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Polybenzimidazole/zwitterion-coated polyamidoamine dendrimer composite membranes for direct methanol fuel cell applications

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ABSTRACT

The zwitterion-coated polyamidoamine (ZC-PAMAM) dendrimer with ammonium and sulfonic acid groups has been synthesized and used as filler for the preparation of PBI-based composite membranes for direct methanol fuel cells. Polybenzimidazole (PBI)/ZC-PAMAM dendrimer composite membranes were prepared by casting a solution of PBI and ZC-PAMAM dendrimer, and then evaporating the solvent. The presence of ZC-PAMAM dendrimer was confirmed by FT-IR and energy-dispersive X-ray spectroscopy (EDS) mapping of sulfur and oxygen elements. The water uptake, swelling degree, proton conductivity, and methanol permeability of the membranes increased with the ZC-PAMAM dendrimer content. For the PBI/ZC-PAMAM-20 membrane with 20 wt% of ZC-PAMAM, it shows a proton conductivity of 1.83×10^{-2} S/cm at 80 °C and a methanol permeability of 5.23×10^{-8} cm² s⁻¹. Consequently, the PBI/ZC-PAMAM-20 demonstrates a maximum power density of 26.64 mW cm⁻² in a single cell test, which was about 2-fold higher than Nafion-117 membrane under the same conditions.

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1. Introduction

Fuel cells are efficient and clean electrochemical power source that convert the chemical energy directly into electricity via electrochemical reaction of fuels and oxygen [1]. Among the

different types of fuel cells, direct methanol fuel cells (DMFCs) have been received much attention because of their high power density, the ease of handling operating conditions, and possible applications in micro fuel cells [2,3]. Proton exchange membrane (PEM) is a key component in DMFC for transferring

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protons from anode to cathode while providing a barrier to fuel crossover between the electrodes. Nafion membranes (DuPont) have long been the standard polymer for use in DMFCs due to their excellent proton conductivity and high chemical durability [4,5]. However, the high methanol permeability decreases the fuel cell efficiency and causes poisoning of the catalyst at the cathode limits the Nafion membranes further commercial application in DMFCs [6]. Therefore, new types of PEMs with high proton conductivity and low methanol crossover is in great demand to promote the development of DMFCs.

In recent years, new types of PEMs based on variety of polymer materials have been synthesized and studied [7–10]. Among the various polymers that have been reported, polybenzimidazole (PBI) has been recognized as a good choice for preparation of PEMs because of its excellent chemical stability, good thermochemical and mechanical stabilities [11,12]. However, the proton conductivity of PBI should be enhanced because it has no proton conducting ability.

Sulfonated polymers with the sulfonic acid groups has become an important approach in enhancing proton conductivity of the PEMs by increasing the water uptake and rendering its ion-exchange properties [13]. A high degree of sulfonation improves the proton conductivity, whereas lead to a high swelling ratio which result in the loss of the mechanical strength and the increase of the methanol permeability of PEMs [14].

Replacement of water with nonaqueous proton carriers such as phosphoric acid, is another simple and powerful method to improve the proton conductivity of PEMs especially at high temperature. However, the performance of fuel cells could be declined by the phosphate anion adsorption on the platinum surface [15]. The performance of fuel cells also could be affected by the release of the phosphoric acid from PEMs [16].

Recently, composite membranes with hydrophilic inorganic fillers have attracted much attention due to the low methanol permeability and high thermal stability [17,18]. Generally, a low content of organic groups of the inorganic fillers is disadvantageous for homogenous and conductive PEMs. To overcome these problems, inorganic fillers with chemical modification have been prepared and used as fillers in PEMs [19]. Chu et al. reported a polybenzimidazole/ H_3PO_4 /zwitterion-coated silica nanoparticle hybrid membranes, and the zwitterion-coated silica nanoparticles showed high compatibility with the polymeric matrix [16]. More recently, zwitterionic cross-linking agent with sulfonic acid and amine groups was synthesized for preparation of PEMs by Shahi et al. [20], and the zwitterionic hybrid PEMs showed high proton conductivity and low methanol crossover. These results suggest that addition of zwitterion-coated fillers can be a promising process to obtain the desired PEMs for DMFCs.

In the present work, zwitterion-coated polyamidoamine (ZC-PAMAM) dendrimer with high concentration of sulfonic acid and amine groups was synthesized and used as fillers of the PBI-based PEMs. PBI/ZC-PAMAM dendrimer composite membranes were prepared by simple solution casting method. The influence of ZC-PAMAM dendrimer content on the membrane properties was systematically described. The

DMFC single-cell performance with the composite membranes was also demonstrated.

2. Experimental

2.1. Materials

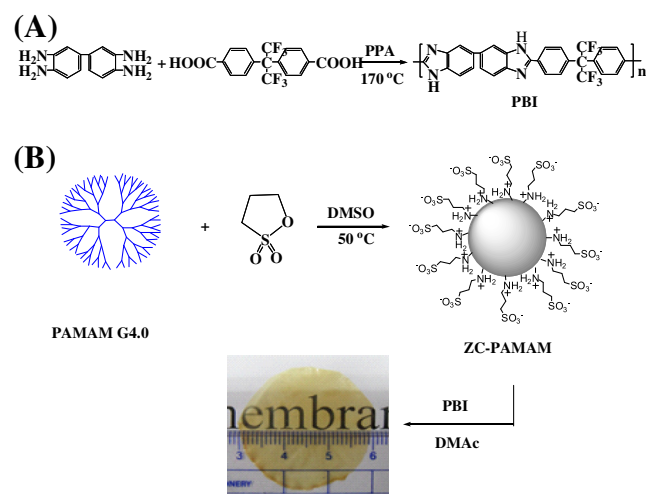
2,2-Bis (4-carboxy-phenyl) hexafluoropropane was purchased from TCI and purified by recrystallization from glacial acetic acid. 3,3'-Diaminobenzidine, 1,2-diaminoethaneanhydrous, 2-propenoicidmethylester, 1,3-propane sultone, poly (phosphoric acid), 1,2-diaminoethane anhydrous, 3,3'-diaminobenzidine, methanol, 2-propenoicidmethylester and poly (phosphoric acid) (PPA) was used as received. N,N-dimethylacamide (DMAc) and dimethylsulfoxide (DMSO), were purified by distillation. Distilled deionized water was used for all experiments.

2.2. Synthesis of zwitterion-coated polyamidoamine dendrimer

Ethylenediamine core PAMAM G4.0 was synthesized as documented in previous literatures [21]. As shown in Scheme 1B, the ZC-PAMAM dendrimer was synthesized as follows: excess 1,3-propane sultone/DMSO solution was slowly added to PAMAM G4.0/DMSO solution at 0 °C, and then the mixture was stirred at room temperature for 48 h. The resultant product was washed with acetone twice and then dried in vacuum at 60 °C for 24 h. ^1H NMR (500 MHz, D_2O), δ : 3.30 (t, $-\text{NCH}_2\text{C}-$), 2.81 (br t, $-\text{CCH}_2\text{CO}-$), 3.32 (br t, $-\text{NCH}_2\text{C}-$), 3.48 (br t, $-\text{CONCH}_2\text{C}-$), 3.59 (t, $-\text{CCH}_2\text{N}-$), 2.59 (br t, $-\text{CCH}_2\text{C}-$). CHNS: calcd (C, 44.20; H, 7.40; N, 15.81; S, 9.48); obsd (C, 43.23; H, 6.58; N, 17.08; S, 10.37).

2.3. Preparation of PBI

PBI was synthesized via the condensation polymerization of 2-bis(4-carboxyphenyl) hexafluoropropane and 3,3'-diaminobenzidine in PPA at 170 °C, as shown in Scheme 1A [16].



Scheme 1 – Reaction scheme for the preparation of PBI and PBI/ZC-PAMAM dendrimer membranes.

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