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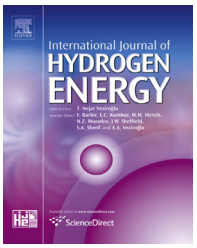

Excellent performance of resistance methanol of a novel sulfonated poly (aryl ether ketone sulfone)/ poly (vinylalcohol) composite membrane for direct methanol fuel cell applications

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ABSTRACT

Composite membrane comprised of the sulfonated poly (aryl ether ketone sulfion) with amino groups (Am-SPAEKS) and poly (vinylalcohol) (PVA) was successfully prepared by the co-solvent coating method. The composite membranes perform a variety of advantages, such as good thermal stability, outstanding water retention, stable mechanical performance and oxidative stability, and the composite membranes have superior water uptake. The proton conductivity of Am-SPAEKS-PVA50% was 0.041 S cm^{-1} at 80 °C and 0.038 S cm^{-1} at 120 °C, and the methanol permeability coefficient of the composite membranes was 2.95×10^{-7} at 25 °C and 8.26×10^{-7} cm^2 s^{-1}, far below the methanol permeability coefficient of Nafion (25.1×10^{-7} cm^2 s^{-1} at 25 °C), so that it could ensures prevent methanol permeation effectively, improve the utilization of methanol. Moreover, the composite membranes show fairly ideal selectivity. These excellent performances show that the composite membranes could be served as new potential membrane materials for direct methanol fuel cells.

Introduction

Along with the excessive exploitation of the energy and the serious environment problem, proton exchange membrane fuel cell (PEMFC) has attracted increasingly keen interest which is regarded as a new type of clean energy [1,2]. Compared with the traditional energy conversion device, PEMFC possesses high energy efficient, non-polluting and good portability [3–6]. Direct methanol fuel cell is one type of PEMFC, which have been widely given attention [7–10]. DMFC has many significant advantages, such as convenient operability, easy to transport, higher energy efficiency, and so on.

At present, Nafion® membrane (the perfluorosulfonate acid membrane) is the only PEM materials which have been commercialized. It has acceptable chemical durability, strong

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mechanical properties, long working life and high proton conductivity. However, high fuel permeability, expensive cost and obvious decrease of proton conductivity on account of low humidity when temperature goes up over 80 °C significantly restrict its application [11–13]. Some investigators, therefore, devote themselves to research some new other way to solve this issue [14]. One of the routes is to modify the Nafion® membrane so that it can make up for weaknesses in these areas. Chen et al. [15] put the modified positively charged silica and heteropolyacids into the Nafion® membrane through the layers of self-assembly method and the membranes could be used as PEM at high temperature (even at 200 °C) or at absolute dry condition. Tsai et al. [16] found that two 1-D channel microporous metal-organic frameworks (MOFs) was used as fillers to optimize the Nafion® membrane in order to make it to increase the membranes ability of absorbing the moisture, this improved the workplace condition of the proton transfer from edgewise. Other routes had been found that several non-fluorinated polymer membranes performances are pretty excellent so that it can be regarded as materials of PEM. Sulfonated polymer is a new kind of material which has some excellent properties. (i). The introduction of the sulfonic acid group could provides a more convenient proton transport channel; (ii). Such polymers can also provide excellent thermal properties, mechanical performances and water retaining capacity.

These sulfonated aromatic polymers include sulfonated poly (ether ether ketone) [17], sulfonated polyimide [18], and sulfonated polybenzimidazole [19], sulfonated poly (ether sulfone) [20] and sulfonated poly (aryl ether ketone) (SPAEKS) [21], and so on. However, with increasing degree of polymerization for polymers, DS value will rise as well. Degrees of the sulfonation (DS) means the content of sulfonic acid groups in the polymer. High DS always leads to poor dimensional stability and high methanol permeability. For these new types of polymers, SPAEKS has many out-bound properties, such as good mechanical property, excellent thermal performance and low cost. Moreover, SPAEKS is an environmentally friendly material. However, high methanol permeability is the biggest problem of this kind of materials [22]. Poly (vinyl-alcohol) (PVA) has excellent water retention capacity; moreover, it has good ability of blocking methanol with high DS [23,24]. Sachan et al. [23] synthesized a composite membrane which is made up by PVA and sulphanilic acid modified poly (methyl vinyl ether-alt-maleic anhydride). This membrane showed higher proton conductivity, with the value 0.0045 S cm^{-1}, better than Nafion-117 membrane. Ebenezer et al. [24] introduced a cross-linked membrane with PVA and sulfosuccinic acid, its proton conductivity could reach 0.14 S cm^{-1} and also has some good performances. Blending method could improve the dimension stability of the membrane and reduce the methanol permeability coefficient in a certain extent [25,26]. The advantage of this method is that it can make the contact between polymer main chains closer [27,28].

In this study, SPAEKS with amino groups (Am-SPAEKS) had been successfully synthesized by condensation polymerization method, and DS value could be controllable by adjusting the content of sulfonated monomer. The composite membranes were prepared by dumping the solution which included the two polymers onto a glass pane. The introduction of PVA not only improves the ability of hindering methanol for composite membranes [22], but also improves the water retention ability of the membrane through strong hydrogen bonding force. The composite membranes were tested particularly and compared to Am-SPAEKS membrane, simultaneously; the dimensional stability, mechanical permeability and proton conductivity of the composite membrane were also investigated.

Experimental

Materials

The raw material of sulfonated poly (arylene ether ketone sulfone) (SPAEKS) polymers which are synthesis by 3.3′-disulfonated 4.4′-dichlorodiphenyl sulfone (SDCDPS), and 4-aminophenyl hydroquinone (4Am-PH) have been successfully synthesized in the previous report [2]. 4.4′-Difluorobenzophenone (99% purity) was purchased from Yanbian Longjing Chemical Company, China. 2.2-Bis (4-hydroxypheny) propane (bisphenol A) (AR grade) was obtained from Tianjin Guangfu Chemical Reagent Company, China. N-methyl-2-pyrrolidinone (NMP) (99% purity), toluene, acetone, and anhydrous potassium carbonate (AR grade) were obtained from Beijing Chemical Reagent Company, China; Poly (vinyl-alcohol) (PVA) was purchased from Shanghai chemical reagent procurement provisions China. The average degree of polymerization of PVA is 1750 ± 50, and the molecular weight is 75000–90000, the sulfonation degree is 120%; The dimethyl sulfoxide (DMSO) was obtained from Tianjin Fuyu fine chemical company.

Synthesis of Am-SPAEKS copolymers

The reactive monomers and reaction process flow chart of the Am-SPEKS copolymers are shown in Scheme 1 [2]. The DS of polymerization is 120% by adjusting the charge ratio of the two monomers (SDCDPS and 4.4′-disfluorbenzophenone). The copolymer was synthesized by polycondensation method and all of the reactive monomers were dried in a vacuum oven (DZF-6050 from Yiheng science Apparatus Company limited, Shanghai) at 60 °C for about 12 h in order that these reagents could be desiccative enough. 4.4′-difluorobenzophenone (0.016 mol), SDCDPS (0.024 mol), 4Am-PHQ (0.008 mol), bisphenol A (0.032 mol) and slightly excess K_2CO_3 were added into a three-necked flask equipped with a mechanical stirring paddle, a condenser pipe with a reflux condenser and a N_2 aeration device. The water azeotropic reagent was toluene; the azeotropic reflux time was 4 h at 128 °C in order to keep the extra moisture away from the reaction system. And then, the temperature was risen slowly so as to distillation all of toluene away. In the final, the temperature of the system was raised to 170 °C and maintain for about 28 h. At the end of the process, the reaction surplus materials were cooled down and poured into 500 mL of acetone to precipitate out the copolymers. Next, the copolymers were ground into a kinematica aiming to make them become powdery substance. Then the water-soluble inorganic salts and residual solvents of the

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