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Performance of H_2/O_2 fuel cell using membrane electrolyte of phosphotungstic acid-modified 3-glycidoxypropyl-trimethoxysilanes

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ABSTRACT

Proton-conducting membranes based on phosphotungstic acid (PWA) and 3-glycidoxypropyl-trimethoxysilane (GPTMS) was investigated as the electrolyte for low temperature H_2/O_2 fuel cell. Parameters determining the conductivity and elastic modulus of the membranes were characterized by thermogravimetry/differential thermal analysis and infrared spectroscopic measurements. The composite containing 5% of PWA exhibited an elastic modulus below 100 MPa at room temperature and a high proton conductivity of 1.0×10^{-2} S/cm at 80 °C and 100% RH. Low elastic modulus of the membrane was found to be useful for both the reduction of the membrane thickness and the better contact with the electrodes. The performance of the membrane electrode assemblies (MEA) was systematically studied as an effect of preparation conditions. A maximum power density of 45 mW/cm^2 and the current density of 175 mA/cm^2 at 0.2 V were achieved at 90 °C and 100% RH for the membrane of 5PWA·95GPTMS composition and 0.2 mm thickness.

1. Introduction

Proton-exchange membrane fuel cells convert chemical energy directly to electrical energy using electrodes and a proton-conducting electrolyte and have much attention from the energy and environmental viewpoints [1,2]. There are a number of fuel cell design parameters with various subjects, usually categorized into two types based on their operating temperature and the electrolytes employed. Our research interesting is to develop a new solid type electrolyte-based fuel cells operating at room temperature. For this purpose, membranes with high proton conductivity and high thermal and chemical stabilities are necessary as the electrolytes. A series of perfluorosulfonate ionomers such as Nafion® are used in actual cells as the electrolytes with high proton conductivity [3–6]. Despite their high conductivities around room temperature, they still have some problems for practical use because of high cost and thermal degradation. Particularly, the decreased conductivity at temperatures higher than ~80 °C limits their practical use. On the other hand, recently, inorganic materials have attracted a lot of interest due to their thermal and chemical stabilities. Many researchers have diverted their interest to the synthesis of proton-conducting inorganic materials.

We were the first to report on the preparation of porous P_2O_5–SiO_2 glasses, which displayed a conductivity of $\sim 10^{-2}$ S/cm at room temperature [7–9]. These glasses were applied to the electrolyte of hydrogen/oxygen fuel cell, exhibiting power densities of order of ~10 mW/cm^2 at room temperature. More recently, we used heteropolyacidic compounds to complex with the P_2O_5–SiO_2 glasses as the fuel cell electrolytes [10–14]. Heteropolyacid such as $H_3W_{12}PO_{40} \cdot nH_2O$ (phosphotungstic acid, PWA, $n \sim 29$) has a Keggin structure and has attracted a lot of interest due to its high protonic conductivity of 10^{-1} S/cm in the crystalline state [15]. The proton conductivities of these glass membranes increased up to $\sim 10^{-1}$ S/cm at 90 °C and 30% RH, and the power density was 23 mW/cm^2 at 30 °C [14]. These inorganic materials are more favorable than polymers as the electrolytes due to their higher thermal stability. Nevertheless, no fuel cell has been exhibited high power densities expected from these high conductivities of electrolytes. One problem is the high resistivities occurred between the electrolyte and electrodes. High elastic modulus of the inorganic compounds impedes good contact with the electrodes, resulting into the decreased performance of the cell. New type electrolytes having both the thermal and mechanical flexible properties would be applicable for practical use in the fuel cells. One is the using of organic compounds with elasticity. Among them, 3-glycidoxypropyl-trimethoxysilane ($(OCH_3)_3Si(CH_2)_3OCH_2CHOCH_2$, GPTMS) GPTNS has been used as precursor of proton conductive organic–inorganic hybrid membranes[16–19]. Three methoxy groups in GPTMS are expected

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to hydrolyze forming the Si–O–Si network structure, resulting into the preparation of structure with thermal, chemical, and mechanical stabilities. On the other hand, the organic phase of polyethylene oxide (pseudo-PEO networks) contributes to improve flexibility and processing suitability, resulting into good contact between the electrolyte and electrodes.

In this study, we also considered to use GPTMS for preparation of hybrid composites with PWA. PWA–GPTMS composite membranes were prepared using a sol–gel method and their elastic modulus, proton conductivity and thermal stability were measured as the function of composition and temperature. Fuel cell performances are discussed in relation to the elastic modulus of the membranes.

2. Experimental procedure

2.1. Preparation of PWA–GPTMS membranes

The hybrid membranes containing PWA of 0–10 mol% were prepared via the sol–gel method using PWA (99.995%, Nacalai Tesque) and GPTMS (98%, Aldrich). GPTMS was hydrolyzed with water (as 0.15N-HCl aq) and ethanol in the ratio of 3:3 for 1 mol of GPTMS under stirring for 1 h at room temperature. Subsequently, PWA was dissolved in ethanol with the mole ratio of 1:10, followed by adding drop-by-drop in the hydrolyzed GPTMS solution. After stirring for 1 h at room temperature, the solution was cast into petri dishes and dried at 70 °C for 2 days to yield a gel. The gel was further heated at 80–150 °C for 12 h to yield a bulk membrane. The sample thicknesses ranged from 0.8 to 0.2 mm.

2.2. Characterization of membranes

Flexural elastic modulus of PWA–GPTMS composites was determined from the stress–strain curves using three-point bending method. Fourier transform infrared (FT-IR) spectra of the composite membranes were obtained with JASCO FTIR-460 Plus spectrometer. The FT-IR spectra were obtained between 4000 and 400 cm^{-1} using the KBr method. The thermal degradation process and stability of the composites were investigated by thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) (Thermoplus 2, TG-8120, Rigaku). The measurements were carried out under dry air and with a heating rate of 1 °C/min. The proton conductivities of composite membranes were determined from the Cole–Cole plots by an AC method using Solartron SI-1260 impedance analyzer with frequencies ranging from 1 to 10^7 Hz. After evaporating the gold electrode with a 0.3 mm diameter onto the PWA–GPTMS membranes, the samples were kept in a constant humidity chamber. The temperature and humidity in the chamber were controlled at 80 °C and 40–100% relative humidity, respectively. The proton conductivity (σ) was calculated from the electrolyte resistance (R) obtained from the intercept of the Cole–Cole plot with the real axis, the thickness (l) and the electrode area (A) according to the equation $\sigma = l/AR$.

2.3. Preparation of membrane electrode assemblies and fuel cell tests

The electrodes were prepared with 5 wt.% Nafion® solution (Aldrich), 10 wt.% polytetrafluoroethylene (PTFE) dispersion (Aldrich), and Pt/C powder, which were ultrasonically stirred for 30 min at room temperature. 40 vol.% ethanol was added and agitated with ultrasonic vibration for 1 h to obtain a catalyst ink. The ink was smoothly painted on a wet-proof carbon paper, followed by holding the membrane. The membrane electrode assemblies (MEA) were prepared by pressing at 1 MPa. The MEA was positioned in a single-cell test station fixture and the performance of a fuel cell was evaluated by measuring the current density versus cell voltage using a Solatron SI-1287 potentiometer at 80 °C and 100% RH under atmospheric pressure. The flow rates of hydrogen for anode and oxygen for cathode were 50 mL/min. Electrochemical measurements were obtained on the operating cells with the potentiometer using an impedance analyzer (Solartron SI-1260). The frequency range was from 10^{-2} Hz to 10^6 Hz with an AC signal amplitude of 10 mV.

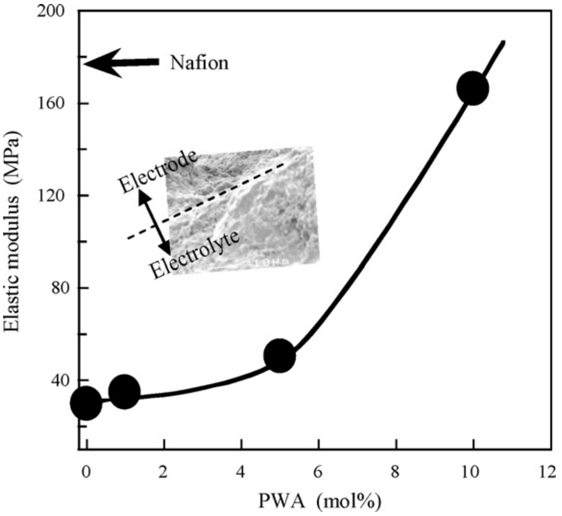

Fig. 1. Elastic modulus, measured by three bending method at room temperature, of PWA–GPTMS composites. The value of Nafion® is also given as the arrow.

3. Results and discussion

3.1. Elastic and proton-conducting properties of PWA–GPTMS composite membranes

When liquid GPTMS is reacted with water, its methoxy groups bound with silicon are hydrolyzed to form three dimensional silica network structures. The other epoxide group forms polyethylene oxides, pseudo-PEO networks, which contributes to its good flexibility and processing suitability of the hydrolyzed GPTMS. The elastic modulus of the hydrolyzed GPTMS was 30 MPa. Fig. 1 shows the elastic modulus, measured at room temperature, of the pre-

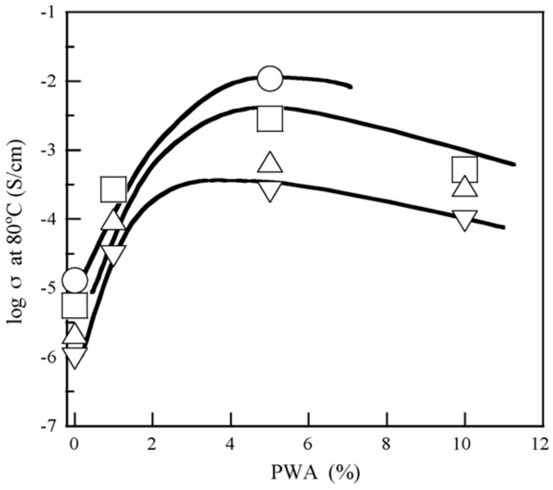

Fig. 2. Conductivity of PWA–GPTMS composites. The conductivities were measured at 80 °C under relative humidities of 40 (▽), 60 (△), 80 (□) and 100% (○).