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Preparation and characterization of composite membranes using blends of SPEEK/PBI with boron phosphate

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Abstract

In this contribution composite membranes have been prepared from acid–base polymer blend and solid inorganic proton conductive boron phosphate (BPO_4). The blends are composed of sulfonated polyether-ether ketone (SPEEK) as the acidic component and polybenzimidazole (PBI) as the basic component. The contents of solid BPO_4 in the composite membrane varied from 10 to 40 wt%. The conductivity of the composite membranes was measured by impedance spectroscopy at room temperature. The conductivity of the composite membranes was found to increase with the incorporation of boron phosphate particles into blend membranes. The highest conductivity of 6 mS/cm was found for composite membrane at room temperature. The membranes were characterized by X-ray diffraction (XRD), differential scanning calorimetry (DSC), and FTIR which showed acid–base interaction in the blend membranes and also confirmed the presence of solid BPO_4 into the composite membranes. These membranes show good perspective in the membrane fuel cell applications.

Keywords: Acid–base blends; SPEEK; Composite membranes; Conductivity; Boron phosphate

1. Introduction

The solid polymer electrolyte membranes (PEM) have received considerable attention over the last few years, due to their use in fuel cells as a portable power source and as a replacement for batteries. It has resulted in the development of various types of membranes with diverse mechanical and electrical properties. So far perfluorosulfonate ionomer membranes such as Nafion 115 (Du Pont), Flemion (Asahi Glass Co.), Acipex (Asahi Chemical.), and Dow (Dow Chemical) have been used as polymer electrolyte membranes in these fuel cells [1]. These perfluorosulfonic acid membranes are not suitable due to their high price, the decreasing conductivity at temperatures higher than 100 °C, and methanol crossover especially in DMFC applications [2,3]. Optimized proton and water transport properties of the membrane 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 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. So, modification of the electrolyte membranes to operate at higher temperatures seems to be an alternative. As a result a number of studies have been reported in the literature to improve the properties of Nafion type ionomer membranes, or develop new ones [4–19]. For this purpose different approaches have been followed in the literature, such as: (1) modifying perfluorinated ionomer membranes or prepare acid–base blends to improve their water retention properties [4–7] at temperature above 100 °C; (2) modifying ionomer membranes to improve conductivity [8–11]; and (3) preparing new electrolyte composite membranes based on proton conducting materials [12–20].

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The composite membrane approach (3) represents one of the ways to improve the properties of the polymer electrolyte membranes as the desired properties of the two components can be combined in one composite. This approach was employed in the previous studies [15,17–19] where in order to improve the proton conductivity of the PEEK, several heteropolyacids and solid boron phosphate (BPO_4) were used as the second phase. However, some of these membranes showed excessive swelling, which makes the membranes brittle upon drying. It has been shown in [21–24] that swelling can be reduced by blending with polymers which are capable of formation of hydrogen bonds. The formation of hydrogen bonds leads to compatibilization of the blend polymer. Recently, it has been reported [24–26] that acid–base blend membranes containing acidic and basic polymers showed reduced methanol permeability and are thermally and chemically stable. Kerres et al. [24] also reported development of blend membranes of SPEEK with polybenzimidazole celazole (PBI), which showed reduction in swelling and methanol permeation, in addition to their high thermal stability and moderate conductivity at higher temperature. In the present work, SPEEK is selected as the acidic polymer and PBI as the basic polymer to make the blend. The acidic polymers are combined with the basic polymers in different acid/base ratios in order to get acid–base blend membranes with improve properties. These blend show moderate swelling with high thermal stabilities. This blend is then used as the polymer matrix to prepare composite membranes containing boron phosphate as the conductive filler. In the acid–base blend 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 [22]. However, their conductivities are lowered due to the reduction in the water uptake (or swelling) as compared to the conductivity of the acidic SPEEK polymers. Their conductivity can be enhanced by the incorporation of an inorganic proton conducting solids.

The present work is an attempt to improve the performance of the SPEEK/PBI blend membranes by introducing the inorganic proton conducting material, BPO_4. Boron phosphate is a solid proton conducting material developed in a previous study [16]. It has been shown previously that BPO_4 under certain conditions reveals the properties of a proton conductor and have a proton conductivity of 6×10^{-2} S/cm at room temperature under full humidification. Another interesting feature of BPO_4 is that it can retain water at high temperature. The composite membranes were prepared from SPEEK/PBI blend suspension and boron phosphate, and their conductivity was monitored by impedance spectroscopy as a function of PBI content for the blend and BPO_4 loading for composite membranes respectively. The contents of solid BPO_4 in the composite membrane varied from 10 to 40 wt%. The membranes were characterized by X-ray diffraction (XRD), differential scanning calorimetry (DSC), and FTIR techniques. The water uptake of these membranes was also investigated.

2. Experimental

2.1. Membrane preparation and characterization

Sulfonated polyether-ether ketone (SPEEK) of ion exchange capacity (IEC) of 1.6 meq/g and polybenzimidazole (AB type) of intrinsic viscosity 1.3 dl/g were procured from FumaTech, Germany. Boron phosphate was synthesized from orthophosphoric and boric acids according the procedure described in [16]. First the membranes were prepared from the blends of SPEEK with PBI and then this blend was used as the polymer matrix for the preparation of composite membranes by incorporation of solid powdered boron phosphate. The blend membranes were prepared by first dissolving the SPEEK and PBI separately in appropriate amounts in dimethylsulfoxide (DMSO), then the two solutions were mixed together and stirred for long periods. The membranes were then cast on the glass plate after evaporation of the solvent. The membranes were first dried at room temperature overnight then at 120 °C for 6–8 h. The composite membranes were prepared from the blend of SPEEK/PBI with powdered solid BPO_4 of particle size less than 0.5 μm in the same way as for the blend membranes. The membrane samples were removed by putting them in water.

Differential scanning calorimetry for the membranes was carried out using METTLER TOLEDO Instruments DSC 2910 equipped with STARe software in N_2 environment. Membrane samples of 6–10 mg were sliced and then compressed into aluminum pans for testing. Samples were heated first from room temperature to 110 °C at a heating rate of 10 °C/min and kept at this temperature for 5 min, then heated at the above mentioned heating rate to 640 °C. Thermal transitions were obtained from the heating cycle. Temperature calibration was performed using indium (T_m = 156.60 °C, ΔH_f = 28.5 J/g). The X-ray diffraction analysis was carried out using Philips Advanced D-8 diffractometer model. Cu Kα irradiation source operated at 35 kV, 25 mA with a step size of 0.1° and a count time of 1.1 s per point is used. FTIR spectra were measured in transmittance mode on a Perkin-Elmer FC-16 FTIR spectrometer. The spectrum for each membrane sample was taken with the above-mentioned spectrometer in the range 400–3500 cm^{-1}.

The water uptake of SPEEK membranes was determined from the difference in weight (W) between the dry and the swollen membranes. The membrane, cast from polymer solution after drying, was weighed and then soaked in water until the weight remained constant. It was then taken out, wiped with blotting paper (soaking paper) and weighed again. The percentage of water absorbed was calculated with reference to the weight of the dry specimen from the following equation:

$$\text{Water uptake}(\%) = \left[\frac{(W_{\text{wet}} - W_{\text{dry}})}{W_{\text{dry}}}\right] \times 100$$