



Short communication

Semi-interpenetrating network electrolyte membranes based on sulfonated poly(arylene ether sulfone) for fuel cells at high temperature and low humidity conditions

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ABSTRACT

Semi-interpenetrating network (semi-IPN) membranes based on sulfonated poly(arylene ether sulfone) (SPAES) were developed for application in polymer electrolyte membrane fuel cells (PEMFCs) operating at high temperature (>100 °C) and low relative humidity (<50% RH) conditions. The semi-IPN membranes were prepared by a heating procedure using SPAES solutions containing vinyl phosphonic acid (VPA) and diethylene glycol dimethacrylate (DEGDMA). When the membrane was prepared using the optimized molar ratio of VPA to DEGDMA, it showed a very high proton conductivity of up to 10 mS cm⁻¹ at 120 °C and 40% RH, and high mechanical property with a tensile strength of 43.2 MPa. Membrane electrode assemblies (MEAs) prepared using this semi-IPN membrane showed a peak power density of 180 mW cm⁻² at 120 °C and 40% RH, which is better than that of the MEAs prepared using SPAES membrane (145 mW cm⁻²). The semi-IPN membranes also showed very good electrochemical stability during the durability test.

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1. Introduction

The development of polymer electrolyte membranes (PEMs) operating at high temperatures (>100 °C) and low relative humidity (<50% RH) is one of the most important issues for the practical applications in polymer electrolyte membrane fuel cells (PEMFCs) in automobile transportations [1,2]. Since the automotive radiators currently used in automobiles are designed to be operated at high temperatures (>100 °C), it is also desirable for PEM operating at the high temperatures, while lower temperatures from 60 to 80 °C have been known to be the optimum operation temperatures for the commonly used PEM based on pure Nafion® [3]. There have been studies on the fabrication of alternative PEMs based on sulfonated aromatic polymers, such as sulfonated poly(arylene ether sulfone) (SPAES), for possible applications at high temperatures due to their thermal stability and excellent mechanical properties as well as inexpensive product process [4]. However, PEMs based on SPAES can have high enough proton conductivity only at a high degree of sulfonation (DS), while SPAES with high DS do not have high enough physicochemical stability for the desirable performance of PEMFC. In this study, we demonstrate a very facile approach to the fabrication of new semi-interpenetrating network

(semi-IPN) membranes based on SPAES showing much improved proton conductivity and electrochemical performance compared with pristine SPAES membrane, without any deterioration of the mechanical stability. The semi-IPNs are composed of cross-linked polymer networks and linear polymer chains penetrated into the polymer matrix (Fig. 1A). They can show the combined chemical properties of the component polymers having the improved physical properties and high conductivities.

A series of semi-IPN membranes were prepared by a simple one step process using the mixtures of vinyl phosphonic acid (VPA), diethylene glycol dimethacrylate (DEGDMA), and SPAES (Fig. 1B). VPA containing a phosphonic acid group was used as a monomer to improve the proton conductivity of SPAES, and DEGDMA was used as a cross-linker to impart the physicochemical stability of VPA. We found that the content of DEGDMA affected the proton conductivity and mechanical strength of the semi-IPN membranes, and the membrane electrode assemblies (MEAs) prepared using the semi-IPN membranes obtained from the optimum cross-linker showed much improved fuel cell performance compared with those prepared using the SPAES membranes.

2. Experimental

2.1. Synthesis of sulfonated poly(arylene ether sulfone) (SPAES)

Sulfonated poly(arylene ether sulfone) (SPAES) was synthesized via nucleophilic aromatic substitution polymerization [5].

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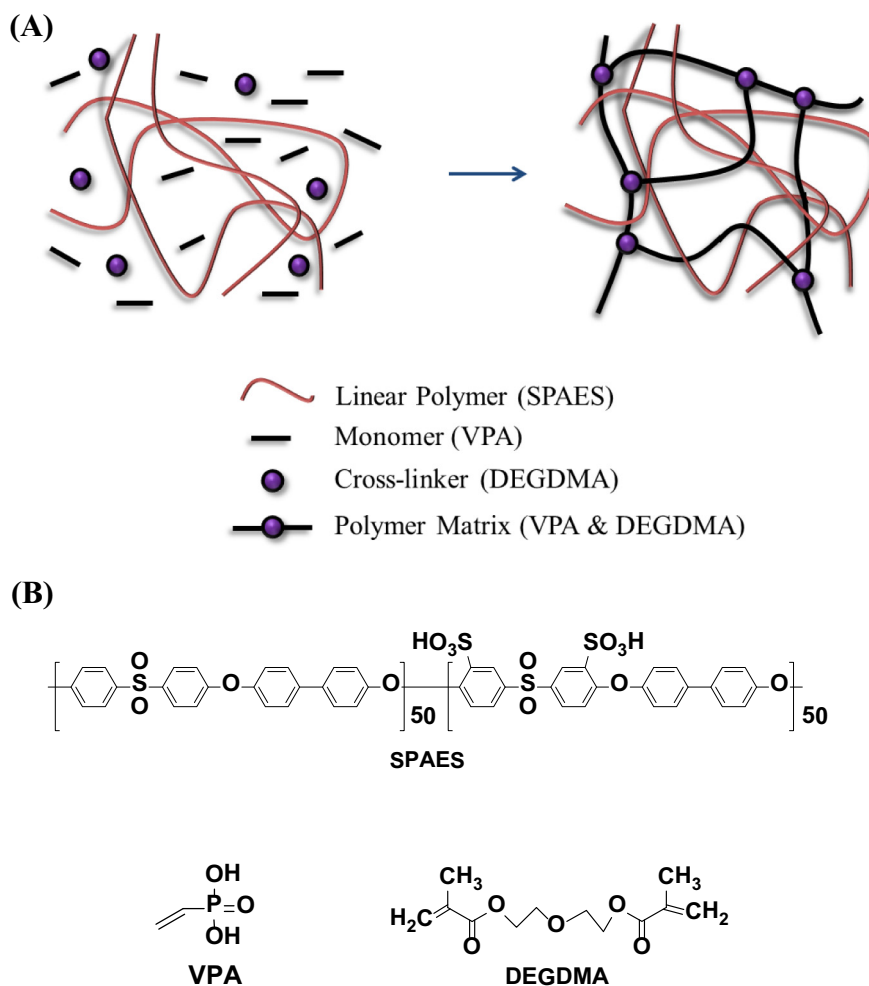


Fig. 1. Schematic illustration of (A) semi-IPN structure and (B) chemical structure of SPAES, VPA and DEGDMA.

SPAES with an ion exchange capacity (IEC) of 1.97 mequiv./g and a degree of sulfonation of 50 mol% was used (M_n : 43,100, M_w : 106,000).

2.2. Preparation of semi-interpenetrating network (semi-IPN) and pristine SPAES membranes

1.0 g of SPAES and 1.0 g of VPA in 13 g of dimethylacetamide (DMAc) were mixed with 0.22, 0.34, and 0.45 g of DEGDMA. Then, azobisisobutyronitrile (1 wt.% of the total amount of VPA and DEGDMA) was injected into the mixture, and then it was spread onto a glass plate. The thickness of the solution could be controlled by a doctor blade applicator. The casted solution was heated stepwise from 25 to 80 °C, then kept at 80 °C for 24 h in a vacuum oven. Flexible polymer films were obtained by the thermal treatment because polymerization of VPA, cross-linking reaction of DEGDMA, and solvent evaporation of DMAc occurred simultaneously. The semi-IPN membranes obtained from 0.22, 0.34, and 0.45 g of DEGDMA were noted as D10, D15, and D20, respectively, because the mole ratios of DEGDMA vs. VPA in the membranes are 10:100, 15:100, and 20:100, respectively. The measured IEC values were 2.15, 2.09, and 2.01 mequiv./g for D10, D15, and D20 samples, respectively. Pristine SPAES membranes were also prepared as a control by the same preparation method. The thicknesses of all the membranes were about 20 μm .

2.3. Characterization and PEMFC tests

Proton conductivity of the samples were measured at 120 °C under different relative humidity (RH) conditions using a conductivity measurement system (BekkTech, BT-552MX) and water uptake was measured at 80 °C under different RHs using a temperature and humidity controllable chamber (Espec, SH-241). Mechanical properties of the membranes were measured using a universal testing machine (Lloyd, LR-10K). Membrane electrode assemblies (MEAs) were fabricated by a decal method. Catalyst layers were comprised of catalyst (50 wt.% Pt/C, Tanaka Kikinokogyo) and Aquivion™ ionomer (EW750, Solvay). The Pt catalyst and ionomer loadings were 0.4 and 0.35 mg/cm², respectively. The membranes with catalyst layers (10 cm² of active area) were sandwiched and hot pressed at 120 °C and 100 kgf cm⁻² for 5 min, then gas diffusion layers (25BC, SGL) were placed on both sides of the catalyst layers. The cell performance and durability tests were executed on a fuel cell test station (Scribner Associates Inc., 850e). Single cells were operated in galvanostatic mode at 120 °C and 40% RH by feeding hydrogen and air (humidified at 93.3 °C) into the anode and cathode, respectively, at a flow rate of 100 and 200 cm³/min, without back pressures. Activation of the MEAs was performed at constant current density of 0.2 A cm⁻² for 24 h. In the durability test, open circuit voltages (OCVs) of the MEAs were monitored and recorded for 100 h at an interval of 10 min, along with the repetitive measurements of cell performance. For a measurement of H₂ leak current through the membranes, a stepwise DC voltage was applied between the electrodes,

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