PBI/Nafion/SiO2 hybrid membrane for high-temperature low-humidity fuel cell applications

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ABSTRACT

A novel composite membrane for fuel cell applications was prepared by incorporating SiO_2 in PBI/Nafion resin by the sol–gel method. Polybenzimidazole (PBI) was blended with Nafion to improve the membrane stability. The presence of PBI also improves the dimensional stability of the composite membrane over a wide range of hydration conditions. Being highly hygroscopic, SiO_2 enhances water absorption and retention in the membrane which improves fuel cell performance under low relative humidity conditions. Scanning electron microscopy showed that the PBI and Nafion polymers can be blended uniformly. Energy dispersive X-ray spectroscopy confirmed the presence of SiO_2 in the composite membrane. Thermal gravimetric analysis confirmed the improved thermal stability of the SiO_2/PBI/Nafion membrane. Tensile strength, water uptake and swelling of the composite membrane were also measured at 60 °C and compared with Nafion. The fuel cell performance of the novel SiO_2/PBI/Nafion composite membrane at 120 °C and 35% relative humidity significantly improved over a pure Nafion membrane of the same thickness.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have been considered one of the most promising clean energy technologies and suitable primary power sources for transportation and stationary applications [1]. Conventional PEMFCs employ perfluorosulfonic acid membranes (such as DuPont's Nafion series) which cannot operate at temperatures higher than 100 °C due to their hydration requirements. Above 100 °C, these membranes dehydrate and their proton conductivity decays sharply [2,3]. As a result, both water and heat management are significant challenges for such membranes. Recently, increased attention has been paid to high temperature PEMFCs (>100 °C) due to their faster electrode kinetics, greater tolerance to impurities in the fuel stream, and easier water and heat management [4]. Therefore, many different approaches have been attempted in the literature to develop novel PEM membranes for high temperature operation.

Phosphoric acid-doped polybenzimidazole (H_3PO_4/PBI) membranes have been investigated intensively and successfully utilized in high temperature PEMFCs (200 °C) because of their excellent thermochemical stability, low gas permeability, good mechanical properties of PBI, and good proton conductivity after doping with H_3PO_4 [5–8]. Most of the research to date has focused on fuel cell demonstration [9–11], catalyst activity [12–14], and physicochemical characterization of H_3PO_4/PBI membrane such as proton conductivity, proton transfer mechanisms, and permeability [15–21].

In the present work, a composite Nafion–PBI membrane was prepared by casting from a blend of Nafion–Na and PBI in *N,N*-dimethylformamide (DMF) solution, according to the acid/basic polymer complexes concept developed by Kerres et al. [22]. The electrical and mechanical properties of the composite membrane were studied by linear sweep voltammetry (LSV), electro impedance spectroscopy (EIS), and tensile strength tests.

Ensuring adequate membrane hydration, especially at higher operating temperatures, is a critical requirement that requires careful water management in PEMFCs. One approach to mitigating this problem is to develop self-humidifying proton exchange membranes. In previous work, many attempts have been made to modify the basic Nafion membrane by developing composite membranes to achieve suitable operation at elevated temperatures. One of these approaches is to add hydrophilic materials to the membrane. Such hydrophilic materials include heteropolyacids (i.e. zirconium phosphate, zirconium sulphophenyl phosphate, etc.) and oxides (i.e. zirconium dioxide, titanium dioxide, and silicon dioxide) [23–27]. These compounds exhibit a high water-retention capability which allows the membrane to retain proton conductivity at elevated temperatures. Experimental data have shown that the addition of inorganic hydrophilic materials can substantially extend the working temperature range of PEMs.

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Recently, composite silica/Nafion membranes were reported to be prepared using a tetraethyl orthosilicate (TEOS) hydrolysis sol–gel reaction followed by the solution casting method [28].

In this paper, we report a novel composite membrane based on Nafion, PBI and hydrophilic SiO_2. The composite membrane exhibited dimensional stability over a wide range of hydration conditions equivalent to pure Nafion. The presence of SiO_2 improved the water uptake of the membrane, which improved the fuel cell performance at low humidity conditions.

2. Experiment

2.1. Membrane preparation

The Nafion–PBI composite membrane was prepared by the following process. First, sodium was introduced into the Nafion resin by adding an appropriate amount of NaOH into Nafion solution (5 wt.%, DuPont, with nominal equivalent weight, EW, of 1100), stirring overnight to neutralize, filtering out the unused NaOH particles, and then heating at 80 °C to evaporate the solvent. An appropriate amount of PBI (PBI Performance, INC) solution (5 wt.%) in DMAC with LiCl was mixed with the Nafion–Na/DMAC solution (10 wt.%) by stirring vigorously for 12 h. Tetraethyl orthosilicate (TEOS) (99+%, Aldrich) was introduced into a beaker with methanol (99.9%, Aldrich) under constant stirring to make a TEOS/methanol solution. Deionized water was added to the TEOS/methanol solution with an H_2O:TEOS molar ratio of 4:1. Next, the Nafion–Na/PBI/DMAC solution was introduced into the beaker containing the TEOS/methanol solution. To promote acid hydrolysis of TEOS, 3–4 drops of acetic acid (99%, Baker) were added. The solutions were further stirred for 24 h at room temperature. The amount of PBI was controlled to achieve 8 wt.%, and the amount of TEOS was calculated to achieve 5 wt.% SiO_2 loading in the final composite membrane.

The composite membranes were prepared by casting the solutions on a glass tray with stainless steel frame with the desired dimensions. The glass tray was placed on a hot-plate at 60 °C for 12 h, and then the temperature was increased to 120 °C for another 12 h. The membranes were then washed using deionized water and 0.5 M H_3SO_4. The thickness of the composite membrane was around 50 μm. The composite membranes were transparent in appearance and slightly more rigid than the pure Nafion membrane. The performance was expected to increase with higher loadings of SiO_2 and PBI. However, membranes with SiO_2 loadings higher than 5 wt.% or PBI loadings higher than 8 wt.% were brittle and could not be used to fabricate membrane electrode assemblies (MEAs).

2.2. Thermogravimetric analysis

A Q500 TGA thermo-gravimetric analysis (TGA) instrument (TA Instruments) was used to study the thermal stability of the prepared membrane samples. The samples (~10 mg) were heated in nitrogen from 25 to 700 °C with a scanning rate of 20 °C/min.

2.3. SEM analysis

The microstructure of the composite membrane was studied using a JSM-7400F high resolution scanning electron microscope (SEM) with an accelerating voltage of 3 kV.

2.4. Tensile strength

Samples of the membrane were dried in a vacuum oven at 80 °C for 12 h. The tensile strength of the recast Nafion and SiO_2/PBI/Nafion membranes was measured in accordance with ASTM Standards [29]. Thirteen mm cardboard end tabs were

bonded to the ends of 51 mm × 6.4 mm membrane samples and thickness measurements were taken at three locations along the gage length of the specimen. The specimens were tested to failure in an Instron Model 5848 Micro Tester at a strain rate of 20 mm/mm-min. The tensile strength was calculated from the maximum load and the average thickness of each specimen. Five replicates of each sample were tested, and the average value was calculated accordingly.

2.5. Water uptake and swelling

Water uptake and swelling were measured using the following procedure. Nafion NR-212 and SiO_2/PBI/Nafion membrane samples were weighed after immersion in deionized water at 60 °C for 8 h. The samples were then dried in a vacuum oven at 80 °C for 12 h and weighed again. Water content (ΔW) was calculated as

$$\Delta W(\text{wt.\%}) = \frac{W_1 - W_2}{W_2} \times 100 \tag{1}$$

where W_1 and W_2 are the wet and dry masses of the sample, respectively.

Membrane specimens with a size 40 mm × 50 mm were dried in the vacuum oven at 80 °C for 12 h and the distance between two specified positions was measured. The measurement was repeated after the samples were soaked in deionized water at 60 °C for 8 h. The dimensional change (ΔL) was calculated as

$$\Delta L \ (\%) = \frac{L_1 - L_2}{L_2} \times 100 \tag{2}$$

where L_1 and L_2 are the distances for the wet and dry samples, respectively.

2.6. Membrane electrode assembly preparation and single cell test

In order to test the performance of the fuel cell, membrane electrode assemblies were fabricated as follows. The membranes were dried and hot-pressed between catalyst-coated gas diffusion media (CCDM) with 0.4 mg/cm² Pt loading at 130 °C for 2 mins to fabricate the MEA. MEAs were prepared similarly using Nafion NR-212 and SiO_2/PBI/Nafion membranes. The performance of the MEAs was then tested in a 10 cm² fuel cell. A polarization curve was obtained for each type of membrane and the results were compared.

The I–V polarization of the fuel cell was conducted and controlled by a fuel cell test station from Arbin Instruments. The fuel cell was started by increasing its temperature to the set point of 70 °C and raising the saturation temperature of the reactant gas streams to their respective values. The H_2 and O_2 pipeline temperatures were maintained 5 °C higher than the saturators to prevent water condensation in the feed lines. The fuel and oxidant were fed in co-flow to the fuel cell. All fuel cell testing was conducted at ambient pressure. The fuel cell was conditioned for 2 h at a current density of 1 A/cm² with fully humidified H_2/O_2 at stoichiometries of 1.5/2. Data were recorded after stable performance was obtained.

After operating the fuel cell at 100% relative humidity at a current density of 1 A/cm² for 2 h, quick scan performance was recorded after stable performance was obtained. Then, the temperatures of the anode and cathode humidifiers were set to 54 °C which reduced the relative humidity in the cell to 50%. After 2 h of operation at 0.5 A/cm² and 50% relative humidity, the fuel cell was maintained at OCV for 5 min before conducting the I–V performance test for each type of membrane. The steady-state performance of the Nafion NRE-212 and SiO_2/PBI/Nafion membranes was evaluated at 0.5 A/cm² with the anode and cathode humidifier temperatures fixed at 90 °C, while progressively raising the cell