



Nanocomposite membranes based on quaternized polysulfone and functionalized montmorillonite for anion-exchange membranes



Xiaofeng Liao, Li Ren, Dongzhi Chen, Xiaohong Liu, Hongwei Zhang*

College of Materials Science and Engineering, Wuhan Textile University, Wuhan 430073, PR China

HIGHLIGHTS

- QPSF/functionalized MMT hybrid membranes for AEMFCs were prepared.
- The AEM containing 5% functionalized MMT showed the best composite performance.
- The highest hydroxide ion conductivity of 4.73×10^{-2} S/cm was achieved at 95 °C.

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ABSTRACT

In this paper, functionalized montmorillonite is intercalated with cetyl trimethyl ammonium chloride and (3-aminopropyl)triethoxysilane. Quaternized polysulfone/functionalized montmorillonite nanocomposite membranes are fabricated to evaluate their potential in anion-exchange membrane fuel cells. Fourier transform infrared spectroscopy, thermogravimetric analyzer and X-ray diffractometer are used to confirm the success of intercalation. The performances of the composite membranes for the anion-exchange membrane fuel cells in terms of their water uptake, mechanical property and ionic conductivity are investigated. Compared with other anion-exchange membranes, the nanocomposite membrane containing 5% montmorillonite modified by cetyl trimethyl ammonium chloride exhibits lower water uptake, higher ultimate stress and larger ionic conductivity. It exhibits an ionic conductivity of 4.73×10^{-2} S cm⁻¹ at 95 °C.

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1. Introduction

Proton-exchange membrane fuel cells (PEMFCs) have been intensively studied in the past decade, but their commercialization is still obstructed by poor durability and high cost [1]. Under these conditions, anion-exchange membrane fuel cells (AEMFCs) are attracting more and more attention, because they have the potential to offer significant performance advantages over PEMFCs, centering on increased material stability at high pH, electrocatalytic activity in alkaline conditions, and fuel choices in basic environments. Meanwhile, they could also decrease the fuel crossover rates and potentially improve the water management [2].

Despite their growing importance of AEMs for application in fuel cells, AEMs have much less reports than PEMs. Moreover, a majority of reports about AEMs is focused on the development of

novel polymer materials with functional groups different from quaternary ammonium [3–21]. Based on a wealth of experience in developing PEMs, it is well-known that another strategy for developing AEMs should be considered, namely, modification to existing polymers. And although modified montmorillonite (MMT) have been used in PEMs, the incorporation of them into AEMs is still scarce.

In this work, we adopted the quaternized polysulfone (QPSF), which had good mechanical and conducting performances [22], and the functionalized MMT to fabricate nanocomposite membranes for AEMFCs. The effect of functionalized MMTs on the properties of nanocomposite membranes was synthetically studied.

2. Experimental

2.1. Chloromethylation of polysulfone

Polysulfone was chloromethylated using chloromethyl ether. A

* Corresponding author.

E-mail address: hanqiujiang@163.com (H. Zhang).

typical example is as follows: Polysulfone (Udel P3500, Solvay) was dissolved in dichloromethane and then treated with chloromethyl ether in the presence of anhydrous tin chloride (SnCl_4) at $30\text{ }^\circ\text{C}$ for 40 min to obtain the chloromethylated polysulfone (CMPSF).

2.2. Functionalization of montmorillonite

In order to modify MMT, two intercalating agents were employed. One was the cetyl trimethyl ammonium chloride (CTAC), the other was the (3-aminopropyl)triethoxysilane (APTES). When CTAC was used, the intercalation procedure was as follows (Scheme 1a): At first 2 g MMT powders was added in deionized water and dispersed homogeneously by vigorous stirring for 12h, subsequently 0.02 mol CTAC was added into the MMT suspension. After being stirred for 12 h at $80\text{ }^\circ\text{C}$, the resulting mixture was filtered and washed thoroughly with deionized water until chlorine ion was removed (silver nitrate test). At last, the product was dried in a vacuum oven at $80\text{ }^\circ\text{C}$ for 24 h. The resulting MMT with long hydrophobic alkyl group was designated as MMT-1.

When APTES was used, the reaction was carried out as follows (Scheme 1b): At first 2g MMT powders was suspended into 200 ml ethanol solution (72%) and vigorously stirred for 6 h at $40\text{ }^\circ\text{C}$. Subsequently, 2.4 ml APTES was dropped into the MMT suspension and the mixture was refluxed gently with stirring for 24 h at $80\text{ }^\circ\text{C}$. The functionalized MMT grafted with amino groups was filtered and washed several times with deionized water. The corresponding MMT with hydrophilic groups was designated as MMT-2.

2.3. Preparation of QPSF membrane and QPSF/functionalized MMT hybrid membranes

The QPSF membrane was fabricated by solution casting. At first, the CMPSF was dissolved in dimethylacetamide (DMAc) to make a 15% w/v solution, stirred, filtrated and casting. Then the obtained film was dried under vacuum at $80\text{ }^\circ\text{C}$ for 24h. The resultant membrane was immersed into 30 wt% trimethylamine (TMA) solution for 24h to induct quaternary groups into the membrane (QPSF), thereafter, the membrane was put into 1M KOH solution for 24 h, and the alkaline QPSF (QPSF-OH) membrane was obtained. At last, the QPSF-OH membrane was washed several times with distilled water, and naturally dried under ambient environment to avoid great shrinkage with water losing. The ionic exchange capacity (IEC) of QPSF-OH membrane was 1.31 mmol g^{-1} , which was determined by the back titration method.

The hybrid QPSF membranes were also fabricated by solution casting. Firstly, MMT or organo-MMT of a prescribed weight was blended with CMPSF/DMAc (15% w/v) solution and the mixture was stirred for 24 h at room temperature. After treated 1h in ultrasonic, the solution was dropped in TMEDA (0.1 mL/10g casting solution)

and kept vigorous stirring for 1 min. Then it was spread on a glass plate with a glass knife. The film was dried under vacuum at $80\text{ }^\circ\text{C}$ for 24h. The obtained hybrid membrane was treated with TMA, KOH solution and distilled water in turn. The resulting hybrid membrane was designated as QPSF/MMT or QPSF/MMT-x membrane, where x was the same number as MMT-x ($x = 1,2$).

3. Characterization methods

3.1. Infrared spectra and membrane morphology measurements

The Fourier transform infrared (FTIR) spectroscopy of powder samples were recorded using a VERTEX70 spectrometer. The surface of the sample was examined through a FE-SEM (Sirion 200). After the sample was dried, it was vacuum-deposited with a thin Pt film for the FE-SEM examination.

3.2. Thermogravimetric analysis

A TA Instruments thermogravimetric analyzer (TGA) instrument Perkin–Elmer TGA-7 was used to measure the content of modification reagent in functionalized MMT. Functionalized MMT samples for TGA analysis were heated to $800\text{ }^\circ\text{C}$ from room temperature at $20\text{ }^\circ\text{C min}^{-1}$ under nitrogen atmosphere.

3.3. XRD measurement

X-ray diffractometer (X'Pert PRO) was adopted to determine the change in d-spacing of MMT crystal before and after the intercalation. Cu K α ($\lambda = 1.54\text{ \AA}$) was used as an X-ray source at d-generator voltage of 45 kV and current of 80 mA. Samples were scanned in 2θ ranges from 2° to 10° , in steps of 0.02° and counting time 2 s per step.

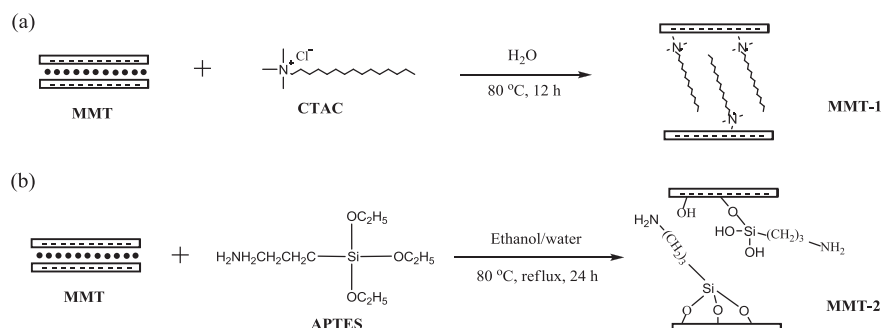
3.4. Mechanical properties

Tensile strength was measured by using INSTRWN5566 Mechanical Testing Machine. The membrane samples were cut into $0.5\text{ cm} \times 5.0\text{ cm}$ and examined at an elongation rate of 10 mm min^{-1} at room temperature. The tensile strength was calculated with the following equation:

$$\text{Tensile strength} = \frac{\text{Maximum load}}{\text{Cross sectional area}} \left(\text{N mm}^{-2} \right) \quad (1)$$

3.5. Water uptake

All membranes were vacuum dried at $120\text{ }^\circ\text{C}$ before water



Scheme 1. Schematic representation of modification processes of MMT.

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