

Surface-modified Y zeolite-filled chitosan membrane for direct methanol fuel cell

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Abstract

Hybrid membranes composed of chitosan (CS) as organic matrix and surface-modified Y zeolite as inorganic filler are prepared and their applicability for DMFC is demonstrated by methanol permeability, proton conductivity and swelling property. Y zeolite is modified using silane coupling agents, 3-aminopropyl-triethoxysilane (APTES) and 3-mercaptopropyl-trimethoxysilane (MPTMS), to improve the organic–inorganic interfacial morphology. The mercapto group on MPTMS-modified Y zeolite is further oxidized into sulfonic group. Then, the resultant surface-modified Y zeolites with either aminopropyl groups or sulfonicpropyl groups are mixed with chitosan in acetic acid solution and cast into membranes. The transitional phase generated between chitosan matrix and zeolite filler reduces or even eliminates the nonselective voids commonly exist at the interface. The hybrid membranes exhibit a significant reduction in methanol permeability compared with pure chitosan and Nafion117 membranes, and this reduction extent becomes more pronounced with the increase of methanol concentration. By introducing $-\text{SO}_3\text{H}$ groups onto zeolite surface, the conductivity of hybrid membranes is increased up to $2.58 \times 10^{-2} \text{ S cm}^{-1}$. In terms of the overall selectivity index ($\beta = \sigma/P$), the hybrid membrane is comparable with Nafion117 at low methanol concentration (2 mol L^{-1}) and much better (three times) at high methanol concentration (12 mol L^{-1}).

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1. Introduction

Direct methanol fuel cell (DMFC), as a novel energy conversion device, is attractive for transportation and portable power generator applications due to its high energy density, simplified system design, convenient storage, recharge and transport of fuels [1]. Polyperfluorosulfonic acid ionomer initially developed by DuPont and successfully used in H_2/O_2 fuel cell, NafionTM, is currently the most commonly utilized proton exchange membrane (PEM) for DMFCs because of its superior chemical stability and high proton conductivity. However, one of the main drawbacks of the NafionTM series membranes is the severe methanol crossover from anode to cathode, resulting in not only a serious reduction in the cell efficiency caused by methanol–oxygen mixed potential at the cathode, but also a considerable decrease in fuel utilization effi-

ciency [2,3]. Alternative PEMs with low methanol permeability and high proton conductivity as well as low swelling, low cost and low toxicity are certainly expected for DMFC exploitation.

Reduction of methanol crossover through PEMs can be achieved by two routes: rational selection or invention of membrane materials, and appropriate manipulation of membrane morphology [4–6]. If a methanol-rejecting and proton conducting DMFC membrane could be viewed as a $\text{H}^+(\text{H}_2\text{O})$ /methanol separation media, membrane materials with excellent alcohol/water separation ability would be considered as appropriate candidates. As a matter of fact, in the field of membrane pervaporation for dehydration of alcohols, many hydrophilic polymers, such as chitosan and polyvinyl alcohol, have been widely used due to their preferential affinity towards water [7–9]. Chitosan is a polysaccharide prepared by the deacetylation of chitin that mainly obtained from the crab and shrimp shells [10]. Due to the inherent characteristics such as hydrophilicity, biocompatibility, antibacterial properties, remarkable affinity towards certain substances and facile film formation, chitosan has been grad-

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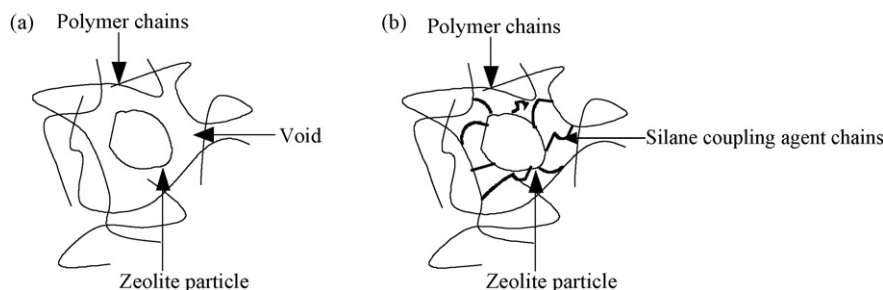


Fig. 1. Schematic illustration of polymer-filled interfacial morphology: (a) voids and (b) transitional phase at interface.

usually regarded as a kind of promising material for membrane fabrication.

Herein, chitosan is chosen as the polymer matrix considering its excellent alcohol-rejecting performance. However, in its normal state, chitosan film has very low conductivity and high degree of swelling [11]. Serious swelling would induce disentanglement within the polymer matrix, thus facilitating the permeation of methanol and water as well as that of the proton to some extent [12,13], resulting in a loss of $\text{H}^+(\text{H}_2\text{O})$ /methanol selectivity. To reduce the swelling degree, chitosan was usually either cross-linked with sulfuric acid or other polyelectrolytes [14,15], or incorporated with some inorganic particles such as silica, zeolites, zirconia and montmorillonite [16–19]. Among these inorganic particles, zeolite, unique for its molecular sieving effect, is attracting considerable research interest due to its well-defined open crystal structures with a pore size of several angstroms, low cost and flexible configurations.

For polymer–zeolite hybrid membranes, the membrane morphology and polymer–inorganic interfacial property are crucial to methanol permeation [20]. Researchers found that when the polymer is in glassy state under preparation or application conditions, nonselective or less selective voids are often present at the interface between the polymer phase and the external surface of zeolite as shown in Fig. 1(a) [21–23]. It is thus reasonable to expect a reduction in methanol crossover by improving the interfacial morphology. In a previous study, plasticizer was used to enhance the polymer–inorganic compatibility by increasing the polymer (chitosan) chain flexibility and thus reducing the stress arisen during the membrane formation process [24]. In this study, another approach involving zeolite surface modification was introduced in hope to create an additional transitional phase between polymer and inorganic phase as schematically illustrated in Fig. 1(b). Two functional organotriethoxysilanes either with $-\text{SH}$ or $-\text{NH}_2$ groups were selected as the modifiers due to their capability of co-condensing with the hydroxyl groups on zeolite surface. Some studies have confirmed the effectiveness of use of silane coupling reagents in membrane preparation for separation and DMFC [25–29]. Sulfuric acid was used as an effective cross-linker for chitosan matrix to prohibit its excess swelling and, meanwhile, to protonate the amino groups on chitosan, endowing the polymer with higher conductivity. In addition, to further increase the membrane conductivity, mercaptosilane-modified zeolite was further oxidized to attach additional $-\text{SO}_3\text{H}$ groups and then incorporated into chitosan bulk to fabricate the membranes. The chemical and physical

properties of the hybrid membranes were characterized and their methanol permeability and proton conductivity were thoroughly investigated.

2. Experimental

2.1. Materials and chemicals

Chitosan (CS) with a degree of deacetylation of 91% was supplied by Zhejiang Golden-shell Biochemical Co. Ltd. NaY zeolite with a Si/Al ratio of 2.50 was purchased from Shanghai Xinnian Shihua Co. Ltd. 3-Aminopropyl-triethoxysilane (APTES) and 3-mercaptopropyl-trimethoxysilane (MPTMS) were purchased from Power Chemical Corporation. Acetic acid, sulfuric acid and methanol were purchased locally. De-ionized water was used throughout the study.

2.2. Surface modification of NaY zeolite

Surface modification of NaY zeolite by organotriethoxysilane was carried out according to the procedure described in the literature [30]: NaY zeolite (1.4 g) and NH_4NO_3 aqueous solution (700 mL, 1 mol L^{-1}) were mixed under stirring at 80°C for 12 h. The zeolite was then filtered and rinsed with de-ionized water till electric neutrality and dried at room temperature followed by calcination at 500°C for 6 h to fully convert NaY into HY form.

HY zeolite, APTES and toluene (mass ratio 1:2:20) were refluxed under stirring at 110°C for 24 h. The zeolite was filtered and rinsed with both ethanol and water to remove the silane residues. The resulting APTES-modified zeolite was dried and denoted as H_2NY zeolite.

For MPTMS-modified zeolite, the above-mentioned procedure was followed except that MPTMS was used instead of APTES. The resulting zeolite with $-\text{SH}$ groups, denoted as HSY, was further oxidized at 25°C in 30 wt.% H_2O_2 solution for 24 h to convert the $-\text{SH}$ groups into $-\text{SO}_3\text{H}$ groups (HO_3SY zeolite).

2.3. Membrane preparation and pretreatment

Chitosan was dissolved in 2 wt.% aqueous acetic acid to acquire a 2 wt.% concentration by stirring at 80°C . A desired amount of zeolite was then added to the above solution and stirred at 80°C for 2 h followed by dispersion under ultrasonic for 1 h. After filtration and degasification, the resulting homoge-

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