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Semi-interpenetrating network based on cross-linked poly(vinyl alcohol) and poly(styrene sulfonic acid-*co*-maleic anhydride) as proton exchange fuel cell membranes

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Abstract

A series of promising proton conducting membranes have been synthesized by using poly(vinyl alcohol), with sulfosuccinic acid (SSA) as a cross-linking agent and poly(styrene sulfonic acid-*co*-maleic acid) (PSSA-MA) as proton source, which form a semi-interpenetrating network (semi-IPN) PVA/SSA/PSSA-MA membrane. A bridge of SSA between PVA molecules not only reinforces the network but also provides extra proton conducting paths. PSSA-MA chains trapped in the network were the major sources of protons in the membrane. FT-IR spectra confirmed the success of the cross-linking reaction and molecular interactions between PVA and PSSA-MA. Associated characteristics of a proton conducting membrane including ion-exchange capacity (IEC), proton conductivity and water uptake were investigated. The measured IECs of the membranes increased with increase of PSSA-MA content varying from 20 to 80% and correlated well with the measured uptake water and proton conductivity. The semi-IPN membranes with PSSA-MA over 60% exhibited a higher proton conductivity than Nafion-115 and also a reasonable level of water uptake. Fuel cell performance of membrane electrode assemblies (MEA) was evaluated at various temperatures with H_2/air as well as H_2/O_2 gases under ambient pressure. A power density of $0.7\,W\,cm^{-2}$ was obtained for the MEA using PVA/SSA20/PSSA-MA80 membrane using H_2/O_2 at 50 °C.

Keywords: Proton conducting membrane; Semi-interpenetrating network; Poly(vinyl alcohol); Poly(styrene sulfonic acid-co-maleic acid); Membrane electrode assembly; Fuel cells

1. Introduction

The proton exchange membrane fuel cell (PEMFC) is one of the most attractive power sources for a variety of applications by virtue of its high efficiency and environmentally friendly nature [1–3]. A PEMFC requires a membrane to separate the chemical reaction at the anode from that at the cathode both chemically and electronically. A successful fuel cell membrane must allow protons to move freely. This requirement has led to great interest in cation exchange membranes. To date, perfluorinated sulfonic acid membrane (Nafion, manufactured by DuPont) has been the most commonly used membrane in a low temperature hydrogen/oxygen fuel cell (H_2/O_2FC) because it combines required chemical, electrochemical and mechanical stabilities with high proton conductivity. However, due to a high production cost, low operating temperature and significant fuel cross-over, considerable efforts have gone into searching for alternative proton exchange membranes for both the H_2/O_2FC and the direct methanol fuel cell (DMFC) [4,5].

Among a variety of different approaches to synthesizing new electrolyte membranes, acid-base polymer blends have become a favorite approach to the design of improved PEM materials due to the interaction (ionically cross-linked) between polymers and these interactions can reduce significantly the swelling and the methanol permeability of membranes [6,7]. A series of different polymer blends, such as sulfonated poly(ether ether ketone) (SPEEK) blended with poly(ether imide) (PEI), poly(amide imide) (PAI), and poly(benzimidazole) (PBI), have been reported in the literature [8–10].

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Due to its high selectivity of water to alcohols, poly(vinyl alcohol) (PVA) membranes have been used in alcohol dehydration to break the alcohol–water azeotrope [11–14]. Taking advantage of this high selectivity, Pivovar et al. [15] explored the potentiality of PVA as proton exchange membrane in DMFC based on proton conductivity and methanol permeability experiments. The authors reported that the PVA membranes employed in a pervaporation process were much better methanol barriers than Nafion. Later, Li and Wang [16,17] prepared proton-conducting membranes based on PVA with embedded phosphotungstic acid (PWA) and found that water uptake, proton conductivity and methanol permeability were increased with PWA content. In order to improve the durability and thermal stability of a PVA/PWA membrane, SiO_2 was incorporated [18]. PVA blends with poly(styrene sulfonic acid-*co*-maleic acid) (PSSA-MA), poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS), and sulfonated phenolic resin (S-Ph) [19–22] have also been investigated. Recently, Rhim and coworkers [23,24] have prepared and characterized cross-linked PVA membranes containing sulfonic acid group for DMFC applications.

Most of the previous studies on PVA-based membranes dealt with preparation and characterizing them towards transport properties but none of them focused on fabricating membrane electrode assemblies (MEA) for fuel cell tests. To our knowledge, this paper is the first one to evaluate the potential of PVA-based membranes for H_2/O_2FC applications. This paper describes the preparation of PVA-based semi-IPN membranes and looks at the influences of the penetrating poly(styrene sulfonic acid-*co*-maleic acid) with the membrane properties such as water uptake, ion-exchange capacity (IEC), proton conductivity. Furthermore, membranes with good physicochemical properties were fabricated into membrane electrode assemblies for fuel cell testing with H_2/air as well as H_2/O_2 at various temperatures.

2. Experimental

2.1. Materials

Poly(vinyl alcohol) (Aldrich, average molecular weight: 89,000–98,000 g mol^{-1}; degree of hydrolysis: 99%; Fluka, average MW: 130,000 and 195,000 g mol^{-1}; degree of hydrolysis: 88% and 99%, respectively), sulfosuccinic acid, as a cross-linking agent (SSA, 70 wt.% solution in water, Aldrich) and poly(styrene sulfonic acid-*co*-maleic acid) (sodium salt, the ratio of styrene sulfonic acid to maleic acid is 3/1, average MW = 20,000 g mol^{-1}; Aldrich) were used to prepare proton conducting membranes. All chemicals were used without further purification. Platinized carbon (46.4% Pt on carbon—TEC1050E) from Tanaka Kikinzoku Kogyo KK, Japan was used as electrocatalyst for fabricating catalyst coated membranes.

2.2. Preparation of membrane

Preparation steps of a semi-IPN membrane are given in Fig. 1 schematically. In brief, PVA powder was dissolved in de-ionized water at 60 °C with continuous stirring. The PVA solution was mixed with a given amount of SSA of the desired concentration and the mixture was stirred continuously at 60 °C until a homogeneous solution was obtained. To facilitate interaction of PSSA-MA with PVA, PSSA-MA was first dissolved in de-ionized water (10 wt.% solution) and then was transformed from Na^+ to H^+ form via Donnan dialysis (two-compartment cell, equipped with Nafion-115 and 1 M HCl).

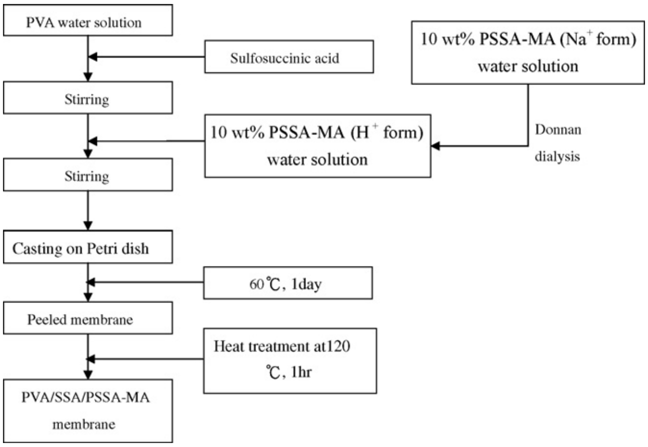

Fig. 1. Schematic illustration of preparation procedures of PVA/SSA/PSSA-MA semi-IPN membrane.

The selected amount of PSSA-MA was added to the PVA/SSA solution and was stirred at 60 °C until homogeneous solution was obtained. The membranes were cast by pouring the solutions onto Petri dishes and evaporating the water at 60 °C for 1 day. Membranes were peeled off from the dish and annealed at 120 °C for 1 h. The amount (%) of SSA and PSSA-MA were determined by the weight of PVA. After cooling down to room temperature suddenly, the resultant membranes were stored in de-ionized water. FT-IR/ATR was used to identify the success of cross-linking reactions and the associated molecular interactions in membrane structure.

2.3. Characterization of proton conductivity membrane

Infrared spectra were recorded in the transmittance mode on a Perkin-Elmer FT-IR spectrometer in the range of wave numbers 600–4000 cm^{-1}. The resolution and number of scans in all spectra were 4 and 16 cm^{-1}, respectively.

Proton conductivity measurements were carried out at ambient temperature after equilibrating the membranes in de-ionized water for 1 day. The proton conductivity cell composed of two stainless steel electrodes of 9.5 mm diameter. The membrane sample was sandwiched between the stainless steel electrodes. AC impedance spectra of the membranes were recorded from 200,000 to 100 Hz with an amplitude of 5 mV by using an Autolab PGSTST 30 instrument. The resistance value associated with the membrane proton conductivity was determined from the high frequency intercept of the impedance with the real axis. The proton conductivity was calculated according to

$$\sigma = \frac{L}{RA}$$