



Preparation of sulfonated zeolite ZSM-5/sulfonated polysulfone composite membranes as PEM for direct methanol fuel cell application



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ABSTRACT

Sulfonated ZSM-5 zeolite was successfully prepared by organo-functionalization method using poly (2-acrylamido-2-methylpropanesulfonic acid) and pAMPS. The modified ZSM-5 zeolite was characterized by TGA, EDX and XRD. The results showed that the organo-functional groups were incorporated onto the ZSM-5 surface. The structures of the modified ZSM-5/sulfonated polysulfone composite membranes were characterized by SEM. The SEM results showed a uniform and homogeneous distribution of the modified ZSM-5 zeolite in the sulfonated polysulfone matrix. The existence of the modified ZSM-5 in the sulfonated polysulfone, (with the degree of sulfonation equal to 70.57%) significantly improved the water uptake, proton conductivity, methanol permeability, and ion exchange capacity of the composite membranes relative to the pristine sulfonated polysulfone.

1. Introduction

Direct methanol fuel cell (DMFC) is one attractive technology as it has been identified as an environmentally attractive energy source for portable power and micro power applications such as laptops, computers, 2-way radios, and etc. [1]. The polymer electrolyte membrane electrolyte membrane (PEM) has been widely used in both the DMFC and PEMFC [2]. The PEM is a semipermeable polymeric membrane generally made from ionomers and designed to conduct protons and to act as an electronic insulator and reactant barrier. The DMFC typically employs the same type of electrolytes as the PEMFC, but it requires a thicker membrane with a greater catalyst loading. Currently, perfluorosulfonic acid polymer namely Nafion as produced by Dupont is one of the widely used PEM. Nafion has excellent proton conductivity when hydrated [3], good chemical and mechanical stabilities [4]. However, the Nafion membrane still has many disadvantages in DMFC applications: reduced water retention at high temperature, high methanol crossover, and high cost [5].

Fluorine-free, aromatic hydrocarbon based membranes have been shown to possess high proton conductivity, excellent mechanical, thermal and chemical stability [6] comparable to Nafion. There have been many directions in the development of less expensive polyelectrolytes [7]: sulfonated polyimide [8]; sulfonated polybenzimidazoles [9]; sulfonated poly(ether ether ketone) [10]; sulfonated poly(phenylene oxide) [11]; and sulfonated polysulfone [12]. Sulfonated

polysulfone (S-PSF) is attractive for fuel cell applications [13]. S-PSF membranes exhibit lower methanol crossover relative to the Nafion 115 membrane for the DMFC application.

Several work developed composite membranes as PEM with high proton conductivity by adding inorganic fillers such as inorganic oxide, clay, and zeolite to enhance and maintain a suitable hydration of the membrane under fuel cell operating conditions, and to improve the mechanical properties [4]. ZSM-5 zeolite has been suggested for the DMFC as the zeolite is hydrated aluminosilicate minerals made from interlinked tetrahedra of alumina (AlO₄) and silica (SiO₄) by sharing all the oxygen atoms to form regular intra-crystalline cavities and channels of molecular dimensions; the structure possesses channels and cages which are large enough to accommodate extra-framework cations and to permit the adsorption and desorption of organic molecules [14]. A composite proton exchange membrane with ZSM-5 as a filler in sulfonated poly(ether ketone ether sulfone) (S-PEKES) possessed the proton conductivity of $1.76 \times 10^{-2} \text{ S}\cdot\text{cm}^{-1}$ and the membrane selectivity of $2.12 \times 10^5 \text{ s}\cdot\text{S}\cdot\text{cm}^{-3}$ [15]. The ZSM-5 zeolite is potentially a suitable filler for the PEM to improve the proton conductivity, water retention, and mechanical strength. However, the ZSM-5 zeolite can generate an agglomeration when excessively added to the polymeric membranes [2].

The objective of this work was to synthesize the sulfonated ZSM-5 zeolite by the organo-functionalization method of grafting poly (2-acrylamido-2-methylpropanesulfonic acid), pAMPS; it has been shown to

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provide higher proton conductivity than the partially hydrated Nafion [3]. The preparation of the sulfonated ZSM-5 zeolite was accomplished through the method of silanization by 3-methacryloxy-propyl-trimethoxysilane (TMSM) as the coupling agent. The fabricated sulfonated ZSM-5 zeolite was added at various amounts to the sulfonated polysulfone matrix. The water uptake, proton conductivity, methanol permeability, and oxidative stability of the fabricated membranes were systematically investigated and compared with the commercial perfluorsulfonic acid polymer, namely the Nafion 117.

2. Experimental

2.1. Materials

Polysulfone (PSF; Aldrich) was used as the polymer based membrane. Sulfuric acid (98%) (H_2SO_4 ; Univar, AR grade) was used as a sulfonating agent. Dichloromethane (DCM; RCI Labscan, AR grade), and dimethylacetamide (DMAc; RCI Labscan, AR grade) were used as solvents. Methanol (Univar, AR grade) was used in the methanol permeation testing. ZSM-5 Zeolite (CBV; Zeolyst International, Si/Al ratio = 23) was used as the filler in the S-PSF membrane. 3-methacryloxy-propyl-trimethoxysilane (TMSM) was used as a coupling agent for the silanization method. Poly(2-acrylamido-2-Methyl-1-propanesulfonic acid), pAMPS, was used in the sulfonation of the ZSM-5 zeolite.

2.2. Preparation of Sulfonated Polysulfone (PSF)

2.0 g of polysulfone (PSF) was dissolved in 10 ml of dichloromethane (DCM) and vigorously stirred at 80 °C until becoming homogeneous. Then 15 ml of sulfuric acid was added into the polymer solution which was stirred continuously for 1 h. The sulfonated polymer was precipitated by pouring cold deionized water into the PSF solution in an ice bath. The precipitate was filtered and washed by using deionized water until the pH of polymer became neutral. The sulfonated polymer was dried at 80 °C for 24 h [16].

2.3. Preparation of Sulfonated ZSM-5 zeolite

2.3.1. Silanization of ZSM-5 zeolite

First, ZSM-5 zeolite of 5 g and 3-methacryloxy-propyl-trimethoxysilane (TMSM) of 5 ml and ethanol of 100 ml were added into deionized water of 50 ml. The solution was adjusted to the pH of 2 by adding hydrochloric acid and vigorously stirred for 15 min. Then, the reaction was carried out at 70 °C by stirring continuously for 2 h. The silanized ZSM-5 zeolite precipitate was filtered and washed by using deionized water mixed with ethanol at the ratio of 1:3 v/v, after which it was washed by deionized water 3 times and filtered again.

2.3.2. Sulfonated ZSM-5 zeolite by grafting with pAMPS

Poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (pAMPS) at 10%wt was dissolved in a three neck round bottom container containing deionized water under a nitrogen flow of 30 min. Then, the ZSM-5 zeolite at the zeolite/TMSM weight ratio of 5% and potassium persulfate 0.05 g were put into the three neck round bottom containing the pAMPS solution and the reaction was carried out at 75 °C by stirring continuously for 5 h. Then, the solution was filtered and washed by acetone 3 times, by deionized water several times, by 0.1 M hydrochloric 4 times, each at the 30 min soaking time. Then the precipitate was washed using methanol several times. The sulfonated ZSM-5 zeolite was dried in a vacuum oven at 80 °C for 24 h.

2.4. Composite membrane preparation

The S-PSF of 1.5 g was dissolved in a 45 ml of DMAc to prepare a polymer solution. The polymer solution was continuously stirred until

homogenous. The ZSM-5 zeolite (at 5, 10, and 15%v/v) was added into the polymer solution and then stirred continuously for 1 h. The membranes were formed by a solution casting technique and then dried in a vacuum at 80 °C for 24 h [16].

2.5. Characterizations

The Fourier Transform Infrared Spectra were taken (FTIR; Nicolet, Nexus 670) to identify the functional groups of PSF and S-PSF. The samples, in a powder form, were grinded and mixed with potassium bromide (KBr; dried at 90 °C for 24 h) as a background material, and then compressed into pellets [16,17]. The FTIR spectra were collected at 64 scans in the 4000–400 cm^{-1} .

The chemical structures of PSF and S-PSF were determined by the nuclear magnetic resonance spectroscopy (Bruker; Biospin Avance 500 MHz NMR spectrometer). The polymer solution 2–5%wt was prepared in deuterated dimethyl sulfoxide ($\text{DMSO}-d_6$) as the solvent and the experiment was conducted at room temperature (27 °C). The NMR data of PSF and S-PSF were analyzed for the degree of sulfonation (DS). The DS was calculated by the following Eq. (1) [16,18]:

$$R = \frac{I(1, 1', 2, 2', 4, 4')}{I(2'', 3, 3')} = \frac{12 - 2\text{DS}_{\text{NMR}}}{4 + 2\text{DS}_{\text{NMR}}} \quad (1)$$

The thermal property of S-PSF and S-ZSM-5 was investigated by a Thermo Gravimetric Analyzer (TGA; Perkin Elmer). The samples were weighed in the range of 4–10 mg. The measurements were carried out under a nitrogen flow between 30 and 800 °C at a heating rate of 10 °C·min⁻¹ [16,19].

The structure of the sulfonated ZSM-5 zeolite was determined by a Single Crystal X-Ray Diffractometer (SC-XRD; Bruker AXS, D8 Discover) using a Cu K α and the scanning angle varied from 5° to 50° with scanning rate of 2°/min [20].

The elements of the ZSM-5 zeolite and sulfonated ZSM-5 zeolite were investigated by the energy-dispersive X-ray spectroscopy (EDX; Hitachi, S-4800). The sample was placed onto a stub with a carbon tape and then coated with gold (Hitachi, E-1010) to be able to conduct electricity where EDX was operated at 8 keV [20].

The morphologies of S-PSF and composite membranes were investigated with a scanning electron microscope (JEOL, JSM-5410LV). Specimens for (SEM) were prepared as dry membrane samples. They were attached to stubs by a carbon tape and the specimen surfaces were coated with gold.

The ion exchange capacity (IEC; mequiv·g⁻¹) of the membranes was determined using the titration method. The dried PSF and composite membranes (0.20–0.30 g) were immersed in a NaCl solution (1 M 50 ml) for 24 h at 27 °C to replace all H⁺ with Na⁺. The amount of H⁺ protons released from the membranes was determined by titration, using a 0.01 M NaOH solution with phenolphthalein as the pH indicator. The IEC value was obtained using the following Eq. (2) [21]:

$$\text{IEC (meq}\cdot\text{g}^{-1}) = \frac{V_{\text{NaOH}} \times M_{\text{NaOH}}}{W_d} \quad (2)$$

where V_{NaOH} is the volume NaOH consumed (ml), M_{NaOH} is the molality of NaOH and W_d is the weight (g) of the dry membranes.

The weight of the dry membrane samples used for the water uptake measurement was between 0.2 and 0.4 g. The membranes were immersed into deionized water for 24 h at 27 °C. Superabundant water was eliminated from the membrane surfaces with a wiping paper and the membranes were then weighed (W_{wet}). The membranes were dried at 80 °C for 24 h in an oven and then weighed again (W_{dry}). The percentage of water uptake was then calculated following Eq. (3) [15,17]:

$$\text{Water uptake (\%)} = \frac{(W_{\text{wet}} - W_{\text{dry}})}{W_{\text{dry}}} \times 100 \quad (3)$$

Proton conductivity of the membranes was measured by an LCR

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