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Electrochemical performance of an air-breathing direct methanol fuel cell using poly(vinyl alcohol)/hydroxyapatite composite polymer membrane

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Abstract

A novel composite polymer membrane based on poly(vinyl alcohol)/hydroxyapatite (PVA/HAP) was successfully prepared by a solution casting method. The characteristic properties of the PVA/HAP composite polymer membranes were examined by thermal gravimetric analysis (TGA), X-ray diffraction (XRD), scanning electron microscopy (SEM), micro-Raman spectroscopy and AC impedance method. An air-breathing DMFC, comprised of an air cathode electrode with MnO_2/BP2000 carbon inks on Ni-foam, an anode electrode with PtRu black on Ti-mesh, and the PVA/HAP composite polymer membrane, was assembled and studied. It was found that this alkaline DMFC showed an improved electrochemical performance at ambient temperature and pressure; the maximum peak power density of an air-breathing DMFC in 8 M KOH + 2 M CH_3OH solution is about 11.48 mW cm^{-2}. From the application point of view, these composite polymer membranes show a high potential for the DMFC applications.

Keywords: Composite polymer membrane; Poly(vinyl alcohol) (PVA); Hydroxyapatite (HAP); Direct methanol fuel cell (DMFC); Alkaline; MnO_2

1. Introduction

Direct methanol fuel cells (DMFCs) [1–43] have recently received a lot of attentions due to their high-energy density (6100 W h kg^{-1}) and low emission of pollutants. The DMFC has attracted much attention because of its use of liquid methanol fuel, which is easy to deliver and store. More importantly, liquid fuel can be used at ambient temperature and pressure, which makes the DMFC easy to use with portable 3C electronic devices [13–18].

However, the development of acidic DMFC has faced several serious problems: (i) slow methanol oxidation kinetics, (ii) the poisoning of CO intermediate on the Pt surface, (iii) the high methanol crossover through the polymer membrane, (iv) the high costs of the Nafion membrane and Pt catalyst.

At the present time, the perfluorosulfonate ionomer membranes, such as Nafion membrane (Dupont), are mainly used on the DMFC. However, the commercial Nafion polymer membranes showed a serious methanol crossover problem [5,9], where methanol permeates from the anode to the cathode. The methanol permeation not only causes fuel loss but also forms a mixed potential at the cathode and reduces the electrochemical performance of the DMFC. Thus, the solid polymer membrane with lower methanol permeability is very important property for DMFC applications. For perfluorosulfonate membrane (Nafion), various ceramic fillers have been added into Nafion membranes to reduce the methanol crossover rate, such as TiO_2 [5,24], SiO_2 [25–32], montmorillonite (MMT) [33,34], zeolite [35,36], and Zr-phosphate [37] all of which have been widely studied. For non-perfluorosulfonate membranes, different composite polymer-based membranes for DMFCs have been extensively studied, for example, PVDF + Al_2O_3 [38], sulfonated styrene–(ethylene–butylene)-sulfonated styrene (SEBSS) + SiO_2 [39], sulfonated poly(ether ether ketone) + ZrO_2 [40], sPEEK + ZrPh [41], sPEEK + MCM-41 [42], etc.

Alkaline polymer electrolytes based on PVA [43–49] have been studied for application on Ni-MH, Zn-air, and DMFC cells. They reported the alkaline PVA-KOH polymer electrolyte exhibiting the ionic conductivity to be around

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10^{-2}–10^{-1} S cm^{-1} at room temperature. Yang [49] also prepared the alkaline crosslinked PVA/TiO_2 nanocomposite polymer membranes applied on the DMFC. The maximum peak power density for alkaline DMFC was about 7.54 mW cm^{-2} at 60 °C and 1 atm.

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAP) has long been used as an implant material due to excellent biocompatibility, bioactivity and chemical stability. The addition of hydroxyapatite (HAP) ceramic filler into a polymer matrix not only facilitated a reduction of the glass transition temperature (T_g) and the crystallinity of the PVA polymer, but also increased the amorphous phases of the polymer matrix as well as its ionic conductivity. As we know, when the HAP filler, which is a stiffer material, is added to the PVA matrix, the swelling ratio of PVA/HAP composite polymer membrane is effectively reduced. As a result, the mechanical properties, dimension stability and swelling ratio of the polymer membrane are also improved.

Yu and Scott [50–52] recently studied the electrochemical performance of the alkaline DMFC with anion-exchange membranes. The DMFC performance with a maximum power density of about 10 mW cm^{-2} was obtained in a commercial quaternary-ammonium anion-exchange membrane (Morgane-ADP, Solvay SA, Belgium). In addition, Rhim et al. [53] and Lin et al. [54] prepared PVA/PWA polymer electrolyte membranes and applied them to the DMFC. Varcoe et al. [55–58] developed and characterized the quaternary-ammonium (as the counter ions bound to the polymer backbone) radiation grafted ETFC [55], PVDF and FEP [58] alkaline anion-exchange membrane (AAEM). They prepared the AAEM-MEAs that do not contain any metal-cation M^{n+} (i.e., K^+, Na^+) to avoid the carbonate precipitation problem and to improve long-term operation stability. This preparation proved to be a breakthrough for alkaline anion-exchange membranes on fuel cell applications. The peak power density of 130 mW cm^{-2} for the H_2/O_2 fuel cell with AAEM membrane was obtained, while the maximum power density of 8.5 mW cm^{-2} was obtained in a metal-cation-free methanol/O_2 fuel cell with 2–2.5 bar back pressure at 80 °C.

Those experimental results indicated that when different ceramic fillers were added into the solid polymer electrolyte (SPE), ionic conductivity, thermal and mechanical properties were improved. The increase of ionic conductivity of the composite polymer electrolyte can be explained by the fact that the HAP fillers in the polymer matrix created some defects or voids at the boundaries of between the ceramic particles and the polymer chain. In this composite polymer membrane there was a dispersion of the HAP ceramic fillers into the PVA matrix, which acted as a solid plasticizer capable of enhancing chemical, thermal and mechanical stabilities for the composite polymer membranes.

TGA was used to analyze the thermal stability properties of the PVA/HAP composite polymer membrane. The crystallinity and surface morphology of the PVA/HAP composite polymer membranes were examined by XRD and SEM, respectively. Micro-Raman spectroscopy was applied to study the chemical composition of the PVA/HAP polymer membranes. The ionic conductivity of alkaline PVA/HAP composite polymer electrolytes was measured by AC impedance spectroscopy. The characteristic properties of the crosslinked PVA/HAP polymer membranes with different weight percentages of HAP fillers (2.5–10 wt.%) will be examined and discussed in detail.

In this work, the alkaline DMFC, composed of the air cathode electrode loaded with MnO_2/BP2000 carbon inks, the PtRu anode electrode (4.00 mg cm^{-2}) and the PVA/HAP composite polymer membranes, was assembled and examined. The PVA/HAP composite polymer membranes were first prepared through direct blending of PVA with HAP fillers under ultrasonic condition. The composite polymer membranes obtained from this process were further crosslinked by adding 5 wt.% glutaraldehyde (GA) solution. For anodic methanol electrooxidation reaction, cathodic oxygen reduction reaction (ORR) and the overall reaction of the DMFC in alkaline media can be described as follows:

- Anodic reaction:

$$CH_3OH + 6OH^- \rightarrow CO_2 + 5H_2O + 6e^-, \quad E_a^0 = -0.810\,\text{V (vs. SHE)}, \tag{1}$$

- Cathodic reaction:

$$1.5O_2 + 3H_2O + 6e^- \rightarrow 6OH^-, \quad E_c^0 = 0.402\,\text{V (vs. SHE)}, \tag{2}$$

- Overall reaction:

$$CH_3OH + 1.5O_2 \rightarrow CO_2 + 2H_2O, \quad E_{cell}^0 = 1.21\,\text{V}, \tag{3}$$

Additionally, the electrochemical characteristics of the DMFCs with alkaline PVA/HAP composite polymer membranes were investigated by the linear polarization, galvonostatic and potentiostatic methods; especially, for the peak power density of the DMFC.

2. Experimental

2.1. Preparation of the PVA/HAP composite polymer membranes

PVA (Aldrich), HAP ceramic fillers (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 PVA/HAP composite polymer membranes were prepared by a solution casting method. The appropriate weight ratios of PVA:HAP = 1:2.5–15 wt.% were dissolved in distilled water by stirring. The PVA/HAP composite polymer membranes were further crosslinked by adding a 5 wt.% glutaraldehyde solution (GA, 25% content in distilled water, Merck) and 1.0 vol.% HCl (HCl used as a catalyst) in the bath. The above resulting solution was stirred continuously until the solution mixture reached a homogeneous viscous appearance at 90 °C for 2 h. The blending time of PVA polymer and HAP fillers was well controlled. The resulting viscous solution was poured out into a Petri dish. The thickness of the wet composite polymer membranes was between 0.20 and 0.40 mm. The Petri