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Conductivity of graphene oxide containing poly (vinyl alcohol) membrane

Abstract

Poly (vinyl alcohol) is used as raw material in this study. With adding graphene oxide, the PVA/GO membrane was prepared with solution casting method. To evaluate the effect of different casting method on the conductivity of PVA/GO membrane, knife casting method with different casting surface were conducted in this study. Ionic conductivity for PVA/GO prepared by solution casting method is about 0.0526 S/cm; whereas the ionic conductivity is sharply improved to 0.1439 S/cm for PVA/GO prepared by casting membrane on the glass with vacuum..

Keywords: Poly (vinyl alcohol), polymer electrolyte membranes, ionic conductivity

Volume 2 Issue 2 - 2018

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Received: September 19, 2018 | **Published:** September 28, 2018

Introduction

Since alkaline polymer electrolytes have been prepared, the conductivity of alkaline electrolytes based on polyvinyl alcohol and polyethylene oxide had been reported.[1–4] Alkaline solid polymer electrolytes (ASPE) or alkaline solid polymer blend electrolytes (ASPBE) using potassium hydroxide (KOH) as ionic dopant had been reported and the results have shown considerable improvement in cell properties. It included poly (vinyl alcohol), poly (ethylene oxide), blends of PVA/PEO, copolymer of epichlorohydrin and ethylene oxide gels of hydrophonics and poly (acrylic acid).[3–13] Graphene oxide (GO) is generated from the oxidation of graphite. It is a nanomaterial with carbon, oxygen, and hydrogen in variable ratios to form a range of reactive groups such as carboxyl, hydroxyl, and carboxylic acid in the material. The typical structure of GO is shown in Figure 1. These reactive groups make GO a good candidate in the various applications and had attracted intensive study.[14]The polymer electrolyte films as well as the electrodes were often prepared by the casting technique.[6] For example, PEO is swollen in water and then mixed with a concentrated aqueous solution of KOH at about 60 °C for 4 h to get viscous homogeneous solution. And then the solution is poured onto a Teflon plate and the water excess is evaporated slowly at ambient temperature for 48h and maintained in a vacuum oven before use. In general, the ionic conductivity increases with increasing the KOH concentration in the preparation. In our previous studies about modification of PVA for alkaline polymer electrolyte membranes and fuel cell,[14-19] the membranes prepared with solution casting method were immersed in 40wt% KOH solution to form the KOH containing polymer electrolyte membranes to evaluate the performance with measuring the KOH uptake, ionic conductivity, methanol permeability, and selectivity of these membranes. As there is not any report about the effect of casting method on the conductivity, the effect of casting method on the conductivity of graphene oxide containing poly (vinyl alcohol) membrane is reported in this study.

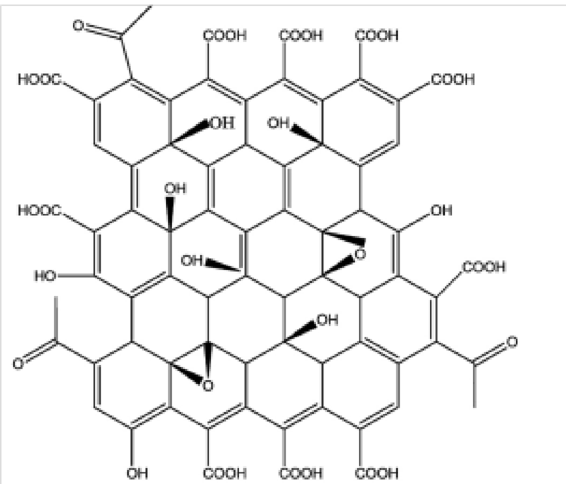

Figure 1 The typical structure of graphene oxide (GO).

Experimental

Poly (vinyl alcohol), (PVA, M_w=70,000-100,000g) was obtained from Sigma. KOH was purchased from Aldrich. Graphene oxide, (20% oxygen content, conductivity 10~30 S/cm, and specific volume higher than 350 m^2g^{-1}), was obtained from Graphage. To evaluate the effect of graphene oxide on the membrane, pure poly (vinyl alcohol) is prepared as control in this study. The solutions of pure poly (vinyl alcohol) is prepared by adding PVA into distilled water at 85°C with stirring for at least 3 h to make sure the solution was completely homogeneous. The solutions were slowly poured onto the prepared glass slides mold and dried in the ambient conditions for 24h. 0.05g graphene Oxide (GO) powder was added in distilled water and sonicated with ultrasonic bath for 1h. Then PVA powder is completely dissolved in the solution with stirring for 4 h at 85 °C to form the homogeneous solution. The solutions were slowly poured onto the prepared glass slides mold and dried in the ambient conditions for 24 h. To evaluate the effect of casting method on the conductivity of PVA/GO membrane, the preparation of the membrane was described in Figure 2. To prepare the alkaline solid polymer electrolyte, the membranes were immersed in 40wt% KOH solution to form the KOH containing polymer electrolyte membranes. Then the ionic conductivity in the KOH containing PVA/GO electrolyte membranes was determined by means of an ac impedance method.[16] The procedure is the same as described in previous study.[16] The membranes were sandwiched between SS316 stainless-steel (SS), ion-blocking electrodes in a spring-loaded glass holder. The impedance of the membranes was measured at different temperature. From the analysis of the experiments, the bulk resistance, R_b (Ω), was obtained. The electrolyte conductance, σ (S/cm) can be calculated according to the formula:

$$\sigma = l / R_b A \qquad (1)$$

Where l is the thickness (cm) of the alkaline solid polymer electrolyte (ASPE), A is the area of the blocking electrode (cm^2).

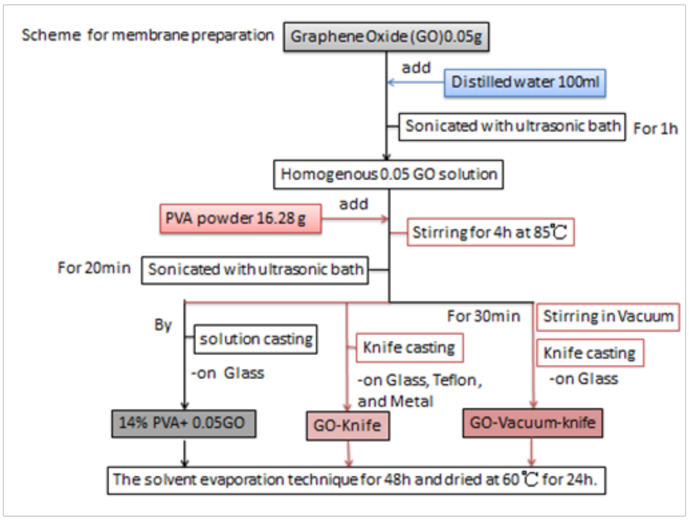

Figure 2 Preparation of PVA/GO membrane with different casting method.

Results and Discussion

Ionic conductivity for different membranes had been reported in references.[1–28] It can be found that the researches emphasize the preparation of different materials with functional group to improve the conductivity. For example, proton conducting polymer derived from poly(etheretherketone) and poly(4-phenoxybenzoyl-1,4-phenylene)[21], sulfonated-fluorinated poly(arylene ether)s membranes for a proton exchange membrane fuel cell[22], solid polymer electrolytes based on statistical poly(ethylene oxide-propylene oxide) copolymers,[23] investigations on the effect of various plasticizers in PVA-PMMA solid polymer blend electrolytes,[24] ionomeric membranes based on partially sulfonated poly(styrene): synthesis, proton conduction and methanol permeation,[25] preparation and characterization of high ionic conducting alkaline non-woven membranes by sulfonation,[26] sulfonated polystyrene grafted polypropylene composite electrolyte membranes for direct methanol fuel cells,[27] sulfonated poly(2,5-benzimidazole) (SABPBI) impregnated with phosphoric acid as proton conducting membranes for polymer electrolyte fuel cells,[28] and so on. Most of Ionic conductivity (S/cm) reported in the references[1–28] is between 10^{-2} to 10^{-5} (S/cm). In our previous studies about modification of PVA for alkaline polymer electrolyte membranes and fuel cell,[14–19] the ionic conductivity can be enhanced to about 0.11(S/cm). In this study, the ionic conductivity of PVA prepared as control is about 0.028(S/cm). With adding GO in to the membrane for PVA/GO membrane, the ionic conductivity is enhanced to 0.0526(S/cm) with solution casting method on glass. An intriguing result is found for the ionic conductivity through PVA/GO membrane prepared with knife casting on glass, Teflon, and metal (Table 1). Compared with the value of ionic conductivity of membrane prepared with solution casting method, the values of ionic conductivity of membranes prepared with knife casting are enhanced. It is about two times of the value of σ obtained from the solution casting membrane. The ionic conductivity was about 0.052(S/cm) for PVA/GO membrane prepared by solution casting method, whereas the ionic conductivity is enhanced to 0.129 and 0.1439(S/cm) with knife casting on the glass without or with vacuum treatment. It seems that the membrane thickness is higher than those prepared with knife casting method. There is not any effect of vacuum treatment of the thickness of membrane, although the ionic conductivity is higher for the membrane prepared with vacuum treatment. Compared with the value of ionic conductivity of membrane prepared with solution casting method, the values of ionic conductivity of membrane prepared with knife casting are enhanced.

Table 1 Ionic conductivity for PVA/GO prepared with knife casting on different membranes

Casting surface	Ionic conductivity (S/cm)	Thickness of membrane (cm)
Solution casting	0.0526	0.042
Glass	0.129	0.028
Teflon	0.0976	0.031
Metal	0.128	0.024
Glass with vacuum	0.1439	0.028

Conclusion

With the different casting method and the different casting surface, the value of ionic conductivity of PVA/GO membrane is changed. It might be due to the effect of casting method on the morphology and resulted in the increased of the ionic conductivity by comparing with the membrane prepared with solution casting method.

Acknowledgements

This work was supported by Ministry of Science and Technology of the Republic of China with grant MOST-104-2211-E-182-054-MY3 and partial financial support of Chang Gung Memorial Hospital with grant CMRPD2F0011 and CMRPD2F0012.

Conflict of interest

Author declares that there is no conflict of interest.

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DOI: 10.15406/mojps.2018.02.00048