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Hybrid anion-exchange membranes derived from quaternized polysulfone and functionalized titanium dioxide

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ABSTRACT

Polysulfone is modified via chloromethylation and TiO_2 is functionalized by three modification reagents (anionic surfactant, 1,3-propane sultone and Dopamine). Based them, a series of promising organic-inorganic hybrid membranes for anion-exchange membrane fuel cells have been prepared by incorporating functionalized TiO_2 submicrospheres into the chloromethylated polysulfone, subsequent quaternization and alkalization. The chloromethylation process is confirmed by Nuclear magnetic resonancespectra. The functionalization of TiO_2 is proved through Fourier transform infrared spectroscopy and Thermogravimetric analysis. The quaternization is testified by contact angle measurement. Associated characteristics of the hybrid membranes were investigated, including water uptake, swelling behavior, mechanical property and ion conductivity. Compared with other anion-exchange membranes, the hybrid membranes containing 5% TiO_2 with $-SO_3H$ groups exhibits higher ionic conductivity because of the acid-base ionic interactions between the inorganic filler and polymer chains. It demonstrates an ionic conductivity of 3.13×10^{-2} S/cm and an acceptable alkaline solution stability at 60 °C.

1. Introduction

Although significant advancements in proton-exchange membranes (PEMs) for fuel cells have been made in the past two decades, the commercialization of proton-exchange membrane fuel cells (PEMFCs) is still not viable because the high cost and low durability of their PEMs and electrocatalysts [1]. In order to evade these problems, more and more researchers pay attention to the anion-exchange membrane fuel cells (AEMFCs).

Compared with the PEMFCs, AEMFCs have many potential advantages, including increased materials stability at high pH (allowing for non-precious catalyst), increased electrocatalytic activity in alkaline conditions (particularly for organic fuels such as methanol or ethanol), increased fuel choices in basic environments (ammonia, borohydride), and decreased fuel crossover rates/potentially improved water management (arising from electro-osmotic drag and the flux of hydroxide ions in the opposite direction of protons in PEMFCs) [2].

As a newly developed field, AEMs had much less reports than PEMs. Moreover, most reports of AEMs centered on the synthesization of polymers with novel structures or functional groups different from quaternary ammonium[3–21]. From the exploration of PEMs, it could be learnt that the modification of the existing polymers is also an important strategy for developing AEMs.

As a consequence, we employed the quaternized polysulfone (QPSF), which had good mechanical and conducting performances [22], and the functionalized titanium dioxide (TiO_2) to fabricate nanocomposite membranes for AEMFCs. And the effect of different functional groups of TiO_2s on the properties of nanocomposite membranes was mainly investigated.

2. Experimental

2.1. Chloromethylation of polysulfone

Polysulfone was chloromethylated using chloromethyl ether (CME). A typical example was 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 °C for 40 min to obtain the chloromethylated polysulfone (CMPSF).

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2.2. Functionalization of TiO_2

In order to modify TiO_2, three modification reagents were employed, including the anionic surfactant (mixture of sodium dodecyl sulfonate and sodium stearate), 1,3-propane sultone and 3-hydroxytyramine hydrochloride (Dopamine).

When the anionic surfactant was used, the facile chemical adsorption procedure was as follows (Scheme 1a): At first a certain amount of TiO_2 powders was suspended in deionized water, subsequently the mixture of sodium dodecyl sulfonate and sodium stearate was added, lastly a small quantity of hydrochloric acid was dropped to keep pH around 2. Then the system was stirred vigorously for 2 h at 80 °C. The functionalized TiO_2 submicrospheres were collected by leaching, washed with distilled water until neutral and dried in a vacuum oven at 80 °C for 24 h. The corresponding functionalized TiO_2 sample was designated as TiO_2-1.

When the 1,3-propane sultone was used, the reaction was carried out as follows (Scheme 1b): At first a certain amount of TiO_2 powders was suspended in toluene, subsequently a large excessive 1,3-propane sultone was added in, lastly the mixture was refluxed gently with stirring for 24 h at 110 °C. The functionalized TiO_2 submicrospheres grafted with sulfonic acid groups were also collected by the same procedure as TiO_2-1. The final TiO_2 sample grafted with sulfonic acid groups was designated as TiO_2-2.

When the dopamine was used, the facile chelation procedure was as follows (Scheme 1c): At first a certain amount of TiO_2 powders was suspended in deionized water, subsequently a small quantity of hydrochloric acid was dropped to keep pH around 2, followed by vigorous stirring for 3 h at 25 °C. Lastly a large excessive dopamine was added in and keeping vigorous stirring for 1 h at 25 °C. The functionalized TiO_2 submicrospheres chelated with amino groups were collected by the same procedure as TiO_2-1. The final TiO_2 sample containing amino groups was designated as TiO_2-3.

2.3. Preparation of QPSF membrane and QPSF/functionalized TiO_2 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 and filtrated. Then the solution was cast onto a flat glass with a glass knife. The film was dried under vacuum at 80 °C for 24 h. The resultant membrane was immersed into 30 wt% trimethylamine (TMA) solution for 24 h to induct quaternary groups into the membrane (QPSF), thereafter, the membrane was put into 1 M 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.

Since the CMPSF with high degree of chloromethylation often led to excess swelling of QPSF-OH membranes, N,N,N′,N′-tetramethylethylenediamine (TMEDA) was added into the CMPSF/DMAc solution as crosslinking agent for forming partial crosslink in QPSF-OH membranes before casting. Hence the resultant QPSF-OH membrane was designated as cQPSF-OH membrane.

The hybrid QPSF membranes were also fabricated by solution casting. Firstly, TiO_2 or functionalized TiO_2 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 1 h in ultrasonic, the solution was dropped in TMEDA (0.1 mL/10 g 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 °C for 24 h. The obtained hybrid membrane was treated TMA, KOH solution and distilled water in turn. The resulting hybrid membrane was designated as QPSF/TiO_2 or QPSF/TiO_2-x membrane, where x was the same number as TiO_2-x (x = 1,2,3).

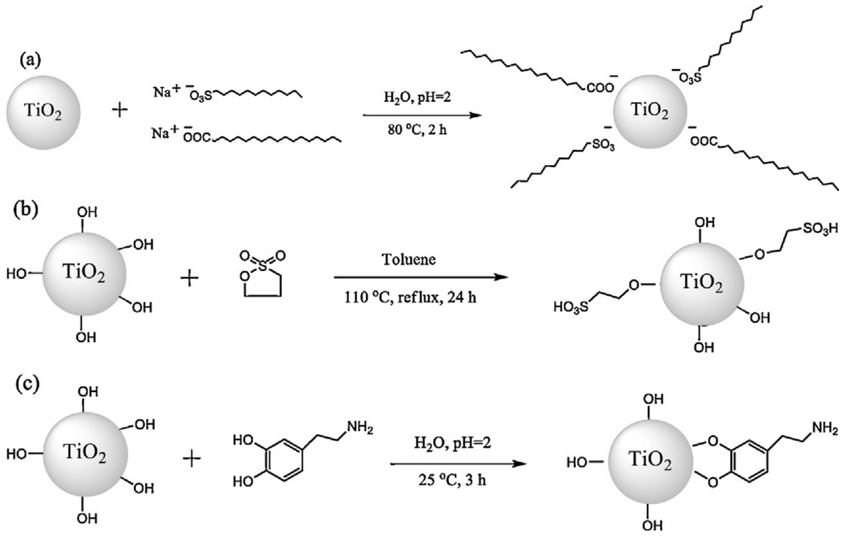
3. Measurements

3.1. Nuclear magnetic resonance (NMR) spectra

In order to study the molecular structure of the polymers and CMPSF degree of chloromethylation, ^1H NMR spectra of CMPSF were recorded using a BRUKER Avance DMX600 NMR spectrometer. Deuterated dimethylsulfoxide (DMSO-d6) as the solvent and tetramethylsilane as the internal standard.

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 TiO_2. Functionalized TiO_2



Scheme 1. Schematic representation of modification processes of TiO_2.