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Long-term durability of radiation-grafted PFA-g-PSSA membranes for direct methanol fuel cells

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ABSTRACT

Poly(tetrafluoroethylene-*co*-perfluoropropyl vinyl ether)-graft-poly(styrene sulfonic acid) (PFA-*g*-PSSA) membranes were prepared by γ-ray radiation-induced grafting of styrene onto 50 μm PFA films and a subsequent sulfonation. The properties of the PFA-*g*-PSSA membranes such as ion exchange capacity, water uptake, proton conductivity, and methanol permeability were evaluated and compared with commercial Nafion 115 membrane. The characteristic properties and direct methanol fuel cell (DMFC) performances with PFA-*g*-PSSA membrane were better than that with the Nafion 115 membrane. The power density of the single cell with PFA-PSSA30, PFA-PSSA50, PFA-PSSA80 membranes having different degree of grafting (DOG), and Nafion 115 membranes was 113, 123, 118, and 111 mW cm^{-2} at 0.4 V, respectively. To study the long-term durability of the prepared membrane electrode assembly (MEA) with a PFA-PSSA50 membrane, the single cell was tested for 2066 h in a galvanostatic mode under a constant load 150 mA cm^{-2} and at a temperature of 60 °C. The performance loss of the MEA after 2066 h operation was about 26.8%. Before and after the long-term performance test, the degradation of MEA with PFA-*g*-PSSA membrane was investigated by polarization curve technique, electrochemical impedance spectroscopy, TEM, X-ray diffraction, and ion exchange capacity.

1. Introduction

Direct methanol fuel cells (DMFCs) using polymer electrolyte membranes have attracted attention for application in portable power sources, material handling vehicles and small transport applications because of their advantages, such as high energy density, low operating temperature, simple system design, and no requirement for fuel processing equipment [1,2]. However, the crucial issues that should be solved for practical applications of DMFCs are their cost and durability. The proton exchange membrane (PEM) is one of the very important components, because PEM is closely related to the performance and durability of the whole DMFC. The PEM has to fulfill several demanding requirements simultaneously including high proton conductivity, low methanol permeability, and long-term durability [3,4]. Perfluorosulfonic acid polymers such as Nafion® are typically used as the electrolyte because of their excellent chemical and mechanical stability and high proton conductivity. However, these polymers have disadvantages in DMFC applications such as high methanol crossover [5]. The crossover of methanol from the anode to cathode reduces the performance of a DMFC and affects the fuel efficiency. Hence, a number of research efforts have been made to develop new alternative PEMs for improving the performance and durability of DMFC.

Sulfonic acid membranes prepared by radiation-induced grafting offers an attractive way to prepare PEM. The advantage of the radiation-induced grafting membrane is the simple method for modifying the base film and imparting new properties without altering their intrinsic properties [6]. Fluorinated polymer films such as poly(tetrafluoroethylene) (PTFE) [7], poly(tetrafluoroethylene-*co*-hexafluropropylene) (FEP) [8], and poly(tetrafluoroethylene-*co*-perfluoropropyl vinyl ether) (PFA) [9,10] or partially fluorinated polymer films such as poly(ethylene-*alt*-tetrafluoroethylene) (ETFE) [11] and poly(vinylidene fluoride) (PVDF) [12] have been used as suitable base polymer films for the radiolytic preparation of PEM owing to their outstanding properties, including chemical, thermal, and mechanical stability. It has been demonstrated that various graft polymers can be grafted onto base polymer films during the radiation-graft polymerization process. Most of those radiation-induced grafted membranes were

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tested for improving the performance and lifetime of a polymer electrolyte membrane fuel cell (PEMFC) [7–12]. Only a few radiation-induced grafted membranes with PVDF, ETFE and FEP as base polymers have been tested for performance in DMFC [13–15].

Among the fluorinated polymer films, PFA film has been less frequently used as a base polymer for radiation-induced grafted membranes. Nasef et al. [8,12] reported the preparation process of sulfonic acid membranes (PFA-*g*-PSSA) by the radiation-induced grafting of styrene into PFA film using simultaneous irradiation followed by a sulfonation. The fuel cell performance of PFA-*g*-PSSA membranes (16% degree of grafting (DOG)) was tested in a PEMFC under H_2/O_2 at 50 °C. However, the performance of this fuel cell was found to be limited to a few hundred hours and was very low (30 mA cm^{-2} at 0.6 V) after the first 50 h of operation [16]. However, the performance evaluation and long-term durability of PFA-*g*-PSSA membrane in DMFC has not yet been reported in the literature.

In this paper, we have prepared poly(tetrafluoroethylene-*co*-perfluoropropyl vinyl ether)-graft-poly(styrene sulfonic acid) (PFA-*g*-PSSA) membranes with different DOG, using PFA as the base film, by a simultaneous radiation grafting of styrene and a subsequent sulfonation. The PFA-*g*-PSSA membranes were characterized according to their ion exchange capacity, water uptake, proton conductivity, and methanol permeability, and the DMFC performance of the membrane electrode assemblies (MEAs) using the prepared PFA-*g*-PSSA membranes were evaluated and compared against Nafion 115 membrane. To investigate the long-term durability of the prepared MEA with PFA-*g*-PSSA membrane for DMFC, a single cell was tested for 2066 h under a constant load of 150 mA cm^{-2} at 60 °C in a galvanostatic mode. Polarization curve technique, electrochemical impedance spectroscopy (EIS), transmission electron microscope (TEM), X-ray diffraction (XRD), and ion exchange capacity (IEC) have been utilized to analyze the degradation of the MEA with PFA-*g*-PSSA membranes.

2. Experimental

2.1. Preparation of the radiation-grafted membrane

Radiation-grafted membranes were prepared by the simultaneous radiation-induced graft polymerization of styrene onto PFA films (Universal Co. Ltd., Japan) [17,18]. The PFA film (7 × 100 cm) with a thickness of 50 μm was washed in acetone and dried in a vacuum oven at 60 °C for 24 h. The pre-treated PFA films were immersed in a styrene/dichloromethane (60:40) mixture solution in a glass ampoule. Styrene (99% purity), dichloromethane, 1,2-dichloroethane, and acetone were supplied by the Showa Company (Japan). The mixtures containing PFA films were purged with nitrogen for 10 min and then irradiated by γ-rays from a ^{60}Co source at a dose rate of 2 kGy/h at room temperature. The grafting reaction was performed for varying reaction time as previously reported [17]. The irradiated films were washed with dichloromethane for 24 h and then dried in a vacuum oven for 12 h at 60 °C. The DOG was calculated from the equation as follows:

$$\text{DOG}\ (\%) = ((W_g - W_o)/W_o) \times 100 \qquad (1)$$

where W_o is the weight of original film and W_g is the weight of grafted film, respectively.

The polystyrene (PS) grafted PFA films (PFA-*g*-PS) were immersed in a 2% chlorosulfonic acid in 1,2-dichloroethane mixture solution for 24 h to introduce a chlorosulfonic moiety into the aromatic ring of the polystyrene grafts. Chlorosulfonic acid (99% purity) was purchased from the Kanto Chemical Company (Japan). The films were then washed several times with dichloroethane and deionized water. The washed films were hydrolyzed in deionized water at 70 °C for 3 h. A complete hydrolysis was confirmed by measuring the pH change of the solution after exchanging of solvent every hour. The hydrolyzed membranes were washed with distilled water and then dried at 60 °C in a vacuum oven. The synthesized membranes with different DOG are denoted as PFA–PSSA*x* (x=DOG of polystyrene, x=30, 50, 80).

2.2. Physical characterization

The ion exchange capacity (IEC) of the membranes was determined by acid–base titration. The membrane samples were immersed into 3 M NaCl at room temperature for 24 h. The solutions were then titrated with a 0.1 M NaOH. From the volume of the NaOH solution consumed in the titration, the IEC of the dry membrane per unit mass (meq/g) was calculated. Water uptake of the membranes was determined as follows: first, the membrane was immersed in distilled water at 25 °C for 24 h. And then, the membrane was taken out and weighed after wiping off the excess surface water. The water uptake was calculated as follows:

$$\text{Water uptake}\ (\%) = ((W_{wet} - W_{dry})/W_{dry}) \times 100 \qquad (2)$$

where W_{wet} and W_{dry} are the membrane weights in the wet and dry states, respectively.

Polystyrene and sulfonic acid groups in PFA-*g*-PSSA membranes was confirmed by Fourier-transform infrared (FT-IR) spectrometer (Tensor-37, Bruker, Germany) in a transmittance mode in the wave number of 4000–500 cm^{-1}. The morphologies of the catalysts were investigated by using field-emission transmission electron microscope (FE-TEM) (Tecnai G2 F30 S-TWIN, FEI Company). X-ray diffraction (XRD) analyses of the catalysts were recorded with a diffractometer (Rigaku DMAX-2500, Japan) using Cu $K\alpha$ radiation in the 2θ range of 20–80° at a scanning rate of 1° min^{-1}.

2.3. Proton conductivity and methanol permeability

The proton conductivity of the membranes was determined by four electrodes ac impedance measurements (IM6&IM6ex, Zahner, Germany) in water-immersed state at 30–60 °C. A conductivity measurement cell having four Pt wire electrodes was used to host the membranes. Membranes of 2 cm long × 1 cm wide were cut and introduced in the conductivity measurement cell. The high frequency intercept on the real axis of the Nyquist plot was used to measure the proton conductivity of the membranes.

The methanol permeability measurements were carried out using a home-made diffusion cell. The diffusion cells consisted of two compartments separated by a membrane having an effective area of 9 cm^2 (3 × 3 cm). One compartment was contacted with 5 M methanol solution and the other with distilled water. Both sides were circulated to avoid concentration gradients of the methanol. The temperature of diffusion cell was controlled at 30–60 °C. The concentration of methanol in the water-side compartment was measured for every 30 min for 2 h using a refractometer.

The methanol permeability of the membranes, P ($cm^2\ s^{-1}$), calculated using the Eq. (3) [19]:

$$P \times (t - t_0) = (C_B(t) \times V_B \times l)/((C_A(t) - C_B(t)) \times A) \qquad (3)$$

where C_A and C_B are methanol concentrations in the methanol and water compartments, V_B is the volume of the water compartment, l is the thickness of the swollen membrane, A is the area of the membrane, t is time of operation, and t_0 is time lag.