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Preparation and characterization of poly(vinyl alcohol)/sodium alginate blended membrane for alkaline solid polymer electrolytes membrane

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ABSTRACT

Novel poly(vinyl alcohol)/sodium alginate membranes (PVASA) are prepared in this study. The PVASA membranes are further treated by chemical crosslinking with glutaraldehyde as a crosslinking agent to get the crosslinked PVASA (PVASA-GA). The thermal property, KOH uptakes, ionic conductivity, and methanol permeability of the PVASA and PVASA-GA membranes are measured. Differential scanning calorimetry, X-ray diffraction, and thermogravimetry analysis are used for the characterization of membranes. It is found that with increasing the content of sodium alginate in the PVASA membrane, the crystallinity and melting point of PVASA decrease. The polymer electrolyte membranes are formed by immersing the various PVASA membranes in KOH solution. The effects of crosslinking time and membrane composition of PVA/SA on ionic conductivity through the polymer electrolyte membrane are studied using AC impedance technique. The ionic conductivity (σ) through the PVASA64 membrane at 25 °C, ($0.091\ \mathrm{Scm^{-1}}$), is higher than the other studies for the different modified PVA membranes. The effect of crosslinking time on methanol permeability is very significant. The methanol permeability (P) of the PVASA-GA membranes is on the order of $10^{-7}\ \mathrm{cm^2\,s^{-1}}$. The value of selectivity, (σ/P), for the PVASA82-GA60 membrane is at about $21.50 \times 10^3\ \mathrm{Scm^{-3}\,s^1}$. Alkaline direct methanol fuel cells comprises of PVASA82-GA membrane is assembled and examined. It shows excellent electrochemical performance. The maximum power density of $20.7\ \mathrm{mW\,cm^{-2}}$ is achieved at $E_{p,max} = 0.232$ V with a peak current density ($i_{p,max}$) of $89.20\ \mathrm{mAcm^{-2}}$ at 30 °C for the direct methanol fuel cell consisting of PVASA82-GA60 membrane.

1. Introduction

Due to the efficient high-power generation, reduced system weight, simplified construction, rapid startup and low or no emissions, polymer electrolyte fuel cells have attracted much interest for solving environmental problems [1]. The main component of the polymer electrolyte fuel cells is the membrane electrode assembly (MEA) which consists of a polymer electrolyte membrane located between two porous, electrically conductive electrodes (anode and cathode) [1]. Electrochemical reactions, both anodic and cathodic, take place at electrodes and promoted by the use of a catalyst.

Polymer electrolyte membranes (PEMs), which serve as both a separator to gas permeation from the anode to cathode as well as a solid electrolyte, have been considered as one of the key components for achieving high fuel cell performance because of their fuel cell properties [2]. Polymer electrolyte membranes for direct methanol fuel cells (DMFCs) with use platinum-based catalysts on high surface area catalyst supports are proposed in current studies [3–7].

Nafion membranes (DuPont), the perfluorosulfonic acid polymers, are considered the state-of-the-art polymer electrolyte membrane materials on the DMFCs because of their excellent chemical and physical stability and their high proton conductivity. However, Nafion membranes suffer critical drawbacks [8–10]. Due to the high cost of Nafion, its application in electrochemical system is limited [11]. In additional, the commercial Nafion membrane showed a serious methanol crossover problem, in which methanol permeates from the anode to the cathode. The methanol permeation not only causes a loss of fuel but also forms a mixed potential at the cathode and leads to a lower electrochemical performance. Thus, it is necessary to use a solid polymer electrolyte with lower methanol permeability in the DMFCs. This has triggered extensive research and development for alternative membrane materials.

As the semi-crystalline polyvinyl alcohol (PVA) is inexpensive and owns excellent properties such as chemical stability, hydrophilicity, high abrasion resistance, suitable mechanical properties including elongation, tensile strength and flexibility with easy processability to film, the preparation and characterization of

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PVA-based polymer electrolytes membranes were evaluated and application for batteries and direct methanol fuel cell have also been reported [12–26].

As described in the previous study [27–29], catalytic activities and stabilities of the catalysts towards methanol and ethanol oxidation reactions in the alkaline solutions were much higher than those in the acid solutions, indicating that the kinetics of the methanol and ethanol oxidation reactions improves in alkaline solutions. When the operational environment is alkaline, it is possible to use non-platinum catalysts for the oxygen reduction reaction [27,30–32]. In addition, the water management is improved due to the electro-osmotic drag transporting water away from the cathode, thus the so-called alcohol 'crossover' problem is highly reduced because of the opposite movement of OH^- anions to the movement of H^+ ions in the acidic membrane [27,33,34]. Recently, great interests have been evoked on alkaline membrane and the evaluations of alkaline membranes for use in direct methanol alkaline fuel cells (DMAFCs) have also been reported [34–40]. However, these polymers are generally of high price and the process is event very toxic and carcinogenic [41].

Alginic acid, also called alginate, is an anionic polysaccharide consisting of (1-4)-linked β-D-mannuronic acid (M) and α-L-gluronic acid (G) units. Alginate exhibits excellent biocompatibility, non-toxicity, non-immunogenicity, biodegradability, and can be easily gelled with divalent cations such as calcium ion [42]. In extracted form it absorbs water quickly; it is capable of absorbing 200–300 times its own weight in water [43]. Sodium alginate is the sodium salt of alginic acid. It has shown excellent performance as a membrane material for the dehydration of ethanol mixture. Blending of alginate with poly(vinyl alcohol) or chitosan had been reported to improve mechanical stability and the evaluation of methanol permeability and proton conductivity [44,45]; whereas the electrochemical performance for the alkaline solid polymer electrolyte (ASPE) was not reported.

Since alginate is a highly water-absorbing polysaccharide, a major research objective is to fix the alginate in stable structures while maintaining its high OH^- conductivity. As chemical crosslinking is a highly versatile method to modify polymers with reducing the swelling and suppress methanol permeability and yielding the dimensional and thermal stability of the membranes [46–52], in this study, the homogeneous, nonporous PVASA membranes were prepared by casting the polymer solutions of PVA with sodium alginate and the PVASA membrane was crosslinked with glutaraldehyde to get the PVASA-GA membrane. For the application in direct methanol alkaline fuel cells, the various PVASA and PVASA-GA membranes were immersed in 40 wt% KOH solution to form the KOH containing polymer electrolyte membranes. The membranes characteristics including differential scanning calorimetry (DSC), X-ray diffraction (XRD), thermogravimetry analysis (TGA), KOH uptake, ionic conductivity and methanol permeability were addressed and compared with other studies. In order to evaluate the applications in practical DMAFC, the potential–current density (*I*–*V*) and the power density–current density curves of the DMAFCs comprised of PVASA-GA membranes at various temperatures is also conducted.

2. Experimental

Both poly(vinyl alcohol) and sodium alginate were obtained from Sigma. The molecular weight for poly(vinyl alcohol) and sodium alginate were about 70,000–100,000 g and 20,000–80,000 g, respectively. 2.5 wt% glutaraldehyde solution and KOH was purchased from Acros and Aldrich, respectively.

2.1. Membranes preparation

A stock 4 wt% PVA aqueous solutions was prepared by dissolving PVA in distilled water at 85 °C. Sodium alginate (SA) was separated prepared. Then SA and PVA solutions were mixed in different proportions with stirring for at least 2 h to make sure that the solution was completely homogeneous. The weight ratio between PVA and SA is 100/0, 80/20, 60/40, 40/60, 20/80, and 0/100, respectively. After degassed in a vacuum chamber, the solutions were poured into plastic dishes, and dried in the ambient conditions. The thickness of the PVASA membrane is about 0.02 cm. These samples were designated as PVA, PVASA82, PVASA64, PVASA46, PVASA28, and NaAlg, respectively.

2.2. Crosslinking of membranes

The various membranes were soaked in a reaction solution consisting of 2.5 wt% glutaraldehyde (Glu) and small amount of HCl in acetone, (volume ratios of $Glu_{(aq)}$:acetone:$HCl_{(aq)}$= 1:2:0.01), at 40 °C for chemical crosslinking with different time. The samples after crosslinking were designated with crosslinking time, for example, the samples for the system of PVASA82 with crosslinking about 30, 60, 120, and 240 min were designated as PVASA82-GA30, PVASA82-GA60, PVASA82-GA120 and PVASA82-GA240, respectively.

2.3. Characterizations of membranes

To examine the variation of crystalline structure of membranes, the X-ray diffraction curve was conducted with XRD (Siemens/D5005). The thermal properties were evaluated with differential scanning calorimetry (DSC) and thermal gravimetrical analysis (TGA). The DSC was carried out with the TA/DSC2010 system. It was scanned from −30 to 250 °C at a heating rate of 10 °C min^{-1} with nitrogen gas flowing as protection. Thermal gravimetrical analysis (TGA) of membranes was carried out with the TA/TGA2050 system. It was measured from 25 to 600 °C at a heating rate of 10 °C min^{-1} with nitrogen gas flowing as protection.

2.4. Properties of polymer electrolyte membranes

Various polymer electrolyte membranes are prepared by immersing the PVA, PVASA and crosslinked PVASA membranes in 40 wt% KOH aqueous solution at 25 °C, respectively. The swelling ratio of absorbed KOH solution in membranes was determined using Swelling (%)$=100\%\,(W_{wet}-W_{dry})/W_{dry}$ where W_{wet} and W_{dry} are the weight of the $KOH_{(aq)}$ absorbed membrane and of the dry membrane, respectively. The membrane was dried in a vacuum oven at about 50 °C and was cut into 2 cm × 2 cm. To evaluate the effect of SA and crosslinking time on the swelling ratio, the weight of the $KOH_{(aq)}$ absorbed membrane was obtained by soaking membrane in 40 wt% KOH aqueous solution at 25 °C for different time; then it was wiped with a filter paper to remove excess water on membranes surface and immediately weighed. The ionic (OH^-) conductivity of the formed polymer electrolyte membranes was measured by an AC impedance technique using an electrochemical impedance analyzer (CHI405A) [53]. Fully swollen polymer electrolyte membranes were sandwiched between SS316 stainless-steel (SS), ion-blocking electrodes, each of surface area 0.785 cm, in a spring-loaded glass holder. The electrolyte conductance, σ (Scm^{-1}) through polymer electrolyte membranes was determined using $\sigma = l/R_bA$ where l is the thickness (cm) of the polymer electrolyte membrane, A is the area of the blocking electrode (cm^2) and R_b (Ω) is the bulk resistance obtained from the analysis of the experiments.