



# Preparation and properties of organic–inorganic alkaline hybrid membranes for direct methanol fuel cell application

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## ABSTRACT

A series of organic–inorganic alkaline hybrid membranes were prepared based on crosslinked quaternized chitosan (QCS, the quaternization degree (DQ) of the QCS was  $80.8 \pm 3.5\%$ ) with different contents of tetraethoxysilanes (TEOS) for alkaline direct methanol fuel cells (ADMFC). These hybrid membranes were characterized by Fourier-transform infrared (FT-IR), thermo gravimetric analysis (TGA). The ion exchange capacity (IEC), water uptake, alkaline stability, methanol permeability and mechanical properties of the membranes were also investigated to evaluate their applicability in ADMFC. The results showed that the anionic conductivities of the hybrid membranes at a level of  $10^{-2} \text{ S cm}^{-1}$  were obtained at  $80^\circ\text{C}$ . The methanol permeability of the membranes was in a range from  $7.5 \times 10^{-6}$  to  $1.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ . The obtained anion exchange membranes (AEM) were stable up to  $200^\circ\text{C}$  in atmosphere according to the TGA analysis. The tensile strength and elongation at break of the membranes were in a range from 15.78 to 27.56 MPa and 10.32% to 3.21% at room temperature, respectively. The results of alkaline stability show that a tensile strength about 20.0 MPa was maintained after immersing the hybrid membrane in a  $10 \text{ mol L}^{-1}$  KOH solution at room temperature for more than 96 h.

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## 1. Introduction

Direct methanol fuel cells (DMFC) represent one of the most attractive power sources because of their stability at relatively low temperatures, high energy density, and operation simplicity [1,2]. One of the vital components of the DMFC is the conductive membrane, which serves as a physical separator between the anode and the cathode with the function of transporting ions and blocking electrons. For a polymer electrolyte membrane to be a candidate for DMFC the following criteria should be met: (i) adequate chemical and electrochemical stability, (ii) high conductivity to enable high current densities and low internal resistance, (iii) low permeability to reactants and products, and (iv) good mechanical stability. Nowadays, the most popular proton exchange membrane (PEM) for DMFC is Nafion, which is a perfluorinated polymeric membrane developed by DuPont in the late 1960s [3]. The working circumstance of the DMFC with Nafion membrane is acidic. However, the acidic DMFC has faced several serious problems: (1) slow methanol oxidation kinetics [4–6], (2) the poisoning of CO intermediate on the Pt surface [7], (3) the high methanol cross-over through the polymer membrane [8–11], and (4) the high costs of the Nafion membrane and Pt catalyst, which have obstructed the commercialization of DMFC. Many efforts, therefore, have been directed towards developing new types of polymer electrolyte membranes for DMFCs. Besides unceasingly exploring new types of proton exchange membranes, anion-exchange membrane (AEM) [12–25] has also aroused

new interest in recent years. This type of membrane works under basic circumstance, where the electrochemical reactions are more facile than in acidic medium, and non-noble metals can be used as catalyst, making the fuel cell more cost effective [26]. Even though there are more and more research focused on the AEM. Unfortunately, until now no commercially available AEM as Nafion does in the field of PEM. For anion exchange membrane fuel cells (AEMFC) applications, AEM needs necessary conductivity, mechanical strength and chemical stability.

As one of the most abundant natural polymers, chitosan has been chosen as the polymer matrix to prepare membrane electrolyte due to its excellent membrane properties, low cost and the feasibility to be modified easily with functional groups in the structure. The quaternization of chitosan can be performed with such as (2, 3-epoxypropyl) trimethylammonium chloride (EPTMAC) by conversion the amino groups into 2-hydroxypropyltrimethyl ammonium chloride [27]. The anion exchange conductor of quaternized chitosan (QCS) is thus obtained by replacement of the chloride ions with hydroxide ions. The high DQ of chitosan results in not only high ionic conductivity, but also significant swelling of the QCS membranes and therefore worse membrane strength. To reinforce the strength of the chitosan based membranes, dialdehydes such as glyoxal [28–30] and glutaraldehyde (GA) [30,31] are normally used to perform the crosslinking. The stable imine bonds between amine groups of the chitosan polymer and the aldehydic group of the glutaraldehyde is then formed [32,33]. However, it was found that crosslinkage is not an effective method to improve the properties of membrane when the quaternization degree of QCS is above 35% due to too high swelling and poor mechanical properties of

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the resultant membranes [31]. Therefore, attempts have also been made to develop AEM by preparation of chitosan composite membranes with other polymers [34] or additives [35,36]. With the aim of enhancement of the mechanical strength of the polymer membranes, a technology has been developed to fabricate composite membranes with inorganic additives of so-called organic–inorganic hybrid membrane [37–43]. Organic–inorganic hybrid materials have been regarded as promising materials for many applications due to their unique performance to combine the remarkable functionality of organic materials with the stability of inorganic materials [44,45]. In PEM fuel cell field, many organic–inorganic hybrid membranes have also been prepared [46–51]. The results showed that the tendency for addition of inorganic materials into the organic polymers are: (1) to reduce the transport channel for methanol resulting in a decrease in the methanol permeability; (2) to enhance the thermal stability and intensity of the membranes; (3) to increase the ion conductivity [52]. However, the similar research in AEM field for DMFC was not “booming”, moreover the organic polymer with high degree of quaternization (DQ) (DQ  $\geq$  50%) was taken as the materials were seldom. Therefore, in this paper we propose a route to prepare a series of organic–inorganic hybrid membranes with organic polymer (QCS, DQ = 80.8  $\pm$  3.5%) and inorganic filler (silica) via sol-gel reaction using TEOS as a precursor. By adding a desired amount of TEOS, a series of hybrid anion exchange membranes with different silica contents have been synthesized. The characteristics of the membranes were evaluated for potential application in alkaline DMFC.

## 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.%) and tetraethoxysilane (TEOS, SiO<sub>2</sub>  $\geq$  28%) were obtained from China National Medicines Corporation Ltd. The deacetylation degree of the Chitosan was 95%, which was determined according to the reference [53]. All the reagents used were analytical grade. The QCS in chloride form was synthesized by quaternization of chitosan in isopropanol with EPTMAC at 85 °C for 10 h and it was afterwards isolated and purified according to the reference described elsewhere [54]. The quaternization degree of the QCS was 80.8 ( $\pm$  3.5) %, which was determined by titration with a standard AgNO<sub>3</sub> solution [55]. The same quaternization degree of QCS was hereafter used for all the membrane preparation.

### 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 chloride form QCS (DQ = 80.8 ( $\pm$  3.5) %) was dissolved in 40 mL 2% (v/v) acetic acid aqueous solution in nitrogen atmosphere at room temperature. Then a required amount of TEOS and 10 mL of ethanol was added into the solution and the mixture was stirred for 1 h at 30 °C to obtain a clear homogeneous solution. Afterward a mixture of ethanol (5 mL) and distilled water (10 mL) containing 0.1 wt.% HCl was slowly added to the solution under continuous stirring. A given amount of crosslinker glutaraldehyde (GA, 2%, v/v) aqueous solution was then added dropwise to the mixture at a feeding rate of 0.5 mL min<sup>-1</sup> to crosslink the QCS (in this research the amount of GA was 0.2 wt.% in all membranes). The mixture was stirred at room temperature for 1 h and it was then sonicated for another 30 min. The resultant mixture was poured onto a glass plate and the solvent was then evaporated in an oven at 40 °C until a constant weight was reached. The alkaline doping of the membranes was performed by immersing the membranes in 1.0 mol L<sup>-1</sup> KOH solution at room temperature for 24 h. The membranes were then washed thoroughly with de-ionized water and dried at 40 °C until a constant weight was reached

to obtain the hydroxide form membranes. By varying the ratio of SiO<sub>2</sub> to QCS, different organic–inorganic hybrid membranes with 3, 6, 9, 12 and 15 wt.% SiO<sub>2</sub> were prepared. The hybrid membranes were designated as M-X, where X is the SiO<sub>2</sub> content (wt.%) in the membrane phase.

#### 2.2.2. Instruments and techniques

The FT-IR spectra of the membrane samples were recorded on a Perkin-Elmer spectrum One (B) spectrometer (Perkin-Elmer, America) and all the samples were prepared as KBr pellets. Thermo gravimetric analysis (TGA) was performed on a TGA 290C analyzer (Netzsch Company, Germany) at a heating rate of 10 °C min<sup>-1</sup> under air atmosphere. The mechanical strength of the dry membranes was determined with an instrument CMT6502 (SANS Company, China). Dumbbell-shaped membrane samples of 25 mm  $\times$  4 mm were prepared and the measurements were carried out by setting a constant separating speed of 5.00 mm min<sup>-1</sup> under the ambient atmosphere. The tensile stress at break  $E$  was calculated by Eq. (1) [56].

$$E = \frac{F}{A_0} \quad (1)$$

Where  $F$  is the applied force at break,  $A_0$  is the initial cross-section area of the sample which is equal to  $4 \times L$  mm<sup>2</sup>, and  $L$  is the thickness of the membrane.

#### 2.2.3. Water uptake and swelling of the membranes

The membrane samples were soaked in de-ionized water for 24 h at room temperature to monitor the variations on weight of the wet membranes. The weight of the wet membrane ( $P_{\text{wet}}$ ) was measured rapidly after wiping the excessive surface water with a tissue paper, and that of the dry membrane ( $P_{\text{dry}}$ ) was obtained by drying the samples at 50 °C in a vacuum oven until a constant weight was reached. The water uptake and the swelling of membranes were determined by Eq. (2):

$$\text{Water uptake or swelling}(\%) = \frac{P_{\text{wet}} - P_{\text{dry}}}{P_{\text{dry}}} \times 100\% \quad (2)$$

#### 2.2.4. Ion exchange capacity

The anion exchange membrane in hydroxide form was washed thoroughly with distilled water and then dried in a vacuum oven at 60 °C to reach a constant weight ( $w_{\text{OH}}$  in gram). It was afterwards immersed in a 0.1 mol L<sup>-1</sup> HCl standard solution at ambient temperature for 48 h under stirring to neutralize the hydroxide ions contained in the membrane. The mole number (equivalent) of the neutralized hydroxide ions ( $n$ ) was determined by titration of the remanent acid with a 0.1 mol L<sup>-1</sup> KOH standard solution. The ion exchange capacity (IEC) of the anion exchange membrane, termed as milli-equivalents (meq) of hydroxide ions per gram of the dry hydroxide form membrane, was obtained by calculation with Eq. (3) [57].

$$\text{IEC}(\text{meq g}^{-1}) = \frac{1000n}{w_{\text{OH}}} \quad (3)$$

#### 2.2.5. Anionic conductivity

The anionic conductivity measurement cell has been described elsewhere [58]. The conductivity of the membrane was measured by using alternating current (AC) with a frequency of 2 KHz supplied via a pair of platinum electrodes. The resistance between the two electrodes was measured with and without the membrane, respectively, to obtain the resistance of the membrane ( $R_M$ ) by comparing the difference. In order to keep that the electrodes were held at a fixed distance apart the mini-gasket was used under the without membrane to cover the distance, which presents the thickness of the membrane, between the

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