorinated materials limit their practical fuel cell applications [2,3].

These limitations have stimulated many efforts in the development of alternative polymeric membrane materials [4]. A series of nonfluorinated sulfonated hydrocarbon polymers such as polyether ketones [5], polyethers [6], polysulfones [7], blend or cross-linked ionomers [8], polyphenylene and polybenzimidazoles [9], and polyimides [10–21] were studied. In general, these nonfluorinated hydrocarbon polymers are expected to have lower production cost as well as satisfactory chemical and mechanical stability for many applications. Through the extensive research works on the sulfonated ionomers, sulfonated polyimides (SPIs) have been developed as proton conductive ionomers with high proton conductivity and substantial stability. We have synthesized several SPIs with aromatic backbone and aliphatic/aromatic side chains terminated with sulfonic acid group based on sulfonated diamines such as bis(3-sulfopropoxy) benzidine (BSPB) and bis(4-sulfophenyl) benzidine (BSPOB). It was found that the membrane properties such as hydrolytic stability could be improved by introducing flexible sulfonated side chains into the polymer structure. The sulfonic acid groups being apart from both the backbone and imide rings tend to give better water stability of the corresponding

* Corresponding author. Tel.: +86 22 87402029; fax: +86 22 27404177.

E-mail addresses: duqing@tju.edu.cn, yinyan221@yahoo.com (Q. Du).

SPIs [3,20]. The properties of aromatic SPIs with different positions of ether linkage in the backbone or in the side group have been described in Ref. [21]. It was concluded that the SPIs with rigid backbone and relatively flexible side chains generally showed better membrane stability toward water. However, the SPIs with much longer aliphatic side chains terminated with sulfonic acid groups have not been studied in details. To better understand the structure–property relationship of the SPIs, a sulfonated diamine monomer with slightly longer sulfonated side group, 2,2'-bis(4-sulfobutoxy) benzidine (2,2'-BSBB), was synthesized and the corresponding SPIs with rigid backbone and longer flexible side chain were prepared. Their physical properties, proton conductivity and methanol permeability are investigated.

2. Experimental

2.1. Materials

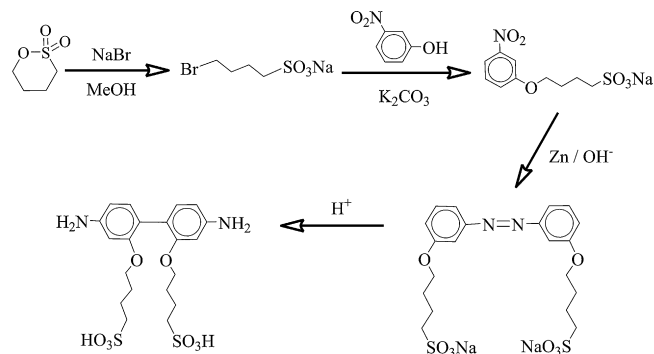
1,4,5,8-Naphthalenetetracarboxylic dianhydride (NTDA) was purchased from Aldrich and purified by sublimation before use. 4,4'-Diaminodiphenyl ether (ODA), bis(4-aminophenyl) sulfone (BAPS), bis(4-aminophenyl) hexafluoro propane (BAHF), 9,9-bis(4-aminophenyl)fluorene (BAPF), and 4,4'-bis(4-aminophenoxy) biphenyl (BAPB) were purchased from Wako Co. and purified by vacuo sublimation prior to use. Triethylamine (TEA, Wako) was purified by distillation under reduced pressure and dehydrated with molecular sieves 4 Å prior to use. *m*-Cresol was dried over molecular sieves 4 Å prior to use. Other reagents were used as received.

2.2. Synthesis of 2,2'-bis(4-sulfobutoxy) benzidine (2,2'-BSBB)

2,2'-BSBB was synthesized from 1,4-butanediol and 3-nitrophenol according to the method described in a previous paper [20]. The synthesis procedure is shown as Scheme 1. The monomer has a total yield of 45% and was characterized by IR and ¹H NMR spectra, and stored in the dark.

2.3. Synthesis of BSBB-based sulfonated polyimides

The homo-SPI was synthesized from 2,2'-BSBB and NTDA directly via a one-step polymerization method. The synthesis of random co-SPIs is shown in Scheme 2 which was similar to that

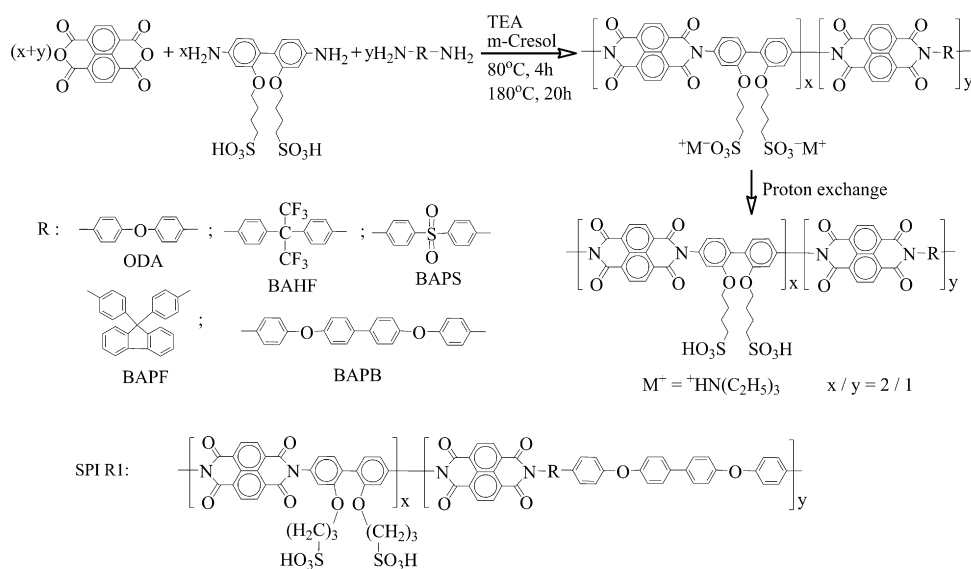


Scheme 1. Synthesis of aliphatic sulfonated diamine of 2,2'-BSBB.

of homo-SPI except for introduction of nonsulfonated diamine monomers. Typical polymerizations of co-SPIs were conducted in a flame dried 3-neck flask which were added 1.952 g (4 mmol) of BSBB, 20 ml of *m*-cresol, and 1.6 ml of TEA, with stirring under nitrogen flow. After BSBB was completely dissolved, 2 mmol of nonsulfonated diamine (ODA, or BAHF, BAPS, BAPF, BAPB), 1.608 g (6 mmol) of NTDA and 1.06 g of benzoic acid were added to the flask successively. The reaction mixture was stirred at room temperature for a few minutes and then heated to 80 °C for 4 h and 180 °C for 20 h, respectively. After cooling to 80 °C, additional 50 ml of *m*-cresol was added to dilute the highly viscous solution, which was then poured into a large excess of acetone. The resulting fiber-like precipitate was collected by filtration, washed with acetone, and dried in vacuo.

2.4. Membrane formation and proton exchange

Membranes of the BSBB-based SPIs were prepared by casting their *m*-cresol solutions (2–5 wt%) onto glass dishes and dried at 110 °C for 10 h. The as-cast membranes were soaked in methanol at 60 °C for 1 h to remove the residual solvent, followed by the proton exchange treatment in 1.0 N hydrochloric acid at room temperature for 10–20 h. The acidification procedure was repeated three times to get proton-exchanged membranes which were thoroughly washed with de-ionized water and then dried in vacuo. The SPI membranes in acid form were obtained with thickness in the range of 40–60 μm.



Scheme 2. Synthesis and chemical structure of aliphatic sulfonated polyimides and SPI R1.

Download English Version:

<https://daneshyari.com/en/article/636032>

Download Persian Version:

<https://daneshyari.com/article/636032>

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