

Formation and evaluation of interpenetrating networks of anion exchange membranes based on quaternized chitosan and copolymer poly(acrylamide)/polystyrene



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ABSTRACT

A high-strength anion exchange membrane with a full interpenetrating network (full-IPN) structure was prepared from quaternized chitosan (QCS), polyacrylamide (PAM) and polystyrene (PS). The influences of the component content of the membrane and crosslinking degree of the QCS on the mechanical properties, anionic conductivity as well as methanol permeability of the membranes were investigated. The results indicated that the full-IPN structure as well as the presence of the hydrophobic PS could improve the mechanical properties and decrease the methanol permeability of the membrane. Corresponding to the increase in the content of PAM/PS (the molar ratio of PAM/PS was 1:1) from 0 wt.% to 40 wt.% in the full-IPN membrane, the tensile stress was increased from 30.1 MPa to 43.9 MPa, the methanol permeability was decreased from $6.64 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ to $6.54 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, respectively. Anionic conductivities of 6.00×10^{-3} – $1.26 \times 10^{-2} \text{ S cm}^{-1}$ were achieved at 80 °C for the obtained membranes. To the membranes with a QCS content of 60 wt.%, the conductivity and tensile stress of about 90% were maintained after soaking the membranes in 1 mol L^{-1} KOH for 120 h, and a 10 mol L^{-1} KOH for 50 h at room temperature, respectively.

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1. Introduction

In recent years, many efforts have been devoted to develop anion exchange membranes (AEMs) for direct methanol alkaline fuel cells (DMFCs) [1–12]. The basic working medium of the AEMs brings about benefits for the DMFCs [2,13,14], which includes: enhanced electro kinetics with the potential for use of non-noble metal catalysts, such as Ag [15]; low alcohol permeability [16]; and improved water management [17]. However, the performance of the fuel cells based on AEMs is inferior to that based on proton exchange membranes due to the needs of superior properties of the AEMs on conductivity, mechanical strength and chemical stability. Therefore, efforts towards improvement of the AEMs are still required.

The AEMs are generally prepared by quaternization of the polymers. For example, quaternary ammonium salts based on polysiloxane [18], poly (oxyethylene) methacrylates [19], polyethersulfone cardo [20], poly (phthalazinone ethersulfone ketone) [21], poly (vinylidene fluoride) (PVDF) and poly (tetrafluoroethane–hexafluoro propylene) (FEP) [14], and chitosan [8,22,23], have been developed to be used as the membrane electrolyte for fuel cells. However, there are some challenges to apply the AEMs in fuel cells practically [24,25]. For

instance, polymers with a high quaternization degree are normally needed in order to obtain an acceptable conductivity [26–28]. However, the highly quaternized polymer membranes may have an excessive water uptake thus bringing on a significant swelling and a deteriorated mechanical strength of the membrane [29]. Meanwhile, serious methanol crossover will be accompanied with the membrane swelling. In general, crosslinking of the polymer chains is a widely used method to reduce the swelling and to improve the strength as well as the stability of the AEMs [30–38]. However, it was found that crosslinking of the polymer is not always efficient. For instance, chitosan is a natural and cheap polymer, which is easy to perform the quaternization. However, both the quaternization and crosslinking occur on the sites of $-\text{NH}_2$ and $-\text{OH}$ groups [22,37,38], which results in a compromise between the conductivity and the mechanical property. Therefore, preparation of composite membranes of quaternized chitosan (QCS) with other polymers [39], employment of supporting meshes [40], and preparation of the membranes with interpenetrated polymer network (IPN) [24,25, 41] are reported to enhance the mechanical strength of the QCS membranes over the crosslinking.

Interpenetrating network (IPN) is defined as a combination of two or more polymers in network form, at least one of which is polymerized and/or cross-linked in the immediate presence of the other. An IPN is a unique type of polymer alloy consisting of two (or more) crosslinked polymers containing essentially no covalent bonds or grafts between

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them [42–45]. The membranes with the interpenetrated network structure are expected to exhibit superior properties than each component material. The IPN can be prepared by simultaneous polymerization, sequential polymerization or latex blending technique [46,47]. In general, phase separation usually occurs during formation of the IPN due to the immiscibility of the multi-components. Therefore the processing of the IPN network structure is normally formed in an emulsion system.

In this work, the full-IPN technology was introduced to prepare the anion exchange composite membrane in order to achieve the membrane with enhanced mechanical strength and stability, low fuel permeation, and meanwhile acceptable conductivity. The QCS was chosen as the conductors of hydroxide ions to fabricate the membrane with full-IPN structure aiming at high mechanical property with low crosslinking degree since both the quaternization and cross-linking of QCS take place on the sites of $-\text{NH}_2$ groups [8]. The other polymer network was formed based on the block polymer of polystyrene (PS) and polyacrylamide (PAM). The hydrophobic PS was employed due to its resistance to methanol permeation, good chemical stability, and assistance for membrane formation. In order to provide amino groups for crosslinking and make the QCS having enough active sites for quaternization as well as to control a suitable phase separation from hydrophobic PS and hydrophilic QCS for ion conduction, monomers of acrylamide (AM) was introduced into the polymerization process of PS to form the block polymer of PAM/PS. The full-IPN structure was obtained through crosslinking reactions with glutaraldehyde (GA) as the cross-linker. The aldehyde groups ($-\text{CHO}$) in GA could react with the amino groups ($-\text{NH}_2$) of block polymer (PAM/PS), hydroxyl groups and/or amino groups ($-\text{NH}_2$) of QCS. Therefore the full-IPN structure could be formed randomly among the polymer chains as illustrated in Fig. 1. The membrane properties including conductivity, ion exchange capacity (IEC), water uptake, methanol permeability, mechanical property, thermal behavior, and alkaline stabilities were investigated to evaluate their applicability in DMFCs.

2. Experimental

2.1. Materials

(2, 3-epoxypropyl) trimethylammonium chloride (EPTMAC, purity $\geq 95\%$) was purchased from Shandong GuoFeng Fine Chemistry Factory. Chitosan, aqueous glutaraldehyde (GA, 50 wt.%), AM and styrene were obtained from China National Medicines Corporation Ltd. All the reagents used were of analytical grade. The deacetylation degree of the chitosan was 95%, which was determined with a titration method [48]. A certain amount of dried chitosan was dissolved in a standard solution of hydrochloride acid at room temperature under stirring to neutralize the acetamides contained in the chitosan structure. The excess acids were titrated with a standard sodium hydroxide solution to obtain the deacetylation degree of the chitosan according to the reacted acids with chitosan. The monomer styrene was pretreated with aqueous NaOH to remove the inhibitor and stored in a refrigerator until use. The QCS chloride was synthesized by quaternization of chitosan in isopropanol with EPTMAC at 85°C for 10 h. The product was isolated by evaporation of the solvent and dried at 85°C in a vacuum oven till a constant weight was reached [49]. The quaternization degree of QCS was determined by titration of the chloride ions with a standard silver nitrate solution using potassium chromate (K_2CrO_4) as an indicator [50], and the QCS with a quaternization degree of $49.8 (\pm 3.5)\%$ was used throughout.

2.2. Methods

2.2.1. Membrane preparation

In a 100 mL round-bottom flask equipped with a magnetic stirrer and a condenser, 2.0 g QCS chloride was dissolved in 40 mL 2% (v/v) acetic acid aqueous solution in N_2 atmosphere at room temperature. A certain amount of AM and styrene monomers (the molar ratio of

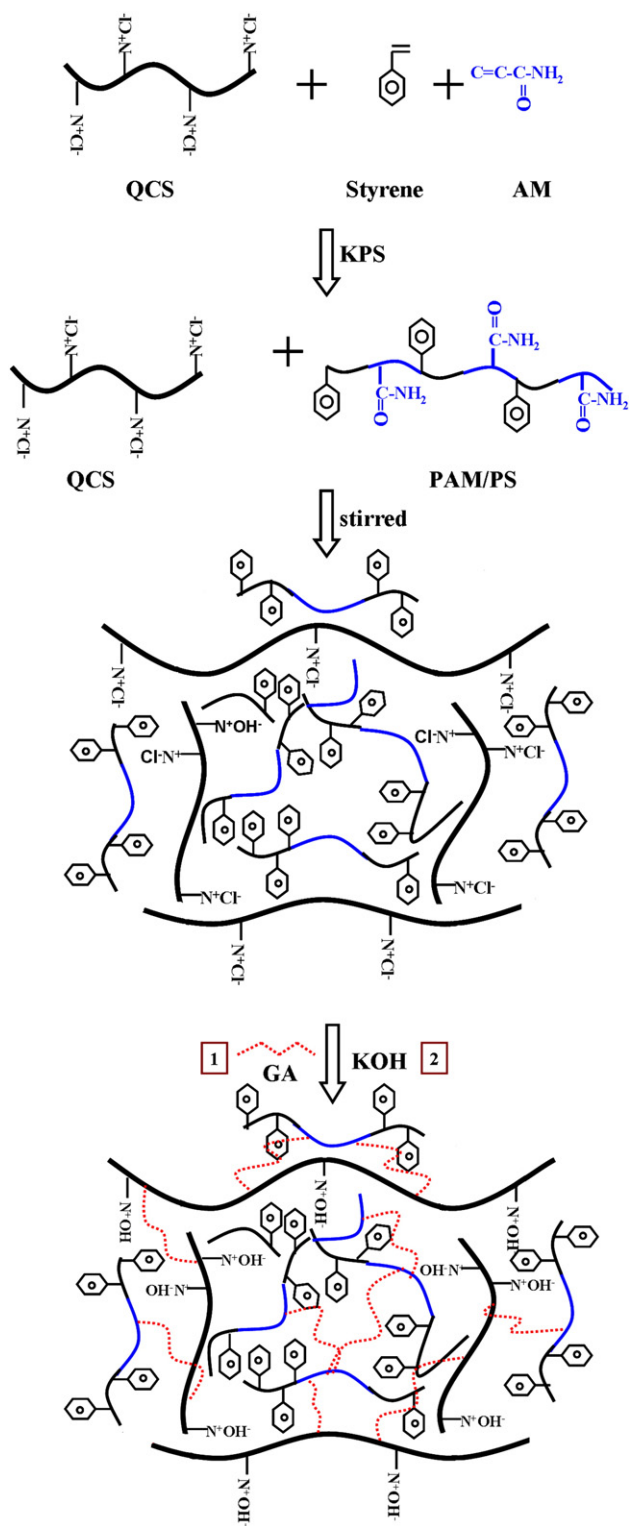


Fig. 1. Schematic diagram of preparation of full-IPN anion exchange membranes.

AM and styrene was 1:1) were added into the flask under stirring. The mixture was first stirred at room temperature for 1 h, afterwards sonicated for 30 min. The resulting solution was then heated to 80°C under N_2 atmosphere. 10 mL 1.6 wt.% potassium persulfate (KPS) initiator was added dropwise into the mixture in four times with an interval of 1.5 h to initiate the polymerization of the styrene and AM. The mixture was afterwards stirred at 80°C for 6 h under

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