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Modified silicon carbide whisker reinforced polybenzimidazole used for high temperature proton exchange membrane

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ABSTRACT

Polybenzimidazole containing ether bond (OPBI) was reinforced with silicon carbide whisker (mSiC) modified by 3-aminopropyltriethoxysilane (KH550), and then doped with phosphoric acid (PA) to obtain OPBI/mSiC/PA membranes. These OPBI/mSiC/PA membranes have excellent mechanical strength and oxidative stability and can be used for high temperature proton exchange membrane (HT-PEM). The tensile strength of OPBI/mSiC/PA membranes ranges from 27.3 to 36.8 MPa, and it increases at first and then decreases with the increase of mSiC content. The high mSiC content and PA doping level contribute to improve the proton conductivity of membranes. The proton conductivity of PBI/mSiC-10/PA membrane is 27.1 mS cm⁻¹ at 170 °C without humidity, with an increase of 55.7% compared with that of OPBI/PA membrane. These excellent properties make OPBI/mSiC/PA membranes promising membrane materials for HT-PEM applications.

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1. Introduction

Proton exchange membrane fuel cell (PEMFC) has received increasing attention as a power generation device for both stationary and transportation applications due to its high efficiency and low emission of pollutants [1]. There are many advantages of operating PEMFCs at high temperatures (100–200 °C), including the reduction or elimination of humidification requirements, increased tolerance to CO, wider fuel choices, improved electrode kinetics, and higher conductivities [2]. Many efforts have been devoted to the development of low cost and high performance proton exchange membranes (PEMs) for high temperature proton exchange membrane fuel cells (HT-PEMFCs) [3], among which phosphoric acid (PA) doped polybenzimidazole (PBI) membrane [4] might be the most promising one because of its high ionic conductivity at high temperatures, excellent thermal and oxidative stability [5]. However, a high PA doping level (PADL) may lead to poor mechanical properties of PA doped PBI membranes [6]. This problem can be overcome by modifying the polymer structure via copolymerization [7], N-substitution [8] or cross-linking of the polymer [9–13] at the reactive benzimidazole N–H sites; or by incorporating

inorganic particles such as hygroscopic oxides (i.e., SiO₂ and ZrO₂) [14–18], perovskite-type oxides (i.e., strontium cerate and barium titanate) [19,20], heteropolyacids [21], zirconium phosphates (ZrP) [22], carbides (i.e., silicon carbide (SiC)) [23], and graphene oxide (GO) [24], which can improve the mechanical properties and acid doping levels of composite membranes because of hydrogen-bond interaction between the oxygen atoms of hydroxyl groups and acid [20].

SiC has many desirable properties, such as high strength, high stiffness, excellent thermal and electrochemical stability [25], making it suitable for the reinforcement of polymer composites for HT-PEMFC applications [26]. Joel [27] reported the effects of SiC on the physical and mechanical properties of PBI membranes. In this report, SiC was introduced to provide additional mechanical stability to the PBI membranes. The results showed that PBI membrane containing 5% SiC was more stable than that containing 1%, 3% and 7% SiC, and it also met the expected conductivity standards (about 0.145 S cm⁻¹ in a temperature range of 22–160 °C). SiC whisker grown by single crystal can also improve various properties of the polymer matrix due to the special fiber-shaped structure. Liepins et al. [28] first introduced β-SiC whisker into PBI to prepare PBI/β-SiC composite by solution-casting method, which, however, was not used for PEM. To our knowledge, there has been no study on SiC whisker for HT-PEMs.

In this study, modified SiC whisker (mSiC) was prepared using a silane coupling agent of 3-aminopropyltriethoxysilane (KH550)

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and then blended with OPBI to obtain a series of OPBI/mSiC membranes. With the aid of the alkaline imidazole ring, silicon hydroxyl, and amino groups, these OPBI/mSiC membranes were further doped with PA to obtain OPBI/mSiC/PA membranes used for HT-PEM. The results clearly show that the introduction of mSiC has a significant effect on the PADL, mechanical properties, microstructure, oxidative stability and proton conductivity of composite membranes.

2. Experimental

2.1. Materials

OPBI polymers were prepared by polycondensation of 3,3-diaminobenzidine (DAB Chemical Technology Co., Ltd., Shanghai) and 4,4-oxybis (benzoic acid) (OBA, Aladdin Industrial Co., Shanghai) in methanesulfonic acid (MSA, Aidie Industrial Co., Ltd., Shanghai) [29]. SiC whiskers were purchased from Alfa Aesar Chemical Ltd. (Tianjin, China) and used without further purification. 3-Aminopropyltriethoxysilane (KH550, Resin Factory Co., Ltd., Shanghai) was used as a coupling reagent to modify SiC. Sodium hydroxide (Lingfeng Chemical Reagent Co., Ltd., Shanghai) was used without further purification. Dimethylacetamide (DMAC, Lingfeng Chemical Reagent Co., Ltd., Shanghai) was purified by distillation under reduced pressure and used as a solvent. All the other reagents were obtained from commercial sources and used as received.

2.2. Preparation of modified silicon carbide whisker (mSiC)

1 mL of KH550 was accurately weighed and mixed with 30 mL of absolute ethyl alcohol and 3 mL of water in a 100 mL beaker. After adjusting the pH to 9–10 with sodium hydroxide, the mixture was subjected to ultrasonic treatment for 30 min. Then 1 g of SiC was added into the solution and stirred at 80 °C for 4 h. The mixture was cooled down to room temperature and continuously stirred for 24 h. The solution was then dried at 80 °C for 18 h to remove the solvent. The obtained product was washed with alcohol and water until the pH of the centrifugate was 7, and then dried at 80 °C to a constant weight.

2.3. Preparation of OPBI/mSiC membranes

OPBI and OPBI composite membranes were prepared by the solution-casting method. mSiC was added into DMAC in an ultrasonic bath for 1 h to obtain a homogeneously dispersed solution. Then, approximately 5 wt% OPBI solution was mixed with mSiC (DMAC) in different proportions under stirring. All homogeneous solutions were cast onto a clean glass plate at 80 °C for 24 h to obtain smooth membranes. Later, these membranes were immersed in water for 24 h to remove residual solvent, and then dried at 80 °C in vacuum overnight. Pure OPBI membrane and OPBI/SiC composite membranes were also prepared by the same procedure and served as the control. OPBI/mSiC membranes and PA doped membranes were 60–70 μm and 100–120 μm thick, respectively.

2.4. Characterization and measurements

The functional groups in mSiC were analyzed using a Nicolet 6700 Fourier transform infrared (FT-IR) spectrometer in the range of 400–4000 cm⁻¹ with a resolution of 4 cm⁻¹, and the element contents were measured using an energy dispersive spectrometer (EDS).

The membranes were immersed in a 14.6 M PA aqueous solution at 80 °C for 48 h and then wiped with filter paper repeatedly

to obtain PA-doped membranes. Then, these membranes were immersed into alkaline aqueous solution to remove absorbed PA and washed several times with water. The obtained membranes were then dried overnight at 80 °C in vacuum. The PADL was determined by the following equation:

$$\text{PADL}(\text{mol PA per repeating unit}) = (W_{\text{PA}} - W_{\text{dry}}) / W_{\text{dry}} \times M_{\text{RU}} / M_{\text{PA}} \quad (1)$$

where W_{dry} , and W_{PA} are the weight of dry and PA-doped membranes, and M_{RU} and M_{PA} are the molar mass of repeating unit of OPBI and PA, respectively.

The mechanical properties of PA-doped membranes were determined using an MTS E43 universal testing machine in ambient atmosphere at a drawing rate of 10 mm min⁻¹. The tensile fracture surface of membranes was observed by a scanning electron microscope (SEM, FE-S4800, Hitachi, Japan) at an acceleration voltage of 15 kV. The thermal stability of PA-doped membranes was measured on an HCT-1 thermogravimetric analyzer (TGA, Beijing Henvin Scientific Instrument Factory, China). Samples were maintained at 120 °C for 30 min to remove absorbed moisture, and then cooled to 80 °C and reheated to 800 °C at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere. The grafting ratio of mSiC was calculated via weight loss in the TGA curves.

Dry membranes were immersed in Fenton's reagent (3 wt% H₂O₂ and 4 ppm Fe²⁺) at 68 °C, and the oxidative stability was evaluated by weight remaining of membranes [30]. All membranes were immersed for 168 h, washed, and then dried at 120 °C to a constant weight. The weight remaining was calculated by:

$$\text{Weight remaining (wt\%)} = W_1 / W_0 \times 100\% \quad (2)$$

where W_0 and W_1 are the weight of initial and final membranes, respectively.

The proton conductivity of composite membranes was determined by AC impedance spectroscopy over a frequency range of 10⁶–10³ Hz at 100–170 °C using a PARSTAT 2273 electrochemical analyzer. All membranes were dried at 120 °C to remove absorbed moisture, and the measurement was carried out under anhydrous conditions. The in-plane proton conductivity (σ , S cm⁻¹) was measured and calculated according to the following equation: $\sigma = L/RS$, where L is the distance between the two electrodes, R is the resistance of the membrane, and S is the cross-sectional area of the membrane.

3. Results and discussion

3.1. Characterization of mSiC

The FT-IR spectra of SiC and mSiC are shown in Fig. 1. Two new absorption peaks observed at about 2848 and 2923 cm⁻¹ in Fig. 1(b) can be assigned to the –CH₂– stretching vibration of alkane chain; and the peak at 1640 cm⁻¹ becomes stronger and is assigned to the –NH₂ group, indicating the successful reaction of KH550 with SiC. This can be further confirmed by the TGA curves in Fig. 2. The weight of pre-dried SiC remains almost constant, whereas that of mSiC decreases at first and then keeps constant after 600 °C. The weight remaining at 600 °C is 99.0 wt% and 93.2 wt% for SiC and mSiC, respectively, indicating that the content of coupling reagent is about 12.1 wt% via the following formula.

$$\text{Grafting ratio (wt\%)} = (m_2 - m_1) \times M_2 / M_1$$

where m_1 and m_2 are the weight remaining of SiC and mSiC at 600 °C and M_1 and M_2 are the molecular weight of thermal decomposition part (–CH₂CH₂CH₂NH₂) and hydrolyzed coupling reagent (–Si(OH)₂CH₂CH₂CH₂NH₂), respectively.

Table 1 shows the EDS results of SiC and mSiC. The atomic ratio of hydrolyzed KH550 should be N/Si=1:1. Thus, the atom percent

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