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Synthesis and characterization of cross-linked quaternized poly(vinyl alcohol)/chitosan composite anion exchange membranes for fuel cells

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ABSTRACT

Novel cross-linked composite membranes were synthesized to investigate their applicability in anion exchange membrane fuel cells. These membranes consist of quaternized poly(vinyl alcohol) (QAPVA) and quaternized chitosan (2-hydroxypropyltrimethyl ammonium chloride chitosan, HACC) with glutaraldehyde as the cross-linking reagent. The membranes were characterized in term of their water content, ion exchange capacity (IEC), ion conductivity and methanol permeability. FTIR, X-ray diffraction and scanning electron microscopy (SEM) were also used to investigate the relation between the structure and performance of the composite membranes. The composite membranes have a high conductivity (10^{-3} to 10^{-2} S cm^{-1}), and a low methanol permeability (from 5.68×10^{-7} to 4.42×10^{-6} cm^2 s^{-1}) at 30 °C. After reviewing all pertinent characteristics of the membranes, we find that the membrane structure is the principal factor affecting the conductivity and methanol permeability of these membranes.

1. Introduction

It is commonly believed that polymer electrolyte membrane fuel cells are destined to become an effective energy alternative [1,2]. Among the various fuel cell technologies, the direct methanol fuel cell (DMFC) holds favor as a promising candidate for its application as a portable power source, owing to its ease of storage and use of methanol as a liquid fuel. DMFCs use currently proton exchange membranes, such as Nafion®, etc., as a barrier to separate the fuel and to transport protons. These membranes can provide high proton conductivity and cell power, but with low methanol barriers, which results in power losses [3,4]. Consequently, alkaline anion exchange membrane fuel cells (AEMFCs) have been developed to avoid the deficiencies of DMFCs containing proton exchange membranes. Because the operational environment is alkaline, AEMFCs have many advantages, including: (1) the methanol oxidation rate is faster in alkaline media than in acid [5]; (2) AEMFCs can use less expensive metal catalysts, such as Ag or Ni; (3) the direction of OH^- anion motion opposes that of the methanol flux through the membrane leading to an intrinsic reduction in methanol permeability.

Research on the application of anion exchange membranes has been underway for several years [6–12]. There are many ways to produce anion exchange membranes, such as radiation grafting, electrophilic substitution or dipping with alkali metal hydroxide, such as KOH. (2,3-Epoxypropyl) trimethylammonium chloride (EPTMAC) is an active electrophilic reagent that can react with $-OH$ or $-NH_2$ groups and hence graft quaternary ammonium groups onto the polymer matrix [13,14]. Therefore, this electrophilic reaction with EPTMAC can be used to synthesize anion exchange membranes. In our previous work, we have investigated quaternized poly(vinyl alcohol) (QAPVA) obtained by the reaction between PVA and EPTMAC and have produced cross-linked QAPVA membranes, which have good conductivity and low methanol permeability [8].

Cross-linked QAPVA membranes have a weak mechanical strength. Their performance can be improved by several means, such as blending with inorganic materials or other polymers. The objective of this work is to blend QAPVA with other materials to produce a composite membrane that has a more compact structure and good mechanical strength.

Chitosan (CS), which has a low toxicity and is biodegradable and biocompatible, is one of the most abundant natural polymers from the ocean. CS has been studied as a membrane material for ultrafiltration, reverse osmosis, pervaporation and fuel cells [15–17]. Because there are no mobile hydrogen ions in its structure, CS has a low electrical conductivity. Quaternized CS (2-hydroxypropyltrimethyl ammonium chloride chitosan, HACC), the product of the reaction of CS and EPTMAC, has exchangeable OH^- anions arising from the quaternary ammonium groups in the matrix. HACC has been used as a flocculant in water treatment [18,19] and is also used as a membrane material for electrolyte separation and pervaporation [20,21]. However, it has not been used in fuel cells.

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Table 1
The characteristics and activation energies (E_a) of the composite membranes

Membrane	P4H1G2	P4H1G4	P4H1G8	P3H2G2	P3H2G4	P3H2G8
QAPVA (wt%)	4	4	4	3	3	3
HACC (wt%)	1	1	1	2	2	2
10 wt% GA (mL)[a]	0.2	0.4	0.8	0.2	0.4	0.8
E_a (kJ mol^{-1})	11.8	16.7	14.4	15.6	13.5	17.9

[a] The quantity of GA is added in a 20-mL composite solution.

Considering the anion exchange groups in HACC, it should be possible to apply HACC in alkaline anion exchange membrane fuel cells.

HACC is a good choice for AEMFCs, since it has —OH and —NH_2 groups that can react with glutaraldehyde (GA) to form a cross-linking network, which reinforces the strength of the membrane [17]. It also has quaternary ammonium groups and exchangeable OH^- anions. When HACC is added into the membranes, its exchangeable groups can improve the ion conductivity of the composite membranes.

According to its good performance and low cost as noted above, HACC was chosen as the polymer material to blend with QAPVA to produce anion exchange membranes for application in alkaline fuel cells. In this paper, we prepared cross-linked QAPVA and HACC composite membranes and assessed their characteristics.

2. Experimental

2.1. Material and membrane preparation

Poly(vinyl alcohol) (polymerization degree of 2400, hydrolysis degree of 98–99%) was supplied by Sinopharm Chemical Reagent Co. Ltd. Chitosan has a degree of deacetylation of approximately 92% (Yuhuan Ocean Biochemical Co. Ltd., China). EPTMAC (purity ≥95%) was purchased from Shandong Guofeng Fine Chemistry Factory. Quaternized poly(vinyl alcohol) was synthesized according to the previously reported study [8]. 2-Hydroxy-propyltrimethy ammonium chloride chitosan was synthesized according to the method reported by Lin et al. [22]. Glutaraldehyde (25 wt% content in distilled water) was supplied by Sinopharm Chemical Reagent Co. Ltd.

QAPVA and HACC were dissolved in deionized water to obtain a solution with a total concentration of 5 wt%. The pH of the solution was adjusted to 5 with 10 wt% sulfuric acid. Then a quantitative amount of 10 wt% GA was added as a cross-linking reagent. After the above solution was filtered with a G3 sand filter, it was coated onto the surface of a glass plate and dried at 45 °C for 6 h. The membrane was removed from the glass plate and dried at 100 °C for 3 h.

Two series of composite membranes were prepared and their characteristics were contrasted as shown in Table 1. The following codes were used to name these composite membranes: P means QAPVA, H means HACC and G means GA. The number behind each letter indicates the weight percent of each composition, except for GA, where the number indicates the number of mL of GA added in a 20-mL mixture to prepare a given membrane. For example, P3H2G2 means that in this membrane the concentration of QAPVA is 3 wt% that of HACC is 2 wt% and the amount of GA added per 20 mL of mixture is 2 mL.

2.2. Structural characterization

The FT-IR absorption spectra of CS, HACC, QAPVA and the composite membranes were recorded using an FT-IR740SX spectrophotometer (Thermo Electron Corporation, USA). The crystal structures of the composite membranes were examined using an X-ray diffractometer (X'Pert Pro, Panalytical, Holland). Also the membrane samples were scanned in the reflection mode with a 2θ angle between 5° and 35°. TGA thermal analyses were carried out using a TG209F1 (NETZSCH, Germany) system. The measurements were conducted by heating from 30 to 600 °C at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere.

The membrane morphologies were investigated by environment scanning electron microscopy (XL30ESEM-TMP, Philips, Holland). Prior to observations, the membrane samples were fractured in liquid nitrogen and then sputtered with gold.

2.3. Water content and ion exchange capacity (IEC)

Water content studies of the composite membranes were carried out by measuring the change in weight of the composite membranes before and after hydration using an electronic scale (AR3130, Ohaus Corporation, USA). The OH^- form composite membranes were immersed in deionized water at room temperature and equilibrated for more than 48 h. The weight of the wet composite membrane was determined after removing excess surface water. Then the wet membrane was dried under vacuum at a fixed temperature of 60 °C until a constant dry weight was obtained. The percentage water content W_c was calculated using the following relation:

$$W_c\ (\%) = \frac{m_h - m_d}{m_d} \times 100 \tag{1}$$

where m_h is the mass (g) of a wet membrane and m_d is the mass (g) of a dry membrane.

The ion exchange capacity was measured using the classical titration method. The composite membranes were soaked in a large volume of 0.1 M NaOH solution to convert them into the OH^- form. They were washed with deionized water to remove excess NaOH and then equilibrated with 100 mL of 0.1 M HCl solution for 48 h. The IEC values were determined from the reduction in acid measured using back titration. The IEC values (mequiv. g^{-1}) were obtained from the following equation:

$$\text{IEC}\ (\text{mequiv. g}^{-1}) = \frac{M_{o,HCl} - M_{e,HCl}}{m_d} \tag{2}$$

where $M_{o,HCl}$ is the milliequivalents (mequiv.) of HCl required before equilibrium, $M_{e,HCl}$ is mequiv. of HCl required after equilibrium, and m_d is the mass (g) of the dried membrane.

2.4. Methanol permeability

The methanol permeability was measured using a diffusion cell comprising two compartments. Magnetic stirrers were used in each compartment to ensure uniformity during the experiments. The membrane was clamped between the two compartments. One compartment was loaded with deionized water and the other with a solution containing 1 M methanol and 0.5 M KOH. The concentration of the permeating methanol was measured by gas chromatography (GC-950, Shanghai Haixin Chromatographic Instruments Co., Ltd.).

2.5. Ion conductivity

The ion conductivity of the membranes was measured by two-probe AC impedance spectroscopy with Parstat 2273 electrochemical equipment (Princeton Advanced Technology, USA) over the frequency range from 0.1 to 1 MHz. Before testing, the OH^- form membranes were hydrated in deionized water for at least 48 h. The testing device with the membrane was placed in a chamber with deionized water to keep the relative humidity at 100% during the measurements.