



Properties and performance of composite electrolyte membranes based on sulfonated poly(arylenethioethersulfone) and sulfonated polybenzimidazole

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ARTICLE INFO

Article history:

Received 15 March 2011

Received in revised form

6 May 2011

Accepted 13 May 2011

Available online 27 May 2011

Keywords:

Sulfonated polyarylenethioethersulfone (SPTES)

Polymer composites

Polymer electrolyte membrane (PEM)

ABSTRACT

A novel composite membranes comprising a sulfonated polyarylenethioethersulfone homopolymer (SPTES-100) and a sulfonated poly(p-phenylene benzobisimidazole) (SPBI), was described in this article. The composite membrane was obtained via a solution cast process in a mixture solvent of N, N-Dimethylacetamide (DMAc) and methanol (MeOH). The proton conductivity of the composite membranes was found to increase with the SPTES-100 content increased. The higher proton conductivity was ~ 110 mS/cm at 85 °C and 85% relative humidity for the SPTES/SPBI 70/30 (wt) composite membrane which was considerably less than that of the 300 mS/cm of the SPTES-100 membrane. The mechanical properties indicated that the swelling of the composite membranes was reduced, which is relative to the SPTES-100 polymers, due to the reduced water uptake of the composite membrane by introducing the SPBI into the SPTES polymer matrix. The morphology of the SPTES/SPBI composite membranes was examined by a combination of techniques such as scanning electron microscopy (SEM) and elemental mapping to confirm the dispersion of the SPBI and study the micro-structure of the composite. The membrane electrode assembly (MEA) performance of the composite membranes was preliminary studied for H₂/Air fuel cells applications.

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1. Introduction

Polymer electrolyte membrane (PEM) fuel cell technology is in an advanced stage of commercialization when compared to other fuel cell technologies. PEM fuel cells based on perfluorinated membranes have successfully been operated in a temperature range of approximately 50–90 °C [1–3]. The most commonly used perfluorinated membrane, Nafion, is an expensive component, adding to the high manufacturing cost of fuel-cell stacks. Cheap engineering thermoplastics, such as polyether ether ketone (PEEK) [4,5], polysulfone (PSU) [6], polybenzimidazole (PBI) [7] etc., are being evaluated as alternatives to Nafion membranes for PEM fuel cell application.

Efforts to develop polymer membranes able to operate above 100 °C have been prompted by the additional benefits of enhanced carbon monoxide (CO) tolerance and improved heat removal [8–11]. The most significant barrier to running a PEM fuel cell at elevated

temperatures is maintaining the proton conductivity of the membranes. Most polymer membranes rely on absorbed water to ionize acid groups and permit proton transport. The conductivity of a dry membrane is several orders of magnitude lower than that of a fully saturated membrane; proton conductivity increases exponentially with water activity in the membranes. So, optimized proton and water transport properties of the membranes and proper water management are crucial for efficient fuel cell operation. Dehydration of the membrane reduces proton conductivity and excess of water can lead to flooding of the electrodes, both conditions may result in poor fuel cell performance. The proton conductivity of the ionomer membranes relies on the presence of water, but because of high evaporation rate at temperature above 100 °C there is a drastic decrease in conductivity. Increasing the fuel cell temperature raises the vapor pressure required to keep a given amount of water in the membrane, thereby increasing the likelihood that water loss will occur and significantly reduce proton conductivity.

The composite membrane approach represents the way to improve the properties of the PEM as the desired properties of the two components can be combined in one composite. Recently, it has been reported [12] that acid–base blend membranes containing acidic and basic polymers showed reduced methanol permeability and are thermally and chemically stable. Kerres et al. [13] also

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reported development of blend membranes of SPEEK with polybenzimidazole celazole, which showed reduction in swelling and methanol permeation, in addition to their high thermal stability and moderate conductivity at higher temperature.

The present work is an attempt to improve the performance of sulfonated polyarylenethioethersulfone homopolymer (SPTES-100) membranes by introducing sulfonated polybenzimidazole (SPBI) proton conducting polymers, which was a rigid rod proton conducting polymer developed in a previous study [14,15]. SPTES-100 is selected as the acidic polymer, and SPBI as the basic polymer to make the composites. The acidic polymers are combined with the basic polymers in different acid/base ratios in order to get acid–base composites membranes with improved properties. In the acid–base composites membranes specific interactions between acidic and basic components are present: hydrogen bridges and electrostatic forces by proton transfer from the acid to the basic group [16]. The composite membranes were prepared using a solution cast method by dissolving SPTES-100 and SPBI in the mixed solvent of methanol and DMAc. The composite membranes were characterized by scanning electron microscopy (SEM) and elemental mapping to confirm the dispersion of SPBI in SPTES-100 polymer matrix. The thermal and mechanical properties of composites membranes were also investigated.

2. Experimental

2.1. Materials

N,N-Dimethylacetamide (DMAc), methanol (MeOH), and triethylamine (TEA) were purchased from Aldrich used as received. Sulfonated polyarylenethioethersulfone homopolymer (SPTES-100) and sulfonated polybenzimidazole (SPBI) were synthesized in our Lab, which have been described elsewhere [14,17]. Both polymers were of high molecular weight and could be solvent-cast into films of outstanding mechanical integrity.

2.2. Preparation of SPTES/SPBI composite membranes

The composite membranes were fabricated via a solvent-cast process in which the rigid-rod SPBI was first solubilized as its triethylammonium salt in a mixture of DMAc and MeOH as solvents followed by the addition of SPTES-100 and the subsequent volatilization of TEA and the solvents. The preparation of SPTES/SPBI composite membranes (SPTES/SPBI = 70/30 (wt) as an example) was as follows: DMAc (40 ml), MeOH (10 ml), and TEA (10 ml) were charged into a three-neck reaction flask equipped with a mechanical stirrer and nitrogen inlet/outlet and were stirred for 30 min at room temperature. SPBI (1.2 g) was added into the flask. The mixture was stirred at 140 °C, in a silicon oil bath, until a solution became clear. Then, SPTES-100 (2.8 g) was added into the SPBI solution. The resulting mixture was stirred under a nitrogen atmosphere at 80 °C for 2–4 h. The SPTES/SPBI composite solution was obtained and was filtered. The SPTES/SPBI composite solution was directly transferred to casting dish, and was dried at 80 °C for 4–8 h in vacuum oven, then at 100 °C for 24 h. Once completed, the membrane was transferred to 2 M sulfuric acid solution bath for 24 h at room temperature. A free-standing SPTES/SPBI (70/30 wt) composite membrane was obtained.

2.3. Proton conductivity measurement

Proton conductivity was measured by using AC Impedance Spectroscopy and utilized a standard 4-electrode measurement setup to eliminate electrode and interfacial effects. Teflon sample fixture was placed inside a temperature and humidity controlled

oven and was adjusted in such a way to allow the sample to be exposed to the humidified air within the chamber. The two outer electrodes were made of platinum foil and these acted as a source for current in the sample. Two inner platinum wire electrodes (spaced 1 cm apart) were then used to measure the voltage drop across a known distance. By measuring the impedance of the material as a function of frequency at a set temperature and humidity, the conductivity of the membranes is obtained using the magnitude of the impedance in a region where the phase angle is effectively zero. The conductivities were calculated by $\sigma = L/(R \times A)$. Here σ : proton conductivity, L : distance between the two electrodes, R : resistance, and A : test area, and is given as $A = T \times W$, where T : thickness of test membrane sample; W : width of test membrane sample.

2.4. Mechanical properties measurement

Mechanical evaluation of the tensile properties was performed on a Tinius Olsen H10KS bench top tensile tester at a speed of 5 mm/min. A stretching force was applied to one pneumatic clamp. Clamp displacement was used to determine elongation ratio and strain. Tensile stresses were calculated from the initial cross-sectional area of the sample and applied load. Young's modulus, E , was determined from the initial slope at $\lambda = 1.025$. Three to five samples per mechanical measurement were used, with estimated error/uncertainty not exceeding 10% in the data. The composite membrane samples were cut into a rectangle shape 50 mm \times 4 mm.

2.5. Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) was performed to determine the influence of the polymer constitution on tensile modulus and mechanical relaxation behavior. A PerkinElmer DMA-7 was run in tensile mode at an oscillation frequency of 1 Hz with a static stress level of 5×10^5 Pa and a superposed oscillatory stress of 4×10^5 Pa. With this stress controlled instrument, the strain and phase difference between stress and strain are the measured outputs. Typically, the resulting strain levels ranged from 0.05 to 0.2% when the sample dimensions were 8 mm \times 2 mm \times 0.1 mm. A gaseous nitrogen purge and a heating rate of 3 °C/min were employed. The temperature scale was calibrated with indium, and the force and compliance calibrations were performed according to conventional methods.

2.6. Thermomechanical analysis

The in-plane coefficient of thermal expansion (CTE) of the polymer composites was measured as a function of temperature via thermo-mechanical analysis (TMA). The technique utilized a TA Instrument TMA 2940 in tensile film mode with a heating rate of 4 °C/min and typical sample dimensions of 100 mm \times 15 mm \times 0.25 mm. The CTE was determined from the slope of the resultant expansion temperature plots.

2.7. Scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDS)

The cross-section of the SPTES/SPBI composite membrane was analyzed by SEM attachment of EDS (JEOL JSM-6360LV model equipped with Oxford INCA X-sight). The distribution of carbon, oxygen, and sulfur elements along the membrane cross-section was determined by an EDS mapping method.

2.8. Fabrication of membrane electrode assembly (MEA)

A painting technique was used to form electrodes on both sides of the composite membranes, using ink slurry. This slurry consisted

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