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Fabrication and physico-chemical properties of iron titanate nanoparticles based sulfonated poly (ether ether ketone) membrane for proton exchange membrane fuel cell application

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ABSTRACT

Novel nanocomposite membranes based on sulfonated poly (ether ether ketone) (SPEEK) and iron titanate, Fe_2TiO_5, (IT) were prepared by dispersion of IT nanoparticles into SPEEK solution with solution casting method. The morphology, thermal and mechanical properties, proton conductivity and fuel cell performance of the nanocomposite membranes were investigated. The nanocomposite membrane with 1 wt.% of IT nanoparticles exhibited the highest proton conductivity of 0.096 S/cm at 80 °C, which is 65.5% and 6.6% higher than that of pristine SPEEK membrane and Nafion 117 membrane, respectively. The excellent proton conductivity of the membranes can be attributed to presence of IT nanoparticles which can perform as pathways for proton transport. Moreover, the as-prepared nanocomposite membranes also showed elevated thermal and mechanical stabilities. A single fuel cell equipped with the SPEEK/IT (1 wt.%) nanocomposite membrane showed a peak power density of 188 mW/cm^2 at 80 °C. The novel SPEEK/IT membranes with the well-defined proton transport channels and enhanced mechanical properties can be the potential alternative materials to Nafion for PEMFC.

1. Introduction

Among the various types of fuel cells, polymer electrolyte membrane fuel cells (PEMFCs) are very attractive for a wide range of applications, especially in vehicular transportation, because of their numerous advantages such as high power density, low operation temperature, quick start up, low cost and simplicity [1,2]. One of the important parts of a PEMFC is polymer electrolyte membrane (PEM) that should have several unique properties such as, high proton conductivity, low electronic conductivity, low permeability to the fuel and the oxidant, low electro-osmotic drag coefficient, good chemical/thermal stability and good mechanical properties for long-term operations.

Various polymers are used to prepare PEMFC membranes. Perfluorosulfonated ionomer, known as Nafion, is the most commonly studied membrane which has high hydrolytic and oxidative stability and excellent proton conductivity in its hydrated state. However, reduction in its proton conductivity and mechanical stability at temperatures above 80 °C and its high cost limit its usage for PEMFC [3]. In recent years, several kinds of proton exchange membranes such as, sulfonated poly (ether sulfone)s (SPES) [4], sulfonated poly(arylene ether sulfone) [5], sulfonated polyimides (SPI) [6], sulfonated polybenzimidazoles (SPBI) [7] and sulfonated poly(ether ether ketone)s (SPEEK) [8–10] have been investigated.

Among them, SPEEK can be easily obtained via post-sulfonation of PEEK by electrophilic substitution of the sulfonic acid groups in the polymer backbone. SPEEK has been greatly considered due to its low cost, high thermal/chemical stability and good proton conductivity. Proton conductivity of SPEEK depends on the degree of sulfonation (DS) which can be controlled by temperature, reaction time and acid concentration [11,12]. To obtain satisfactory proton conductivity, sulfonated polymer should have high DS. However, increase of DS values usually leads to increase of swelling and the loss of mechanical strength at high temperature and humidity; and long-term stability decreases by the degradation by hydroxyl radicals [13,14]. Whereas, membranes with low DS show low proton conductivity, they have high thermal and mechanical stability [15]. The addition of an inorganic component is known to limit swelling by restraining polymer chains [16].

On the other hand, the proton exchange membranes, such as Nafion and SPEEK, require water to preserve their proton conductivity. Thus, to prevent drying of the membrane and keep the membrane at most conductive state, without external humidification, many composite membranes with self-humidifying ability have been developed. For example, incorporating hygroscopic metal oxides, such as silica [17–21], titania [13,22–24], zeolites [25,26] montmorilonite [27], iron titanate [28], zirconia [29], strontium cerate [30] and barium zirconate [31,32]

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were developed to absorb water and accordingly improve the proton conductivity. These prepared nanocomposite membranes have presented good interfacial compatibility, enhanced water retention property and mechanical stability. Also, good dispersing of inorganic fillers in the polymeric matrices has been known as an effective method to overcome fuel cross-over [33,34]. In this respect, it appears possible to improve the performance of membranes by incorporating a suitable inorganic phase in a polymeric network.

Fe_2TiO_5 (IT) is a multiple oxide with pseudo-brookite structure. The surface hydroxyl groups of IT nanoparticles provide strong hydrogen bonding sites with water molecules, which act as water reservoir in the membrane matrix. Furthermore, Ti^{4+} and Fe^{3+} cations, which are classified as hard acids, react with —OH groups of water. It seems that when Fe^{3+}cations are placed near Ti^{4+}cations in the IT structure, result in strengthening of acidic effect and make strong bonds with —OH groups of water [35].

In this work, for the first time, a novel nanocomposite membrane is developed by incorporating IT nanoparticles as filler into SPEEK. The —OH groups of IT nanoparticles provide strong hydrogen bonding sites with water molecules and —SO_3H groups of the SPEEK polymer and increase the contents of the bound to free water ratio into the membrane matrix. It is expected that IT nanoparticles can help to achieve the nanocomposite membranes with enhanced proton conductivity. The microstructure and physic-chemical properties of the membranes were evaluated. The as-prepared nanocomposite membranes were characterized by Fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FESEM), XRD and TGA while the membranes performance were extensively evaluated in terms of mechanical stability, water uptake, membrane swelling, proton conductivity as a function of temperature and fuel cell performance. Compared with SPEEK membrane, the swelling of the nanocomposite membranes is reduced with increasing of IT content. These observations imply that incorporating the inorganic IT is conducive to the membrane dimensional stability. The DS of SPEEK polymer was set at 68%, to ensure the optimum range based on the proton conductivity and mechanical properties [23].

The as-prepared nanocomposite membranes were characterized by Fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FESEM), XRD and TGA while the membranes performance were extensively evaluated in terms of mechanical stability, water uptake, membrane swelling, proton conductivity as a function of temperature and fuel cell performance.

2. Experimental section

2.1. Materials

Poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene) (PEEK) (M_W = 28,800 g/mol) was purchased from Sigma Aldrich. N, N-dimethylacetamide (DMAc) and Sulfuric acid was supplied from Merck. Other reagents and solvents were achieved from Sigma-Aldrich.

2.2. Synthesis of IT nanoparticles

IT nanoparticles were prepared by our group by wet-chemistry synthesis method as following procedure [36]: first, a suitable amount of stearic acid was melted in a beaker at 73 °C and then iron acetyl acetonate was added to it under stirring until a transparent brown solution is obtained.

After that, stoichiometric tetrabutyl titanate was added to the above solution and stirred to form a homogeneous light brown sol. It was cooled down at room temperature and dried in an oven for 12 h to obtain a dried gel and finally the gel was calcined in air atmosphere to obtain IT nanoparticles between 48 and 80 nm in size.

2.3. Sulfonation of PEEK

Two gram of the PEEK pellets were dissolved in 20 mL concentrated sulfuric acid at room temperature. The sulfonation reaction was performed at 60 °C for a certain time period under nitrogen atmosphere. The reaction was terminated by dropping the polymer solution in cold water. The product was washed repeatedly with deionized water till pH became 6.0, and dried at 70 °C for 24 h. The degree of sulfonation was determined by conventional titration method [37]. 0.2 g of the sulfonated polymers were placed in 20 mL of 1 M NaCl and kept for 1 days in the shaker, and the resultant were titrated with 0.02 M NaOH aqueous solution using phenolphthalein as an indicator. The DS was calculated as follow:

$$DS = \frac{10^{-3} \times 288.31 \times C_{NaOH} V_{NaOH}}{W - 0.081 C_{NaOH} V_{NaOH}} \times 100 \quad (1)$$

Where C_{NaOH} is the molarity of the NaOH solution, V_{NaOH} is the amount of NaOH solution consumed, W is the weight of the sample, 288.31 is the molecular weight of the repeating unit of PEEK, and 81 is molecular mass of SO_3H. The DS of SPEEK was obtained 68%.

2.4. Membrane preparation

The SPEEK/IT nanocomposite membranes were prepared by a solution casting method. 0.5 g of SPEEK powder was dissolved in 1.5 mL of DMAc with stirring at room temperature. Different weight percentages of IT nanoparticles with respect to the sPEEK polymer (0.25–2%) were dispersed in 1 mL DMAc under sonication for 30 min and then combined with the SPEEK solution under stirring for 30 min. The homogeneous mixture was directly cast onto a glass plate by using a doctor blade at a constant speed, and dried at room temperature overnight then dried at 70 °C for 24 h. The prepared membranes (SPEEK and SPEEK/IT) were nominated as SP and SP/ITx respectively, where x present the weight percent of IT in the SPEEK membranes. The membranes were immersed in 2 M sulfuric acid solution for 24 h before use. The thicknesses of the dried membranes were between 60 and 80 μm.

2.5. Characterization

Morphology and size of IT nanoparticles were performed by transmission electron microscopy (TEM) (Zeis EM900, 80keV). IT nanoparticles were dispersed in ethanol by ultrasonication, afterward one drop of this suspension was applied on the TEM sample grid; dried and then used for TEM observation. FTIR spectra of the nanocomposites were recorded in the wave number range of 500–4000 cm^{-1} on an attenuated total reflection Fourier transform infrared spectrophotometer (ATR-FTIR, Bruker Equinox 55). Thermogravimetric analysis (TGA) was performed under nitrogen atmosphere on a Hi-Res TGA 2950 thermogravimetric analyzer with a temperature range of 25–550 °C at a heating rate of 10 °C/min. The cross-sectional morphology of the membranes was examined by field emission scanning electron microscope (FESEM, TESCAN). Prior to SEM analysis, the samples were prepared by freeze-fracturing in liquid nitrogen, and then their surfaces were coated with gold sputtering. Element mapping was accomplished with an energy dispersive X-ray spectroscopy (EDX (.

The crystal structure of pristine SPEEK and nanocomposite membranes was investigated by X-ray diffraction scattering (XRD) operated on an INEL model EQUINOX 3000, France X-ray Diffractometer in an angular range of 5–80°. The mechanical properties of the membranes were investigated using a tensile test machine with an elongation rate of 1 mm min^{-1} at room temperature.