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Synthesis and characterization of sulfonated mutiphenyl conjugated polyimide for PEMFC

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ABSTRACT

A new monomer, di-sulfuric acid-1,1-bis(4-aminophenyl)-2,2-diphenylethylene (SBAPDPE), was synthesized by direct sulfonation of the parent diamine, 1,1-bis(4-aminophenyl)-2,2-diphenylethylene (BAPDPE) using concentrated sulfuric acid. A series of the side-chain-type sulfonated conjugated tetraphenylethylene polyimides (SCTPPIs) with different degrees of sulfonation were prepared from dianhydrides with SBAPDPE and non-sulfonated diamine. The SCTPPIs generally showed good solubility in *m*-cresol and DMSO. The membranes were studied by FT-IR, ¹H NMR spectroscopy, and TGA. Sorption experiments were conducted to observe the interaction of sulfonated polymers with water. The ion exchange capacity (IEC) and proton conductivity were evaluated with increase of degree of sulfonation. © 2017 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved.

Introduction

Proton exchange membranes (PEMs) used as electrolyte in polymer electrolyte membrane fuel cells (PEMFCs) with excellent properties, such as high chemical stability against oxygen and free radicals, good mechanical flexibility, and high proton conductivity, have attracted lots of attention nowadays [1–3]. Membranes currently used in PEMFC are perfluorinated polymers, such as Dupont Nafion, which are perfluorosulfonic acid copolymer, commercially used as the polymer electrolyte membrane because of its excellent chemical, physical, and electrical properties. However Nafion is not suitable in use of above 100 °C. Thus new polymer membranes for fuel cells are being explored and developed by chemical modification. To overcome these kinds of drawbacks, extensive efforts have been made to develop alternative proton-conducting membranes based on sulfonated aromatic hydrocarbon polymers [4–8], such as sulfonated poly (arylether sulfone) [9,10], sulfonated polyphenylene [11], sulfonated poly (ether ether ketone) [12], sulfonated polybenzimidazoles (SPBI), and sulfonated polyimides (SPIs) [13]. Polyimides are an attractive material for the preparation of membranes because it possesses excellent film and membrane-forming properties as well as high thermal and chemical stability. Much endeavor has been focused on synthesizing tractable

and processable polyimides with no reasonable sacrifice of their own excellent properties [14]. Many novel side-chain-type and main-chain-type sulfonated diamines are prepared to develop high performance SPI ionomers [13–17]. Research efforts have been aimed at the development of novel sulfonated aromatic polymers with pronounced hydrophilic/hydrophobic separation by changing of chemical modification using sulfonic acid groups on side chain rather than main chain [15–17]. Recently Chen et al. and Fang et al. [16,17] reported the relationship between the structures of sulfonated diamines and the properties of the resulting polyimide membranes have been intensively studied by developing novel main chain and side chain types of sulfonated diamines. The side-chain-type sulfonated monomer with sulfonated pendant groups are favorable for preparing high performance SPIs, due to the formation of the microphase-separated structure composed of hydrophilic side chain domains and hydrophobic polyimide main chain domains. Tian et al. [18] also investigated the effect of the different sized hydrophilic block segments in the main chain on the morphology of membranes as well as and the effect of the side-chain-type sulfonated polymer. The polymer membranes obtained with better hydrophilic/hydrophobic microphase separation exhibit much better single fuel cell performance. We also studied the the side-chain-type sulfonated polymer membranes which are consisted tetraphenyl groups on a polymer backbone, and selectively sulfonated on side chain phenyl ring [19].

The purpose of this work is to prepare the side-chain-type sulfonated and conjugated planar structure of polymer membrane

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having characteristics of low solubility in water, low water uptake, and high conductivity. This work is an attempt to synthesize side-chain-type sulfonated polyimide with the conjugated phenyl rings in side chain of polymers. The sulfonic acid on side chain would be provided better clustering effect and hydrophilic/hydrophobic separation. And also the conjugated planar structure provides better dimensional stability by generating π - π interaction between phenyl rings of polymer chains. The synthesized copolymers were characterized by FT-IR, ^1H NMR spectroscopy, thermo gravimetric analysis (TGA), the proton conductivities, water uptake, and ion exchange capacity (IEC).

Experimental

Materials

3,3',4,4'-Biphenyltetracarboxylic dianhydride (BPDA), 4,4'-diaminodiphenylmethane (DADPM), concentrated sulfuric acid (95%), *m*-cresol, DMSO, triethylamine (Et_3N), sodium chloride, sodium hydroxide, and benzoic acid were purchased from Aldrich Co. Other commercially solvents such as acetone, methanol, and water were also used without further purification.

Synthesis of di-sulfuric acid-1,1-bis(4-aminophenyl)-2,2-diphenyl ethylene (SBAPDPE)

Under an N_2 atmosphere, a three-necked flask equipped with a magnetic stirrer was charged with 1,1-bis(4-aminophenyl)-2,2-diphenyl ethylene (5.00 g, 13.70 mmol) and 15 mL of concentrated sulfuric acid (165.50 mmol). The reaction mixture was stirred at room temperature for 4 h until the starting monomer was consumed (monitored by TLC). The reaction mixture was poured into distilled water and then washed with distilled water until the pH of residual water was 6. The brown powder was filtered and then dried at 60 °C in vacuum oven. Thus, 4.5 g of brown powder product was obtained. Yield: 90%. ^1H NMR (400 MHz, DMSO-*d*₆), δ = ppm: 7.35–7.39 (d, 4H, 2 ortho C_6H_2 – SO_3H), 7.10–7.19 (d, 4H, 2 meta C_6H_2 – SO_3H), 7.10–7.00 (d, 4H, 2 meta C_6H_2 – NH_2), 6.89–7.00 (d, 4H, 2 ortho C_6H_2 – NH_2), FT-IR: 1249 cm^{-1} , 1026 cm^{-1} , 690 cm^{-1} (stretching O–S–O), 2500 cm^{-1} –3250 cm^{-1} (stretching $^+\text{NH}_3$), 3500 cm^{-1} (b, N–H, –OH near $^+\text{NH}_3$ and $-\text{SO}_3\text{H}$).

Synthesis of sulfonated conjugated tetraphenylethylene polyimides (SCTPPIs)

A series of sulfonated polyimides containing conjugated tetraphenylethylene were prepared via one-step polycondensation from dianhydrides (BPDA) with sulfonated diamine (SBAPDPE) and non-sulfonated diamine (DADPM), respectively. The molar ratio of BPDA to SBAPDPE to DADPM was 100:30:70, 100:40:60, and 100:50:50. To a 100 mL three-necked flask equipped with a mechanical stirrer, a nitrogen inlet, and a thermometer, SBAPDPE (1.42 g, 2.71 mmol), DADPM (0.83 g, 4.07 mmol), *m*-cresol (13 mL) and TEA (2.02 mL, 14.60 mmol) were fitted. The mixture was stirred at 50 °C under nitrogen flow until diamine monomers were completely dissolved to give a homogeneous solution. Then BPDA (2.06 g, 6.79 mmol) and benzoic acid (1.66 g, 13.58 mmol) were added to the solution. The 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 the solution was cooled to 80–100 °C, 10 mL of additional *m*-cresol was added to dilute the highly viscous solution. The fiber-like precipitate was obtained as the solution was poured into methanol, and then collected by filtration, washed with methanol, acetone, and dried in vacuum at 100 °C for 24 h. ^1H NMR (400 MHz, DMSO-*d*₆), δ = ppm: 8.18–8.47 (b, 6H, $\text{C}_{16}\text{H}_6\text{N}_2\text{O}_4$), 7.90–

8.18 (b, 4H, 2 ortho C_6H_2 – SO_3H), 6.90–7.51 (b, 8H, C_6H_4 – CH_2 – C_6H_4 , 12H, $2\text{C}_6\text{H}_2$ – SO_3H , $2\text{C}_6\text{H}_4$ – NH_2), 4.07–4.25 (b, 2H, C_6H_4 – CH_2 – C_6H_4), FT-IR: 1710 cm^{-1} (C=O, symmetric), 1670 cm^{-1} (C=O, asymmetric), 1365 cm^{-1} (C–N, asymmetric), 3500 cm^{-1} (b, –OH near $-\text{SO}_3\text{H}$).

Membrane preparation and characterization

Membranes (25 μm) of the sulfonated polyimides (0.2 g) were prepared by casting the *m*-cresol and DMSO solutions (3 mL/7 mL) of polymers in TEA salt form (20 wt.%) on glass plates ($3 \times 3 \text{ cm}^2$) and drying at 120 °C for 12 h. The casted membranes were soaked in 1 M H_2SO_4 solution at room temperature for 12 h. The samples of polymer membranes were washed with deionized water several times before test. The data point was collected from average value of five each samples. The proton exchanged membranes were thoroughly washed with water at several times and then dried in vacuum at 150 °C for 12 h. The polymers structure was confirmed by Fourier transform infrared (FT-IR) spectroscopy. Measurements were recorded using a MIDAC FT-IR spectrometer with thin homogeneous cast films. The ^1H NMR spectra were recorded on a Bruker DRX (400 MHz and 900 MHz) spectrometer using DMSO-*d*₆ as solvent and tetramethylsilane (TMS) as internal standard. Thermo gravimetric analyses (TGA) were performed Perkin-Elmer TGA7 analyzer respectively. The molecular weight of polymers was determined relative to polystyrene standards by gel permeation chromatography (GPC) in THF as the eluent on a Perkin Elmer series 200 with RI detector. The membranes were vacuum dried at 100 °C for 24 h, weighed and immersed in deionized water at 30 °C and 80 °C for 24 h. The wet membranes were wiped to dry and quickly weighed again. The water uptakes of membranes are reported in weight percent as follows: water uptake = $\{(m_{\text{wet}} - m_{\text{dry}})/m_{\text{dry}}\} \times 100\%$ where m_{wet} and m_{dry} are the weights of the wet and dry membranes, respectively. The titration technique was used to determine the IEC of the membranes. The membranes in the acid form (H^+) were converted to the sodium salt form by immersing the membranes in a 1 M NaCl solution for 24 h to exchange the H^+ ions with Na^+ ions. Then, the exchanged H^+ ions within the solutions were titrated with a 0.02 N NaOH solution. The theoretical IEC calculated from sulfonated degree was obtained from the formula: IEC (meq./g) = Ionic mmol concentration/Mass of dry membrane at 25 °C. Proton conductivity of membranes was determined from the membrane resistance measured by electrochemical impedance spectroscopy (EIS) using a Bekktech membrane & single-cell test systems (BT-512) at 40, 60, 80 °C under 0–100% humidity. EIS was conducted at the open circuit condition by applying a small alternating voltage (10 mV) and varying the frequency of the alternating voltage from 1×10^5 to 1 Hz. After assembling the single cell, the MEAs were fully hydrated by feeding a fully humidified N_2 into the single cell for 2 h. During the operation, fully humidified H_2 and air at 70 °C were fed into the anode and cathode, respectively. The stoichiometry of hydrogen and to air was maintained to be 1.5/2.0 and the relative humidity 100/100%. After the activation procedure, polarization curves were measured with a commercial test station (Scitech, Korea Inc) at the temperature of 70 °C and ambient pressure. Polarization measurements were started at the OCV and the cell was operated in the galvanostatic mode with a scan rate of 36 mA/s for each step. The tensile stress–strain properties of the membranes were tested using a Com-Ten Industries 95 T series load frame equipped with a 200 lbf load cell and computerized data acquisition software. Samples of 9 mm width were deformed at a crosshead speed of 5 mm/min with gauge length of 30 mm.

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