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Blends based on sulfonated poly[bis(benzimidazobenzisoquinolinones)] and poly(vinylidene fluoride) for polymer electrolyte membrane fuel cell

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ABSTRACT

A new blend system consisting of an amorphous sulfonated poly[bis(benzimidazobenzisoquinolinones)] (SPBIBI) and the semi-crystalline poly(vinylidene fluoride) (PVDF) was prepared for proton exchange membranes. The miscibility behavior of a series of blends of SPBIBI with PVDF at various weight ratios was studied by WXRD, DSC and FTIR. The properties of the blend membranes were investigated, and it was found that the introduction of PVDF in the SPBIBI matrix altered the morphological structure of the blend membranes, which led to the formation of improved connectivity channels. For instance, the conductivity of the blend membrane containing 10 wt% PVDF displayed the highest proton conductivity (i.e., 0.086 S cm^{-1}) at room temperature, a value almost twofold that of the pristine SPBIBI membranes (i.e., 0.054 S cm^{-1}) under identical conditions. The result was thus comparable to the proton conductivity of Nafion 117 (i.e., 0.09 S cm^{-1}). Moreover, the dimensional stability, the elongation at break, the methanol permeability and the oxidative stability were enhanced in various extents by introducing PVDF into the blend membranes.

1. Introduction

Polymer electrolyte membranes (PEMs) constitute an important class of polymeric materials for use as ion-exchangers, electrolytes for batteries and sensors, and dopants for electronic conductors. Recently, studies on PEM materials have been strongly promoted as a result of a considerable interest in the development of high-performance polymer electrolyte membrane fuel cells (PEMFCs) for transportation, stationary and portable power applications [1,2]. In order for a fuel cell to work effectively and to be widely adapted, the PEM must present a portfolio of properties including an acceptable cost, a high proton conductivity, good chemical and thermal stabilities, a decent mechanical strength, and a low fuel crossover [3].

Nafion (from Dupont) is a perfluorosulfonated membrane material with a hydrophobic fluorocarbon backbone and hydrophilic sulfonic pendent side-chains, and is capable of satisfying a large number of the requirements concerning polymer electrolyte membranes. Nafion has found practical use in PEMFCs [4]. However, various limitations exist for Nafion membranes, and these include a very elevated cost, a high fuel permeability, and the loss of the preferable properties at temperatures >80 °C [5–9].

In view of this, numerous efforts have been focused on developing more economical alternatives based on non-fluorinated or partially fluorinated polymers. Up to now, a large number of sulfonated aromatic polymers such as poly(ether ether ketone) [10–14], poly(ether sulfone)s [15–18], poly(arylene ether)s [19,20], polyimides [21–26] and poly(p-phenylene)s [27,28,20] have been developed. Generally, such polymer membrane materials for PEM fuel cells rely on the presence of absorbed water and its interaction with acid groups to produce proton conductivity. To ensure high proton conductivity, polymers presenting significant ion-exchange capacities (IECs) have been utilized, but these materials were found to swell excessively in water (thereby losing their mechanical properties) and were moreover brittle when dry.

Previous papers [29] have reported on poly[bis(benzimidazobenzisoquinolinones)] ionomers, a class of ladder polymers, that are hydrolytically and dimensionally stable. This enhanced stability toward water has been attributed to the acid–base interactions between the pyridinone ring and sulfonic acid groups. However, the proton conductivity and oxidative stability for practical applications requires further improvement. The present study thus attempts to investigate the possibility of obtaining, through blending, a membrane demonstrating high proton conductivity as well as high oxidative stability.

Polymer blending has been known to be the most frequently used means of overcoming the shortcomings of an individual polymer and of obtaining inexpensive materials with desirable

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properties by combining the advantages of two or more individual polymer components. A key factor in acquiring polymer electrolyte membranes via blending relies on finding an optimum combination of thermal, chemical and mechanical properties with hydrophilicity in the employed polymers. Among various counter-polymers, poly(vinylidene fluoride) (PVDF), a semi-crystalline and chemically resistant material, is well suited for the fuel cell environment [30]. Blends of PVDF with Nafion [31,32] and sulfonated poly(ether ether ketone) [33,34] have been prepared for potential use in a direct methanol fuel cell. PVDF also demonstrates sufficient dimensional stability and mechanical strength. Thus, a successful combination of the conducting characteristics of SPBIBI and the physical stability of PVDF should be able to be achieved provided that it is possible to obtain a miscible blend of the two materials.

The present article reports on a blend of SPBIBI with PVDF for use as a proton exchange membrane for fuel cells. The effect of the PVDF content on water uptake, swelling ratio, oxidation stability, proton conductivity and methanol permeability of the prepared SPBIBI/PVDF membranes were investigated to evaluate their potential applications in direct methanol fuel cells (DMFCs).

2. Experimental

2.1. Materials

PVDF was purchased from Aldrich having a weight average molecular weight (Mw) of 530,000. Dimethylsulfoxide (DMSO) was dried over CaH_2, then distilled under reduced pressure, and stored over 4 Å molecular sieves under nitrogen in the dark. 4,4′-Binaphthyl-1,1′,8,8′-tetracarboxylic dianhydride disulfonic acid (SBTDA) was prepared according to a previously reported method [35]. All other reagents were obtained from commercial sources and used as received.

2.2. Synthesis of SPBIBI

The sulfonated poly[bis(benzimidazobenzisoquinolinone)] (SPBIBI) was synthesized in the laboratory using the method described below. To a 100-mL completely dried, three-necked flask were successively charged 0.5545 g (1 mmol) of SBTDA, 10 mL of m-cresol, 0.68 mL (about 2 mmol) of Et_3N, and 0.2143 g (1 mmol) of 3,3′-diaminobenzidine (DAB) successively under a flow of nitrogen. After obtaining a homogeneous solution, 0.2442 g (2 mmol) benzoic acid was added. The mixture was stirred at room temperature for a few minutes and then heated to 80 °C. It was maintained at this temperature for 4 h, heated to 180 °C and kept there for 20 h. After cooling to 80 °C, an additional 6 mL of m-cresol was added so as to dilute the highly viscous solution, after which the solution was poured into 200 mL of acetone. The result polymer has an inherent viscosity value of 1.67 dL g^{-1} in DMAc at 30 °C. The polymer was treated with 1.0N sulfonic acid at room temperature for 24 h for proton exchange and dried in a vacuum oven for 12 h at 150 °C before blending.

2.3. Blend membranes preparation

Blends were prepared by dissolving the two polymers (5%, w/v) in DMSO at the required ratio for 12 h. The homogeneous blend solutions were filtered through a 0.5 μm PTFE membrane and then poured into a glass Petri dish at 80 °C to cast the blend films. Transparent homogeneous thin films (30–50 μm) were boiled in water thoroughly and dried in a vacuum oven at 100 °C for 48 h to remove the solvent completely. The proton exchanged membranes were thoroughly washed with deionized water and then dried in vacuum at 100 °C for 10 h.

2.4. Polymer characterization

2.4.1. Measurements

FTIR spectra were obtained with a Bio-Rad digilab Division FTS-80 FTIR spectrometer. Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC-7 system at a heating rate of 20 °C min^{-1} under nitrogen atmosphere. The X-ray diffraction data were collected on a Rigaku D/max-2500 X-ray diffractometer with a Cu Kα ($\lambda = 0.154$ nm) source operating at 40 kV and 200 mA at 293 K. The XRD patterns were obtained at a scanning rate of 5° min^{-1}. Tensile measurements were carried out with an Instron-1211 mechanical testing instrument at a speed of 1 mm min^{-1}.

2.4.2. Water uptake and dimensional change

The membranes (30–40 mg per sheet) were dried at 100 °C under vacuum for 10 h until constant weight to obtain the dry material. They were then immersed into deionized water at room temperature for 4 h. After this time, the membranes were taken out, wiped with tissue paper, and quickly weighed on a microbalance. The water uptake of the membranes was calculated according to:

$$\text{water uptake}\,(\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \qquad (1)$$

where W_{dry} and W_{wet} are the weight of the dry and the corresponding water-swollen membranes, respectively.

Water swelling ratio of the membranes were investigated by immersing the round shape samples into water at room temperature for a given time, the changes of through-plane and in-plane direction were calculated as following:

$$\Delta T_c = \frac{T - T_s}{T_s}, \qquad \Delta L_c = \frac{L - L_s}{L_s} \qquad (2)$$

where T_s and L_s are the through-plane and in-plane direction of the membrane at dry state, respectively; T and L refer to those of the membrane immersed in liquid water for 5 h.

2.4.3. Proton conductivity

The proton conductivity (σ, S cm^{-1}) of each membrane (size: 1 cm × 4 cm) was obtained using $\sigma = d/L_sW_sR$ (d: distance between reference electrodes, and L_s and W_s are the thickness and width of the membrane, respectively). Here, ohmic resistance (R) was measured by four-point probe alternating current (ac) impedance spectroscopy using an electrode system connected with an impedance/gain-phase analyzer (Solatron 1260) and an electrochemical interface (Solatron 1287, Farnborough Hampshire, ONR, UK). The membranes were sandwiched between two pairs of gold-plate electrodes. The membranes and the electrodes were set in a Teflon cell and the distance between the reference electrodes was 1 cm. The cell was placed in a thermo-controlled chamber in liquid water for measurement. Conductivity measurements under fully hydrated conditions were carried out with the cell immersed in liquid water. All samples were equilibrated in water for at least 24 h before the conductivity measurements. At a given temperature, the samples were equilibrated for at least 30 min before any measurements. Repeated measurements were then taken at that given temperature with 10-min interval until no more change in conductivity was observed.

2.4.4. Methanol permeability and oxidative stability

The methanol permeability was determined by using a cell basically consisting of two half-cells separated by the membrane, which was fixed between two rubber rings. Methanol (2 mol L^{-1}) was placed on one side of the diffusion cell, and water was placed on the other side. Magnetic stirrers were used on each compartment to ensure uniformity. The concentration of the methanol was measured by using a Shimadzu GC-1020A series gas chromatograph.