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Methanol permeability and proton conductivity of a semi-interpenetrating polymer networks (IPNs) membrane composed of Nafion® and cross-linked DVB

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Abstract

The problem of methanol crossover through a Nafion® membrane is one of the challenges in the application of direct methanol fuel cells (DMFCs). In order to reduce methanol crossover, a semi-interpenetrating polymer networks (IPNs) membrane composed of Nafion® and cross-linked DVB was prepared. This new membrane was found to be effective in reducing methanol permeation compared with unmodified Nafion® membrane. Although the conductivity and H_2/O_2 fuel cell performance were still lower than those of unmodified Nafion® membrane, the present results demonstrate the potential for using semi-IPN membranes as an electrolyte for DMFC.

Keywords: Proton-conducting polymer electrolyte; Methanol crossover; Interpenetrating polymer networks; Nafion®; Direct methanol fuel cells

1. Introduction

Direct methanol fuel cell (DMFC) systems have attracted the attention of many researchers, and their merits have been widely investigated, i.e., the simple system-structure, reduced system size and weight, and high power-generation efficiency. Recent reports have demonstrated relatively high performance with solid polymer electrolytes such as Nafion® and with Pt–Ru alloys used as the anode catalyst [1,2].

Perfluorocarbon-type polymer electrolyte membranes such as Nafion® show high proton conductivity associated with ion percolation phenomena and chemical stability [3–5], but the methanol permeability is too high. When these membranes are applied to DMFC, methanol permeates the membrane (crossover) from the anode to the cathode, where it directly reacts with oxygen [6,7]. This phenomenon leads to an efficiency reduction. There is a strong need for suitable membranes with high proton conductivity and low methanol permeability [7,8]. In order to reduce the methanol crossover, a number of techniques have recently been reported. One technique involves modification of the existing commercial membranes such as Nafion® [9–16].

Nafion® combines the extremely high hydrophobicity of a perfluorinated backbone with the extremely high hydrophilicity of sulfonic acid functional groups. The sulfonic acid functional groups of Nafion® aggregate to form hydrophilic domains (ion clusters), which leads to some hydrophobic/hydrophilic phase separation [17]. The well-connected hydrophilic domain (channel) is responsible for proton transport. In order to maintain high proton conductivity to Nafion®, sufficient H_2O must be present to be incorporated in the channel. However, the methanol permeability is known to increase according to the H_2O content. There have been some reports of suppressing methanol permeability by controlling the channel structure of Nafion® [13–16]. These results suggest that by reducing the channel size or introducing huge ions or molecules, the free volume of a channel filled with H_2O can be regulated and that methanol permeability can be successfully suppressed. The permeation rate is also determined by restrictions on the polymer swellability. The polymer swellability can be reduced by crosslinking or copolymerization with other suitable polymers.

Interpenetrating polymer networks (IPNs) are polymer alloys consisting of two or more cross-linked polymers held together by permanent entangles [18]. When IPN consists

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of one polymer network and a linear polymer, it is referred to as a semi-IPN. There is no doubt that IPNs can act as a powerful tool in simultaneously carrying out a reduction in the methanol permeability and the mechanical stability of polymer electrolytes. However, there have been no reports on the use of this technique for fuel cell application.

In the present study, in order to prepare proton-conducting polymer electrolytes that would also reduce methanol crossover, semi-IPN membranes composed of Nafion® and cross-linked divinylbenzene (DVB) were synthesized. In these semi-IPNs, the linear Nafion® carries the ionic groups. The cross-linked DVB exhibits a number of desirable properties, including good mechanical strength and low affinity to methanol and water. If the chains of both polymers are entangled, the methanol permeable characteristics of the Nafion® membrane are expected to be kinetically controlled and promote both mechanical strength and stability. By regulating the mole ratio of incorporated DVB per sulfonate group of Nafion®, a semi-IPN membrane with different methanol permeability and proton conductivity can be manufactured. Since emphasis in the present study was placed on preparation and characterization of the new membrane, only the test-cell performance using pure H_2 and pure O_2 was measured, while the performance of the DMFC was not investigated.

2. Experimental

2.1. Preparation of the semi-IPN membrane

2.1.1. Materials

Five-percent Nafion® solution and a Nafion® 117 membrane were purchased from Aldrich Chem. Co. Before use, the Nafion® 117 membrane was cut into a small square suitable for each measurement and pretreated in the following conventional way. First, it was boiled in 3% H_2O_2 aqueous solution for 2 h, followed by soaking in 0.01 M H_2SO_4 aqueous solution for 12 h. Finally, the membrane was repeatedly rinsed in deionized water until the water became neutral. After this treatment, the membrane was stored in deionized water. DVB (Tokyo Kasei Kogyo Co., Ltd.) was washed twice with 1.0 M NaOH aqueous solution to remove the polymerization inhibitor.

2.1.2. Preparation of semi-IPN coating film

The semi-IPN coating films were prepared by solution casting and a solvent evaporation technique. Five-percent Nafion® solution was mixed with DVB monomer at the prescribed mole ratio. A small amount of benzoyl peroxide (BPO) as a radical initiator was added to the mixture. The solution was heated at 80 °C for 3 h under N_2 bubbling, and the prepolymerized solution with the appropriate viscosity was then obtained. Graded amounts of BPO were added to the above prepolymerized solution, followed by drop-coating on an alumina substrate (1 cm × 1 cm) with a Pt lower electrode. The film on the substrate was post-cured and dried at 70 °C for 12 h in a N_2 atmosphere. These coating films were used for the dielectric loss measurement and the proton-conductivity measurement. For the solvent uptake measurement, coating films were also prepared on an AT-cut quartz crystal oscillating element (4 MHz) with a silver electrode plated on both sides using a similar procedure.

2.1.3. Preparation of semi-IPN casting membrane

The semi-IPN casting membranes were also prepared by solution casting and a solvent evaporation technique. Five-percent Nafion® solution was mixed with DVB monomer at the prescribed mole ratio. A small amount of benzoyl peroxide (BPO) as a radical initiator was added to the mixture. The solution was heated at 80 °C for 24–48 h (depended on the mole ratio) under N_2 bubbling. It was poured in a glass Petri dish (60Ø) and post-cured at 70 °C for 12 h in N_2 atmosphere. The membrane was peeled from the Petri dish and boiled in 3% H_2O_2 aqueous solution for 2 h, followed by soaking in 0.01 M H_2SO_4 aqueous solution for 12 h. Finally, the membrane was repeatedly rinsed in deionized water until the water became neutral. After this treatment, the membrane was stored in deionized water. The composition of each membrane (mole ratio of incorporated DVB per sulfonate group of Nafion®) was determined by elemental analysis. The membranes were clear, transparent, and flexible when the composition of DVB was lower. With increases in the DVB composition, the membranes became brittle in the dry state. However, when hydrated, the membranes also became flexible.

2.1.4. Preparation of semi-IPN dipping membrane

The pre-treated small square pieces of Nafion® 117 membranes were dried over silica gel for 12 h. After each membrane was conditioned in a humid atmosphere for 3 h, they were dipped in DVB monomer containing a small amount of benzoyl peroxide (BPO) as a radical initiator with vigorous stirring. DVB monomer penetrated into the Nafion® matrix, and excess DVB monomer attached to the surface of the membrane was then removed in toluene solution under ultrasonic irradiation for 10 s. Finally, the membrane was heated at 70 °C for 6–24 h in N_2 atmosphere, and the polymerization of DVB was completed. The membrane was boiled in 3% H_2O_2 aqueous solution for 2 h, followed by soaking in 0.01 M H_2SO_4 aqueous solution for 12 h. The membrane was then repeatedly rinsed in deionized water until the water became neutral. After this treatment, the membrane was stored in deionized water. The composition of each membrane was also determined by an elemental analysis. The prepared membranes were clear and transparent, while deformation twinning was observed.

For better sample identification, all membranes prepared in the present study were listed in Table 1.

2.2. Measurement

2.2.1. Dielectric loss measurement

The effects of DVB composition on the microstructure of the semi-IPN membrane was examined based on dielectric loss measurement. For this purpose, three kinds of sandwich-type samples were prepared. One was based on the semi-IPN coating film on the alumina substrate (see Section 2.1.2), and an upper gold electrode (4 mm × 4 mm) was deposited on the membrane by a vacuum evaporation technique. Others were based on