

Composite Anion Exchange Membrane for Alkaline Direct Methanol Fuel Cell: Structural And Electrochemical Characterization

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ABSTRACT: A copolymer of 4-vinylpyridine (4-VP) and styrene was synthesized by radical mass polymerization using 2,2'-azobisisobutyronitrile as initiator. An insoluble (linear) pyridinium-type polymer was prepared by the reaction of P (4VP-St) with 1-bromooctane. An anion exchange membrane was prepared using a composite of pyridinium-type polymer and a fibrous woven structure for use in electrochemistry. The composite membrane was characterized by X-ray diffraction, tensile strength, scanning electron microscopy, and electrochemistry measurements. The experimental results showed that the fibrous woven product

had improved the tensile strength more than had the membrane made of a pyridinium-type polymer alone. The composite membrane was used in alkaline fuel cells, and its properties were measured by electrochemical analysis. The ionic conductivity of the membrane was acceptable, but its performance as a direct methanol fuel cell (DMFC) was not. The primary reason for this was analyzed, and research is ongoing, with analysis to be discussed in later reports. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 2248–2251, 2006

Key words: alkaline; SPE; DMFC

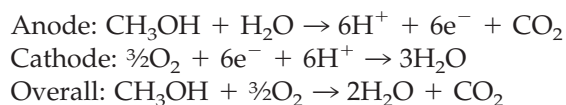
INTRODUCTION

Fuel cells are electrochemical energy converters, transforming chemical energy directly into electricity.¹ Several kinds of fuel cell exist, the most important being the proton exchange membrane fuel cell.² This kind of fuel cell uses an acidic membrane (commonly named Nafion) as electrolyte and gives excellent results, but its high cost has limited its development. So it is desirable to determine the feasibility of using an anion exchange membrane or an alkaline solid polymer electrolyte (SPE) in a fuel cell.

SPEs can be divided into two classes that differ mainly in the ionic conduction model within the polymer structure. Polymer-salt complexes are part of this first class of ionic conducting polymer materials. The principle of ionic conduction within the structure is based on heteroatom-cation interactions and on the mobility of amorphous chains. This kind of SPE commonly is in gel form and has been widely used in lithium batteries.³ Another class of SPE is a polyelectrolyte or ionic polymer. The ionic sites are fixed in the skeleton of the polymer chain. A mobile counterion is associated with each ionic function. Conduction of the SPE relies on counterion exchange. Nafion belongs to this class of SPEs.

Nafion is a hydrated perfluorosulfonic polymer, in which sulfonate is grafted onto the C-F skeleton of the polytetrafluoroethylene main chains. Although Nafion can be used in direct methanol fuel cells (DMFCs), but two major obstacles have hindered their use⁴: limitations on development from the activity of the anode catalyst and the noble metal electrode and the serious problem of methanol crossover. Thus, a series of membrane materials have been produced to substitute for Nafion. For example, poly(tetrafluoroethylene-hexafluoropropylene) film was first irradiated, and then styrene groups were grafted to it, using divinylbenzene as a crosslinker.^{5–7} The performance of this membrane was promising. In developing polymer electrolytes for use in fuel cells, the systems most widely investigated include sulfonated polysulfone,⁸ sulfonated poly(ether sulfone),⁹ sulfonated poly(ether ether ketone),¹⁰ sulfonated polybenzimidazole,¹¹ and sulfonated poly(ether ether ketone ketone).¹² These materials have shown some good characteristics, such as high intensity and high heat resistance. All these membranes are all based on perfluorosulfonic acid, in which conductivity relies on proton transport. The fuel cell reactions in a DMFC with proton transport through an acid membrane are:

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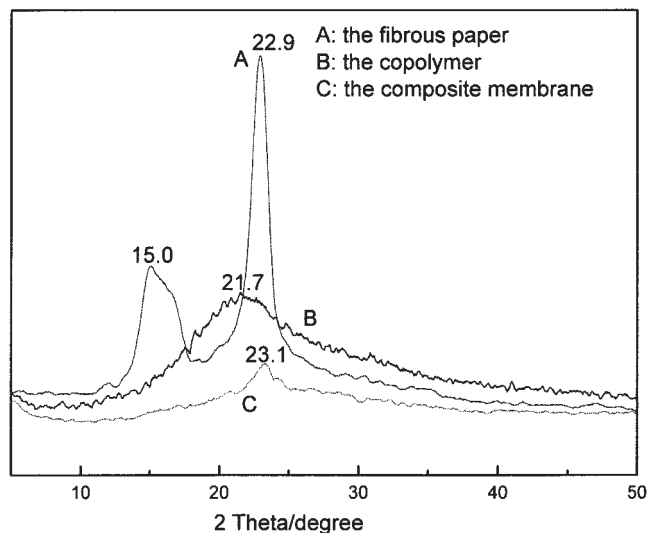
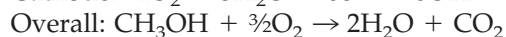
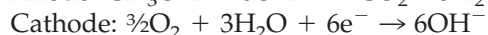


Figure 1 X-ray diffraction patterns of the membranes.

The problem of the anode catalyst using a noble metal has not been settled, which led to the idea that an alkaline anion exchange membrane might overcome the problem. The fuel cell reactions in a DMFC with hydroxyl transport through an acid membrane are:



In such cells, cheaper non-noble metal catalysts such as nickel and silver can be used.^{13–16}

In a previous work, we produced a series of solid polymer electrolytes (SPEs) containing a 4-vinylpyridinium salt unit and a styrene unit.¹⁷ The anion exchange membrane was made from the SPE. A fibrous woven-reinforced membrane was applied in the fuel cells. The properties of this composite membrane were described in the article on this study.

EXPERIMENTAL

Preparation of composite membranes

A piece of fibrous woven material (Yihecheng Company, Shandong, China) was placed on a Teflon gasket. A solution of 10 mL of nitromethane in which the copolymer (1.0 g), made as described previously,¹⁷ had been dissolved was cast on the fibrous woven material, and the nitromethane was allowed to evaporate at room temperature. The membrane was dislodged carefully and then subjected to further drying under vacuum for 2 days. A dried membrane with a thickness of 65 μm was obtained. The composite membrane was so transparent that the fibrous woven material was not evident. The 2 cm^2 membranes, made by quaternized copolymers, were immersed in a 0.1

mol/L NaOH solution (25°) for 30 min. The color of the membrane changed from colorless to red. This process can be reversed when the red membrane is immersed in 0.1 mol/L HCl. Obviously, groups were exchanged between the OH^- and the halogen ions. The ionic conductivity of the composite membrane exchanged by OH^- was measured by an electrochemistry workstation.

Model and structure of DMFC

The model and structure of the DMFC are shown in Figures 3 and 4, respectively. Figure 4 shows the membrane-electrode assembly (MEA), the heart of the DMFC, which consists of an anode, a cathode, and an SPE membrane (compound C). The testing conditions were: temperature, 45°C; anode—1M CH_3OH , flux density, 2 mL/min; cathode— O_2 , flux density, 10 mL/min.

Characterization of membranes

The wide-angle X-ray diffraction (XRD) patterns of the 65- μm -thick membranes were recorded with a Shimadzu XRD-6000 (Kyoto, Japan) diffractometer by using a Cu $\text{K}\alpha$ target at 40 KV and 30 mA with a scan rate of 4°/min. The diffraction angle ranged from 5° to 45°. The tensile strength and breaking elongation of the membranes were measured on an electron tensile tester (XINSANSI-cmt6202, Shenzhen, China) with a tensile rate of 5 mm/min, at a gauge length of 50 mm and a gauge width of 10 mm. The temperature and relative humidity were 25°C and 60%, respectively. The morphology of membrane surfaces was examined by a Hitachi-570 scanning electron microscope (SEM; Japan). The membranes were frozen under liquid nitrogen in order to fracture and were coated with gold under a vacuum of 13.3 prior to the SEM experiment. The ionic conductivity of the composite membranes was obtained by AC electrochemical impedance spectroscopy measurement carried out on an electrochemistry workstation (Chenhua CHI660, Chenhua Company, Shanghai, China).

RESULTS AND DISCUSSION

WXRD of membranes

The X-ray diffraction spectra of the membranes, shown in Figure 1, revealed two clear peaks at 2θ

TABLE I
Mechanical Performance of the Membranes

	Thickness (mm)	Tensile strength (M Pa)	Elongation at break (%)	Elastic modulus (M Pa)
A	0.025	75.96	3.29	4218.0
B	0.060	7.59	4.80	310.0
C	0.065	50.01	7.42	1081.4

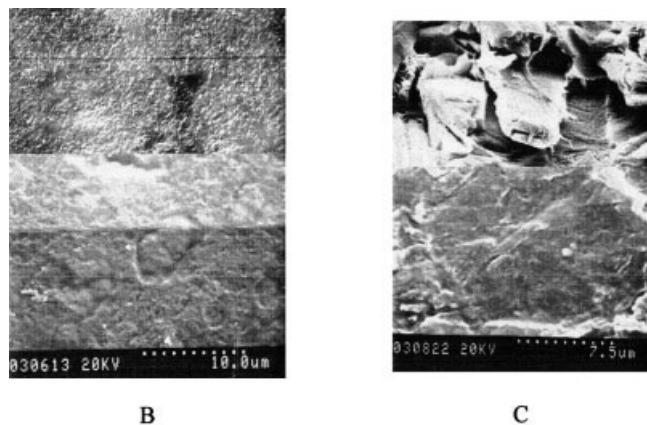


Figure 2 Scanning electron microscopy (SEM) of the membranes.

= 15.0° and 22.9°, suggesting a high degree of crystallization in the fibrous woven material (compound A), whereas a wide peak in the copolymer containing 4-vinylpyridinium salt and styrene (compound B) suggested an amorphous structure. An obvious distinction can be seen in the X-ray diffraction spectrum of the composite membrane (compound C), with the wide peak suggesting an amorphous structure. This implies interaction between the copolymer containing 4-vinylpyridinium salt and styrene (B) and the fibrous woven material (A). According to the classical theory, if there were no interaction, the X-ray diffraction spectrum of compound C would have been the sum of the X-ray diffraction spectra of compounds A and B. What actually occurred suggests that this interaction of compounds A and B destroyed the crystallinity of compound A. This interactive behavior can be explained as chain interaction between the two polymers, that is,

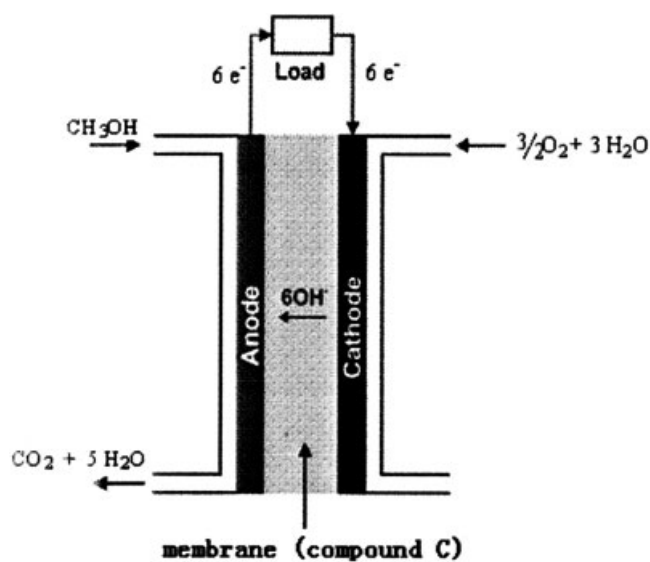


Figure 3 Model of the DMFC.

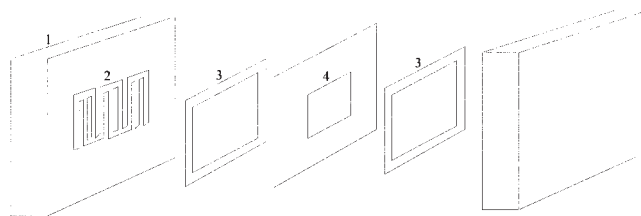


Figure 4 Structure of the DMFC.

interaction between the 4-vinylpyridinium salt unit of compound B and the OH group in compound A.¹⁷ Another phenomenon is that the peak height shown in the X-ray diffraction spectrum of compound C was lower than that in the spectrum of compound B, implying that the structure of the composite membrane (compound C) was more irregular than that of compound B.

Mechanical properties of membranes

The mechanical properties of the membranes are shown in Table I, which shows that the tensile strength of compound A was higher than that of compound C, which was higher than that of compound B. Indeed, compound B was enhanced by compound A because of the fibrous paper loading most of the stress in compound C. The thickness of compound C was less than the sum of the thicknesses of compounds A and B. This may be explained as compound B permeating compound A, dispersing the latter's stress concentration.¹⁸ Another phenomenon is that the elongation at break of compound C was higher than that of compounds A and B. This phenomenon has no reasonable explanation, but it hints that there is interaction between compounds A and B.

Morphological characteristics of membranes

In the Figure 2 photographs the upper section of each photograph shows a cross section of the membrane and the bottom section shows the surface of the membrane. Figure 2 shows that the degree of coarseness of compound C was higher than that of compound B. The phenomenon may be explained as compound B filling in the holes in compound A and the chains of compounds B and A intermingling with each other.¹⁹ Compound B dispersed the strain energy of compound A, and compound A shackled compound B [Fig. 2(c)].

Electrochemical performance of DMFC

The performance of the DMFC is shown in Figure 5. The ionic conductivity of the composite membrane was 0.008 S/cm at 25°C by the alternating current

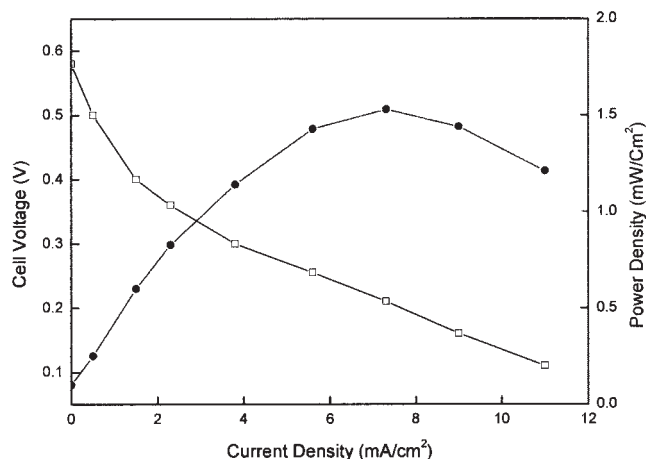
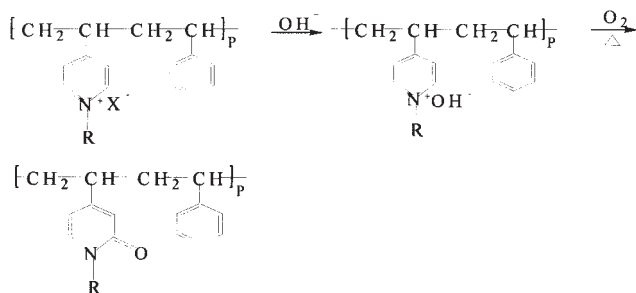


Figure 5 Performance of the DMFCs.

impedance method using a electrochemistry workstation. Figure 5 shows the natural behavior of a working cell, but its performance was inadequate. Open circuit voltage (OCV) was 0.58V, and power density was 1.5 mW. There are two reasons that may have led to the unsatisfactory performance of the cell. First, methanol crossover is a serious problem and induces lower electromotive force; second, the thermal endurance of the copolymer containing of a 4-vinylpyridinium salt unit and a styrene unit (compound B) in alkaline conditions was inadequate. Perhaps there is the same degradation of compound B as described earlier.²⁰



This mechanism implies that thermal endurance of the copolymer containing a 4-vinylpyridinium salt unit and a styrene unit (compound B) in alkaline conditions would not be adequate, although by itself it was relatively heat resistant. So the working temperature of DMFC could not go higher, leading to power density being lower. We need to find an SPE membrane containing aliphatic quaternary amines units for fuel cells to improve the performance of the DMFC, the subject of ongoing work.

CONCLUSIONS

In the present study, an anion exchange membrane enhanced by fibrous paper (compound C, a composite

membrane) was produced, and its characterization and application were studied. Through the characterization of the membranes, it was shown that the fibrous paper (compound A) and the copolymer containing a 4-vinylpyridinium salt unit and a styrene unit (compound B) had good compatibility. The tensile strength of the composite membrane was higher than that of compound B. The performance of the DMFC made of the composite membrane and other components was tested. Natural behavior of a working cell was shown, but its performance was inadequate. There were several reasons for this poor performance. The thermal stability of the copolymer containing a 4-vinylpyridinium salt unit and a styrene unit (compound B) in alkaline conditions should be emphasized over the thermal stability of the copolymer itself containing a 4-vinylpyridinium salt unit and a styrene unit (compound B). Through this study, a direction was clear: we have to find SPE membranes containing aliphatic quaternary amines units because this type of membrane has higher thermal stability in alkaline conditions. Work on such an SPE membrane is underway.

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