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Journal of Membrane Science 279 (2006) 570–577

journal of MEMBRANE SCIENCE

www.elsevier.com/locate/memsci

Synthesis and characterization of new sulfonated polyimides as proton-exchange membranes for fuel cells

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Received 9 July 2005; received in revised form 8 December 2005; accepted 24 December 2005
Available online 15 February 2006

Abstract

The synthesis and characterization of a series of new sulfonated polyimides are described. One-step high temperature polymerization method was used to prepare the sulfonated polyimide copolymers from 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA), 4,4′-diaminostilbene-2,2′-disulfonic acid (DSDSA), and other three common diamines, i.e., 4,4′-oxydianline (ODA), 4,4′-methylene dianiline (MDA), and 4,4′-(9-fluorenylidene)dianiline (FDA). The sulfonation degree of the copolymers was regulated through variation of the molar ratio of DSDSA to the common diamines. Flexible, transparent, and mechanically strong membranes were successfully obtained. The membranes were characterized with Fourier transform infrared spectra, thermogravimetric analysis, ion-exchange capacity, and proton conductivity measurements. These results showed that the membranes had good thermal stability and exhibited high conductivity at high relative humidity levels, especially in liquid water at 70 °C. At high temperatures of above 140 °C, the membranes displayed higher conductivities than Nafion® membranes because of their high activation energies.

Keywords: Sulfonated polyimides; Proton-exchange membranes; Proton conductivity; Copolymer; Fuel cell

1. Introduction

Proton-exchange membrane fuel cells (PEMFCs) have attracted much attention because of their high power density and high energy conversion efficiency as well as low pollution levels [1–3]. One of the main components of a PEMFC is proton-exchange membrane (PEM) itself. Dupont Nafion® or other perfluorinated sulfonic acid membranes are currently popular membranes for low temperature PEMFCs due to their high proton conductivity, good mechanical strength, and high chemical stability. However, some disadvantages such as high cost, strong dependence of proton conduction on the water content of the membrane, and low conductivity at high temperatures (above 100 °C) and low relative humidities (RHs) seriously limit their industrial applications [4]. It is desirable for a PEMFC to operate at high temperatures (120 °C or higher) and low humidities (<50% RH). Such operation can increase the anode's tolerable level of CO in the fuel, accelerate the reaction rates at the anode and cathode, ease or eliminate the water management, and improve thermal management and heat utilization of the fuel cell stack [5,6]. So, it is necessary to develop alternative membranes that have low cost and good performance at high temperatures and low humidities.

Recently, sulfonated polyimides (SPIs) have been studied and expected to be promising materials for PEMFCs because of their many desirable characteristics including excellent mechanical and thermal properties as well as chemical stability [7–26]. The sulfonic acid groups may be introduced either by direct sulfonation of the parent polymers or by polymerization of sulfonated monomers. Very few results can be found in the literature for the direct sulfonation of polyimides because of difficulty in sulfonating polyimides with a stable structure or the resulting sufonated polyimides possessing undesirable properties such as poor stability. Sulfonated polyimides were mostly realized by polymerization of sulfonated monomers. The sulfonation degree was carefully controlled by regulating the molar ratio between a sulfonated diamine and a common diamine.

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doi:10.1016/j.memsci.2005.12.049

Pineri and co-workers [7] firstly synthesized sequenced five-membered and six-membered ring sulfonated polyimides from 4,4′-diaminobiphenyl-2,2′-disulfonic acid (BDSA), 4,4′-oxydianiline (ODA), and two types of dianhydrides, oxydiphthalic dianhydride (ODPA) and 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA), respectively. To maintain a good compromise between the conductivity and hydrolysis stability, they controlled the ion-exchange capacity (IEC) value of the membranes from 1.1 to 1.3 meq/g. They studied membrane properties such as swelling and conductivity [8], water vapor sorption and diffusion coefficients [9–11], and stability in aqueous medium [12] and tested their fuel cell performance based on a new design of the membrane electrode assembly (MEA) [13]. Their results showed that the sulfonated polyimide membranes had fairly good fuel cell performance while the proton conductivity was rather low (less than 0.01 S/cm at 100% relative humidity). They concluded that the ODPA-based sulfonated polyimides were not stable in fuel cell conditions, whereas NTDA-based sulfonated polyimides were fairly stable (maximum: 3000 h). To improve the hydrolysis stability and conductivity of the membranes, they also developed aromatic ether diamines having different amino-substituted positions or bulky groups in their structure and used them with NTDA and BDSA to synthesize several series of SPIs. But no better results had been achieved [14].

Based on the idea that bulky or angled comonomers can push the polymer rigid rod backbone apart and produce nano-sized pores inside the membrane, Litt and co-workers [15–17] have developed various sequenced and random SPIs using BDSA, NTDA, and unsulfonated diamines with a bulky and/or angled structure. They reported that most membranes showed high conductivity (as high as Nafion® membranes at moderate relative humidity values and higher at high relative humidity levels). However, these membranes had poor hydrolysis stability and poor mechanical strength, and no fuel cell testing data were reported.

McGrath and co-workers [18–20] prepared a series of SPIs using different sulfonated diamines, a commercially available sulfonated diamine, 2,5-diaminobenzene sulfonic acid (DABSA), and two self-synthesized sulfonated diamines, 3-sulfo-4,4′-bis(3-aminophenoxy)triphenyl phosphine oxide sodium salt (SBAPPO) and 3,3′-disulfonic acid-bis[4-(3-aminophenoxy)phenyl]sulfone (SA-DADPS). But no conductivity and fuel cell performance data have been reported.

Okamoto and co-workers [21–26] have developed two types of SPIs (main-chain type and side-chain type) intending to study systematically the structure–property relationship of SPIs. They synthesized aromatic sulfonated diamines such as 4,4′-diaminodiphenyl ether-2,2′-disulfonic acid (ODADS) [21], 9,9′-bis(4-aminophenyl)fluorene-2,7-disulfonic acid (BAPFDS) [22], and 4,4′-bis(4-aminophenoxy)biphenyl-3,3′-disulfonic acid (BAPBDS) [23] and prepared several series of main-chain type sulfonated polyimides by their copolymerization with NTDA and several common diamines. They found that the resulting ODADS- and BAPFDS-based SPI membranes displayed higher proton conductivities and better hydrolysis stability than the corresponding BDSA-based ones. The BAPBDS-based SPIs showed greatly improved hydrolysis stability and similar or higher proton conductivities than Nafion® membranes. Although these membranes might be good candidates for low temperature (<80 °C) fuel cell system, they might not have sufficiently good stability for high temperature application (>80 °C) [22,25].

To create a microphase-separated structure and ion-rich domain form channels being favorable for proton transport similar to those in Nafion® membranes, Okamoto and his co-workers [24–26] also synthesized a novel type of side-chain SPIs using their self-developed sulfonated diamines, e.g., 2,2′-bis(3-sulfopropoxy)benzidine (2,2′-BSPB), 3,3′-bis(3-sulfopropoxy)benzidine (3,3′-BSPB), and 3-(2′,4′-diaminophenoxy)propane sulfonic acid (DAPPS). Their results showed that the side-chain type SPIs, especially NTDA-2,2′-BSPB-based SPIs, had high proton conductivities of 0.2 S/cm at 80% RH and 105 °C and 0.05 S/cm at 50% RH and 120 °C. These SPIs might be expected to be good candidate membranes for high temperature PEM fuel cell application, but their thermal stability was not reported.

In this paper, a series of random sulfonated polyimides with controlled sulfonation degrees were synthesized using a new commercially available sulfonated diamine, 4,4′-diaminostilbene-2,2′-disulfonic acid (DSDSA), NTDA, and other common diamines. The physical properties and proton conductivities of the membranes at 70 °C and high temperatures above 100 °C were investigated, and their potential application for high temperature PEM fuel cells was explored.

2. Experimental

2.1. Materials

NTDA, DSDSA, FDA, MDA, and ODA were purchased from TCI America (Portland, OR) and were dried in a vacuum oven at 120 °C overnight prior to use. Triethylamine (TEA, 99.5%), *m*-cresol (99.0%), and benzoic acid (>99.5%) were purchased from Aldrich (St. Louis, MO) and were used as received.

2.2. Synthesis of DSDSA-based SPI copolymers

A typical procedure for preparation of sulfonated polyimide copolymers is described below using the copolymer of NTDA-DSDSA/ODA (70/30) as an example. In the preparation, 2.593 g (7.0 mmol) of DSDSA, 50 ml of *m*-cresol, and 1.700 g (16.8 mmol) of triethylamine were charged to a 250 ml, completely dried four-neck flask equipped with a mechanical stirring device. The mixture was heated to 80 °C and was stirred under nitrogen flow until DSDSA was completely dissolved. Then 0.613 g (3.0 mmol) of ODA, 2.682 g (10.0 mmol) of NTDA, and 2.442 g (20.0 mmol) of benzoic acid were added successively. Additional 15 ml *m*-cresol was added to have a 10 wt% solid concentration. The reaction mixture was stirred at 80 °C for 4 h, at 180 °C for 16 h, and at 200 °C for 4 h, respectively. After cooling to room temperature, 50 ml *m*-cresol was added to dilute the highly viscous solution, and then the solution was precipitated into excess isopropyl alcohol (IPA). The precipitate was filtered