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Cross-linked poly(vinyl alcohol) and poly(styrene sulfonic acid-*co*-maleic anhydride)-based semi-interpenetrating network as proton-conducting membranes for direct methanol fuel cells

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Abstract

A series of semi-interpenetrating network (SIPN) membranes was synthesized by using poly(vinyl alcohol) (PVA) with sulfosuccinic acid (SSA) as a cross-linking agent and poly(styrene sulfonic acid-*co*-maleic acid) (PSSA-MA) as a proton source for direct methanol fuel cell (DMFC) application. A bridge of SSA between PVA molecules not only reinforced the network but also provided extra proton-conducting paths. PSSA-MA chains trapped in the network were the major proton conduction path of the membrane. The SIPN membranes with 80% PSSA-MA (SIPN-80) exhibited a higher proton conductivity value of 2.59×10^{-2} S cm^{-1} and very low methanol permeability (4.1×10^{-7} cm^2 s^{-1}). More specifically, the SIPN membranes exhibited very high selectivity (proton conductivity/methanol permeability). Membrane characteristics such as water uptake, proton conductivity and methanol permeability were evaluated to determine the effect of PVA molecular weights. The SIPN membranes with higher PVA molecular weight were also evaluated using methanol and oxygen gas in a single cell fuel cell at various temperatures. Power density value of over 100 mW cm^{-2} was obtained for SIPN membrane-based membrane electrode assembly at 80 °C and using commercial binary alloy anode catalysts and 2 M methanol.

Keywords: Proton-conducting membrane; Semi-interpenetrating network; Poly(vinyl alcohol); Membrane electrode assembly; Direct methanol fuel cells

1. Introduction

Direct methanol fuel cell (DMFC) is one of the most attractive power sources for widely differing applications, ranging from vehicles to portable devices, due to its inherently high efficiency and low emission [1,2]. Despite its advantages, there are several obstacles preventing commercialization of DMFC. The main issue is the non-availability of a suitable proton-conducting membrane due to the unacceptably high methanol crossover of currently used perfluorosulfonic acid membranes such as Nafion® (DuPont). This not only reduces the fuel efficiency but also causes performance loss at the cathode due to the consumption of oxygen and catalyst poisoning [3,4]. The polymer electrolyte is one of the critical components dictating the size, cost, power and efficiency of DMFCs. Early commercialization of DMFC requires new proton-conducting membranes that can significantly reduce methanol permeability with suitable proton conductivity.

In the past, several attempts have been made by researchers around the world to minimize methanol crossover by developing new membranes from non-fluorinated and partially fluorinated hydrocarbon-based polymers [5–8] or by modifying Nafion® membranes [9–13]. Among the variety of different approaches to synthesizing new electrolyte membranes, acid–base polymer blends have become a favorite approach to the design of improved proton exchange membrane (PEM) materials due to the interaction (ionically cross-linked) between polymers. These interactions can significantly reduce the swelling and the methanol permeability of membranes [14,15]. However, membranes with physically cross-linked structure can become disentangled in water and even in methanol, resulting in large swelling and mechanical disintegration [16]. Specific attempts to reduce the excessive swelling of the membranes have been made, such as using chemical cross-linking structure

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and higher molecular weight polymers to modify membranes [16–19].

Poly(vinyl alcohol) (PVA) membranes are used in pervaporation-based dehydration of alcohols because they preferentially permeate water and retain alcohol [20–23]. Taking advantage of its high selectivity, Pivovar et al. [24] explored the possibility of using PVA as the proton exchange membrane in DMFC by using proton conductivity and methanol permeability experiments. They reported that the PVA membranes employed in pervaporation process were much better methanol barriers than Nafion® membranes.

A series of PVA acid–base polymer 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) have also been investigated [25–28]. Recently, Rhim et al. [29,30] prepared and characterized cross-linked PVA membranes containing sulfonic acid group for DMFC applications. Most of the previous studies on PVA-based membranes have focused on preparation and transport properties but few of them were devoted to fabrication of membrane electrode assemblies (MEA) and evaluation of fuel cell performance [25–30]. In this paper, a series of semi-interpenetrating network (SIPN) membranes was 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 sources, and their physico-chemical and electrochemical characterizations are reported. More importantly, the SIPN membranes with high molecular weight PVA were fabricated into membrane electrode assemblies for direct methanol fuel cell testing with methanol/O_2 at various temperatures and a power density of >100 mW cm^{-2} at 80 °C was observed.

2. Experiment

2.1. Materials

Poly(vinyl alcohol) (Aldrich, average M_W = 89,000–98,000 g mol^{-1}; degree of hydrolysis, 99%; Fluka, average M_W = 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 M_W = 20,000 g mol^{-1}; Aldrich) were used to prepare proton-conducting polymers. All chemicals were used without further purification. Pt/C (46.4% Pt on carbon, TEC1050E) from Tanaka Kikinzoku Kogyo KK, Japan, was used as a cathode electrocatalyst and Pt–Ru (58.1% Pt:Ru on Vulcan XC-72; 1:1 a/o Pt:Ru, E-Tek, USA) was used as an anode electrocatalyst.

2.2. Membrane preparation

The SIPN membranes were prepared by casting PVA/SSA/PSSA-MA solutions onto Petri dishes and evaporating water at 60 °C in an oven for 1 day. The membranes were peeled off the dishes and then annealed at 120 °C for 1 h, described in detail elsewhere [31]. The thicknesses of the membranes were controlled in a range of 100–120 μm.

2.3. Characterization of proton conductivity membrane

The water uptake of the membranes was determined by measuring the change in the weight before and after the hydration. Pre-dried membranes were immersed in de-ionized water for 24 h, and then surface-attached water onto the membrane was removed with filter paper. After that, the wetted membrane weight (W_{wet}) was determined as quickly as possible. The weight of the dry membrane (W_{dry}) was determined after completely drying it in vacuum at 60 °C for 24 h. The water uptake (%) value of the membranes was calculated by using the following equation [32]:

$$\text{water uptake} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100$$

A titration method was used to determine the ion-exchange capacity (IEC). Each membrane was soaked in 1 M sodium chloride aqueous solution for 1 day to exchange protons with sodium ions. The ion-exchanged solution was then titrated with 0.005 M sodium hydroxide solution. The IEC value was calculated using the following equation [32]:

$$\text{IEC} = \frac{M_{\text{i,NaOH}} - M_{\text{f,NaOH}}}{W_{\text{dry}}} = \frac{\text{H}^+\,(\text{mmol})}{W_{\text{dry}}}$$

where $M_{\text{i,NaOH}}$ is the initial mmol of NaOH of titration and $M_{\text{f,NaOH}}$ is the mmol (m_{eq}) of NaOH after equilibrium. In addition, H^+ is the molar number of proton sites presented in the membrane and W_{dry} is the weight of dry membrane.

Proton conductivity measurements were carried out at ambient temperature after equilibrating the membrane in de-ionized water for 1 day. The proton conductivity cell was composed of two 9.5 mm diameter stainless steel electrodes. The membrane sample was sandwiched between the stainless steel electrodes. The ac impedance spectra of the membranes were recorded from 200,000 to 100 Hz with amplitude of 5 mV by using an Autolab PGSTAT30 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

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

where σ, L, R and A denote, respectively, the proton conductivity of the membrane, thickness of the membrane (which was measured with a micrometer in each case), the measured resistance of the membrane, and the cross-sectional area of the membrane perpendicular to current flow. The temperature dependence of proton conductivity was determined by using the same piece of membrane and controlling the temperature in a range starting from 20 to 50 °C. The conductivity at each temperature was measured several times until the reading remained unchanged.

Methanol permeability of membranes was determined by using a home-made side-by-side glass diffusion cell. Prior to all experiments, the membrane was equilibrated in water for