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Quaternized poly(vinyl alcohol)/alumina composite polymer membranes for alkaline direct methanol fuel cells

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ABSTRACT

The quaternized poly(vinyl alcohol)/alumina (designated as QPVA/Al_2O_3) nanocomposite polymer membrane was prepared by a solution casting method. The characteristic properties of the QPVA/Al_2O_3 nanocomposite polymer membranes were investigated using thermal gravimetric analysis (TGA), scanning electron microscopy (SEM), dynamic mechanical analysis (DMA), micro-Raman spectroscopy, and AC impedance method. Alkaline direct methanol fuel cell (ADMFC) comprised of the QPVA/Al_2O_3 nanocomposite polymer membrane were assembled and examined. Experimental results indicate that the DMFC employing a cheap non-perfluorinated (QPVA/Al_2O_3) nanocomposite polymer membrane shows excellent electrochemical performances. The peak power densities of the DMFC with 4 M KOH + 1 M CH_3OH, 2 M CH_3OH, and 4 M CH_3OH solutions are 28.33, 32.40, and 36.15 mW cm^{-2}, respectively, at room temperature and in ambient air. The QPVA/Al_2O_3 nanocomposite polymer membranes constitute a viable candidate for applications on alkaline DMFC.

1. Introduction

Direct methanol fuel cells (DMFCs) are recently gaining much attention for their highly potential applications on the electric vehicles (EVs), stationary applications, and portable power sources, such as cellular phones, notebook computers, etc. At the present time, direct methanol fuel cell (DMFC) is being actively studied and a lot of progress is made during the past few years [1–15]. However, the development of the DMFC has been hampered due to several serious problems, which are slow methanol oxidation kinetics and incomplete electrooxidation of methanol, the poisoning of adsorbed intermediate species on the Pt surface, the high methanol crossover through the solid-state polymer Nafion membrane, and the high costs of the Nafion (Du pont) polymer membrane and Pt catalyst.

Recently, Yang et al. [1,2] synthesized the cross-linked PVA-based composite polymer membranes and applied in an alkaline DMFC. More precisely, the carbonation problem of alkaline DMFC can be greatly reduced by using an alkaline solid polymer membrane instead of an alkaline solution [3–6]. In addition, as we know, the anodic electrooxidation of methanol in an alkaline media shows much faster kinetics than that in an acidic media [7]. The works on the preparation of the anion exchange polymer membrane for alkaline DMFC have been studied intensively [8–15]. Recently, many kinds of anion exchange polymer membrane based on quaternized polymers applied for the alkaline alcohol fuel cells have been investigated [9,15].

Interestingly, Xiong et al. [16] studied a quaternized poly(vinyl alcohol) (here designated as QPVA) polymer membrane for applications in DMFC. The quaternary ammonium groups were grafted onto the backbone of the PVA host. The ionic conductivity of QPVA exchange polymer membrane was 7.34×10^{-3} S cm^{-1} in deionized water at 30 °C. Moreover, Xiong et al. [17,18] also prepared and examined two organic–inorganic hybrid anion exchange membranes based on QPVA and tetraethoxylsilanes (TEOS) [17] and QPVA/chitosan [18]. These composite polymer membranes show a high ionic conductivity of 10^{-3} to 10^{-2} S cm^{-1} and a low methanol permeability of 5.68×10^{-7} to 4.42×10^{-6} $cm^2\ s^{-1}$ at 30 °C. However, they did not show any electrochemical data for applications in an alkaline DMFC [16–18].

There are several ceramic fillers being used on the polymer electrolyte membrane, for examples, TiO_2 [1], SiO_2 [6], α-Al_2O_3 [19], bentonite [20], which are blended into the PVA polymer. Alumina (Al_2O_3) [19] was used owing to its good physical (hydrophilic) and chemical (inert) properties. Alumina is typically used in the form of nano-particles providing with high surface area and activity, and excellent chemical stability. The addition of hydrophilic Al_2O_3 fillers into the polymer matrix reduces the crystallinity of the PVA polymer, therefore increasing the amorphous phases of PVA polymer matrix, resulting in an increase of its ionic conductivity. As we know, when Al_2O_3 filler used as a stiffener material added to the PVA matrix, the mechanical properties of the QPVA/Al_2O_3

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nanocomposite polymer membrane greatly enhance. The thermal property, dimensional stability, and swelling ratio could also be improved.

In this work, we attempt to disperse these nano-sized Al_2O_3 ceramic fillers into the QPVA matrix to act as a solid plasticizer capable of enhancing the chemical and thermal properties, and dimensional stability for the QPVA/Al_2O_3 nanocomposite polymer membrane. Alkaline DMFC, comprised of the air cathode loaded with MnO_2/BP2000 carbon ink on a Ni-foam, the PtRu anode based on a Ti-screen, and using a QPVA/Al_2O_3 nanocomposite polymer membrane, was assembled and investigated. The QPVA/Al_2O_3 composite polymer membrane was prepared by a direct blend of QPVA polymer (PVA being amination by GTMAC first) and nano-sized Al_2O_3 fillers under a stirring condition. A 5 wt.% glutaraldehyde (GA) solution was finally directly added to the composite polymer membrane for the cross-linking reaction. In comparison, among three methanol concentrations (1–4 M), were tested. The electrochemical characteristics of alkaline DMFC using a QPVA/Al_2O_3 nanocomposite polymer membrane were investigated by the linear polarization and galvanostatic methods; especially for the peak power density of alkaline DMFC in ambient conditions.

2. Experimental

2.1. Preparation of the QPVA/Al_2O_3 composite polymer membrane

PVA (Aldrich), nano-sized Al_2O_3 fillers (10–30 nm, 200 $m^2\,g^{-1}$, CBT, Taiwan), glycidytrimethyl ammonium chloride (GTMAC) (Aldrich), and KOH (Merck) were used as received without further purification. Degree of polymerization and saponification of PVA were 1700 and 98–99%, respectively. The QPVA/Al_2O_3 nanocomposite polymer membrane was prepared by a solution casting method [8–10].

The appropriate quantities of the PVA polymer were dissolved in distilled water under stirring. The above resulting solution was stirred continuously until the solution mixture became homogeneous with viscous appearance at 85 °C for 3 h. The temperature of the viscous mixture was cooled to 65 °C, then a suitable amount of GTMAC, KOH (GTMAC:KOH = 1:1 in mole ratio) was added to the resulting mixture solution under a continuous stirring condition for 4 h. The resulting viscous polymer mixture was washed using anhydrous alcohol to obtain yellow precipitates. Then, these quaternized poly(vinyl alcohol) precipitates (the so-called QPVA) were dried at 65 °C in a vacuum oven.

The QPVA/Al_2O_3 mixture solution was prepared by using a suitable amount of as-prepared QPVA precipitates, 0–10 wt.%Al_2O_3 fillers, and 5 wt.% GA (a cross-linking agent), 1 vol.%HCl at 85 °C for 3 h under a continuous stirring condition. The resulting viscous blend polymer solution was poured out on a glass plate. The thickness of the wet composite polymer membrane was between 0.020 and 0.040 cm. The glass plate with viscous QPVA/Al_2O_3 composite polymer sample was weighed again and then the excess water was allowed to evaporate slowly at 60 °C at a relative humidity of 30%. After evaporation of water solvent, the glass plate with the composite polymer membrane was weighed again. The composition of QPVA/Al_2O_3 polymer membrane was determined from the mass balance. The thickness of the dried composite polymer membrane was controlled in the range of between 0.010 and 0.020 cm.

2.2. Crystal structure, morphology, and thermal analyses

TGA thermal analysis was carried out using a Mettler Toledo TGA/SDT 851 system. Measurements were carried out by heating from 25 to 600 °C, under N_2 atmosphere at a heating rate of 10 °C min^{-1} with about 10 mg samples. The surface morphology and microstructure of the QPVA/Al_2O_3 nanocomposite polymer membrane were investigated by a scanning electron microscope (SEM) (Hitachi S-2600H).

2.3. Ionic conductivity and methanol permeability measurements

Conductivity measurements were carried out on QPVA/Al_2O_3 nanocomposite polymer electrolytes via an AC impedance method. The QPVA/Al_2O_3 nanocomposite samples were immersed in a 4 M KOH solution for 24 h before measurement. Alkaline QPVA/Al_2O_3 nanocomposite polymer membranes were clamped between stainless steel (SS304), ion-blocking electrodes, each of surface area 1.32 cm^2, in a spring-loaded glass holder. A thermocouple was kept in close proximately to the composite polymer membrane for temperature measurement. Each sample was equilibrated at the experimental temperature for at least 30 min before measurement. AC impedance measurements were carried out using an Autolab PGSTAT-30 equipment (Eco Chemie B.V., Netherlands). The AC spectra in the range of 300 kHz to 10 Hz at an excitation signal of 10 mV were recorded. AC impedance spectra of the nanocomposite polymer membrane were recorded at a temperature range between 30 and 70 °C. Experimental temperatures were maintained within ±0.5 °C by a convection oven. All QPVA/Al_2O_3 nanocomposite polymer electrolytes were examined at least three times.

Methanol permeability measurements [21,22] were conducted by using a diffusion cell. The cell was divided into two compartments, in which one compartment was filled with D.I. water (called B compartment) and the other compartment filled with a 20 wt.% methanol aqueous solution (called A compartment). Prior to testing, the QPVA/Al_2O_3 nanocomposite polymer membrane was hydrated in D.I. water for at least 24 h. The composite polymer membrane with a surface area of 0.58 cm^2 was sandwiched by O-ring and clamped tightly between two compartments. A stir bar was kept active in the glass diffusion cell during the experiment. The concentration of methanol diffused from compartment A to B across the QPVA/Al_2O_3 nanocomposite polymer membrane was examined using a density meter (Mettler Toledo, DE45). An aliquot of 0.20 mL was sampled from the B compartments every 30 min. Before the permeation experiment, a calibration curve for the value of density vs. the methanol concentration was prepared. The calibration curve was used to calculate the methanol concentration in the permeation experiment. The methanol permeability was calculated from the slope of the straight-line plot of methanol concentration vs. permeation time. The methanol concentration in the B compartment as a function of time is given in Eq. (1) [21,22]:

$$C_B(t) = \frac{A}{V}\frac{DK}{L}C_A(t - t_o) \quad (1)$$

where C is the methanol concentration, A and L are the composite polymer membrane area and thickness, D and K are the methanol diffusivity and partition coefficient between the membrane and the solution. The product DK is the membrane permeability (P), t_o, a time lag, is related to the diffusivity (D): $t_o = L^2/6D$.

2.4. Micro-Raman spectroscopy analyses

Micro-Raman spectroscopy is a quick tool to characterize pure PVA and the QPVA polymer membranes. The micro-Raman spectroscopy analysis was carried out using a Renishaw confocal microscopy Raman spectroscopy system with a microscope equipped with 10×, 20×, and 50× objectives, and a charge coupled device (CCD) detector. Raman excitation source was provided by a 632.8 nm He–Ne laser beam, which had the beam power of 17 mW and was focused on the sample with a spot size of about 1 μm in a diameter.