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Development of cesium phosphotungstate salt and chitosan composite membrane for direct methanol fuel cells

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ABSTRACT

A novel composite membrane has been developed by doping cesium phosphotungstate salt ($Cs_xH_{3-x}PW_{12}O_{40}$ ($0 \leq x \leq 3$), Cs_x-PTA) into chitosan (CTS/Cs_x-PTA) for application in direct methanol fuel cells (DMFCs). Uniform distribution of Cs_x-PTA nanoparticles has been achieved in the chitosan matrix. The proton conductivity of the composite membrane is significantly affected by the Cs_x-PTA content in the composite membrane as well as the Cs substitution in PTA. The highest proton conductivity for the CTS/Cs_x-PTA membranes was obtained with $x = 2$ and Cs_2-PTA content of 5 wt%. The value is 6×10^{-3} S cm^{-1} and 1.75×10^{-2} S cm^{-1} at 298 K and 353 K, respectively. The methanol permeability of CTS/Cs_2-PTA membrane is about 5.6×10^{-7}, 90% lower than that of Nafion-212 membrane. The highest selectivity factor (φ) was obtained on CTS/Cs_2-PTA-5 wt% composite membrane, 1.1×10^4/S cm^{-3} s. The present study indicates the promising potential of CTS/Cs_x-PTA composite membrane as alternative proton exchange membranes in direct methanol fuel cells.

1. Introduction

Direct methanol fuel cells (DMFCs) have been considered as attractive alternative energy supply for future portable electronic devices due to their capability of high energy density, simplified system design and convenient fuel transportation and storage (Jiang, Zheng, Wu, Wang, & Wang, 2008; Tang, Wang, Pan, Jiang, & Ruan, 2007). The most common proton exchange membranes used in DMFCs are the state-of-the-art perfluorosulfonic acid (PFSA) based membranes such as Nafion due to their high proton conductivity, high structural and chemical stability and mechanical strength (Chai et al., 2010; Tang, Pan, & Wang, 2008). However, PFSA based membranes such as Nafion exhibit two technical challenges. One is their high cost (Sancho, Soler, & Pina, 2007), and the other is methanol crossover from anode to cathode through the membrane which results in a significant reduction in the electrical performance of DMFCs (Du, Zhao, & Yang, 2007; Eccarius, Garcia, Hebling, & Weidner, 2008; Qi & Kaufman, 2002; Tang, Pan, Jiang, & Yuan, 2005; Yang & Bae, 2008). It has been reported that over 40% of methanol could be lost in a DMFC due to crossover across the membrane (Tricoli, Carretta, & Bartolozzi, 2000).

In the past several years, much effort has been made in the development of polymer electrolyte membrane with inherent low methanol permeability, high conductivity and lower cost. Among them, chitosan (CTS) based materials have shown promising properties for applications as proton exchange membranes of low temperature fuel cells (Ma & Sahai, 2013; Odeh, Osifo, & Noemagus, 2013). Chitosan is an abundant natural polymer with low toxicity, biodegradable and biocompatible properties (Muzzarelli, 2011) that has been intensely used as a promising and low cost source of membrane material (Cui et al., 2008; Ma, Sahai, & Buchheit, 2012; Osifo & Masala, 2012). The wide application of chitosan on pervaporation membrane revealed its fine methanol permeability (Ghazali, Nawawi, & Huang, 1997; Mochizuki, Amiya, Sato, Ogawara, & Yamashita, 1989). Furthermore, chitosan based materials exhibit good thermal/chemical stability and mechanical properties due to the ring structure of the

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Abbreviations: CTS, chitosan; PTA, phosphotungstate salt; Cs_xPTA, cesium phosphotungstate salt ($0 \leq x \leq 3$); CTS/Cs_xPTA, cesium phosphotungstate salt and chitosan composite membrane; φ, selectivity factor; HPAs, heteropolyacids; WU, water uptake; W_{wet}, weight of wet membrane; W_{dry}, weight of dry membrane; ΔS, swelling degree; S_{wet}, area of wet membrane; S_{dry}, area of the dry membrane; σ, proton conductivity; GC, gas chromatography; FID, hydrogen flame ionization; P, methanol diffusion coefficient; NPs, nanoparticles.

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chitosan molecular, which would be beneficial to the fuel cell operation. However, pristine chitosan has low conductivity and there are no mobile hydrogen ions in its structure. It has been reported that the proton conductivity of the dry chitosan film without cross-linking and modification is very low, $\sim 10^{-9}$ S cm^{-1} at room temperature (Suzuki, Saimoto, & Shigemasa, 1999; Wan, Creber, Peppley, & Bui, 2003a). In order to increase the ionic conductivity of CTS membranes, structural modification (Chávez, Oviedo-Roa, Contreras-Pérez, Martínez-Magadán, & Castillo-Alvarado, 2010; Wan, Creber, Peppley, & Bui, 2003b), blending (Seo, Koh, Roh, & Kim, 2009; Smitha, Sridhar, & Khan, 2005), proton acid doping (Cui, Xing, Liu, Liao, & Zhang, 2009; Ma et al., 2012; Smitha, Devi, & Sridhar, 2008; Yamada & Honma, 2005) and inorganic salts doping (Khiar, Puteh, & Arof, 2006; Majid & Arof, 2005; Wu, Hou, Wang, Xiao, & Jiang, 2010) methods have been introduced. These studies have showed that the proton conductivity of the chitosan membrane could be improved while maintaining its good mechanical properties, methanol permeability and thermal/chemical stability.

Heteropolyacids (HPAs) are well known as superionic conductors in their fully hydrated state, particularly those with Keggin structure (Yang et al., 2005) and have been used to enhance the proton conductivity, water retention and resistance to methanol crossover properties of Nafion or other proton exchange membranes (Li, Xu, & Wang, 2003; Yang, Lu, Lu, Jiang, & Xiang, 2010). Among HPAs, cesium phosphotungstate salt (Cs_x-PTA, $0 \leq x \leq 3$) which contains the characteristic structure of phosphotungstic acid (PTA), has excellent conductive capability and increased stability in aqueous medium (Matsuda et al., 2007). It has been shown that addition of Cs_x-PTA enhances the proton conductivity and reduced methanol permeability of host matrix materials including sulfonated poly (ether-ether ketone) (SPEEK) (Doğan, Inan, Unveren, & Kaya, 2010; Zhang, Zhang, & Bi, 2008), Nafion (Amirinejad, Madaeni, & Navarra, 2011; Amirinejad, Madaeni, & Rafiee, 2011), chitosan-hydroxy ethyl cellulose (CS-HEC) (Mohanapriya et al., 2009), polybenzimidazole (PBI) (Li, Shao, & Scott, 2008; Oh et al., 2010), Nafion/polytetrafluoroethylene (PTFE) (Li, Shao, & Zhang, 2006) and polyethyleneoxide (PEO)/polyvinylidene fluoride–chlorotetrafluoroethylene (PVDF–CTFE) copolymer (Amirinejad, Madaeni, Navarra, Rafiee, & Scrosati, 2010), etc. As indicated by Hacer Dogan (Doğan et al., 2010), the methanol permeability was reduced to 4.7×10^{-7} cm^2/s for SPEEK/Cs-PTA membrane with 10 wt% Cs-PTA concentration, and acceptable proton conductivity of 1.3×10^{-1} S/cm was achieved at 80 °C under 100% RH.

In the present study, CTS/Cs_x-PTA composite membrane was prepared by blending Cs_x-PTA ($0 \leq x \leq 3$) with chitosan/acetic acid solution for potential application as proton exchange membranes of DMFCs. The composite membranes were characterized in details by Fourier transform infrared (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray (EDS) and thermo-gravimetric analysis (TG). Moreover, the effects of Cs_x-PTA content on the mechanical property and the proton conductivity at different temperatures, as well as the selectivity factor of CTS/Cs_x-PTA composite membrane has been investigated.

2. Experimental

2.1. Preparation of Cs_x-PTA and composite membranes

$Cs_xH_{3-x}PW_{12}O_{40}$ ($0 \leq x \leq 3$) were synthesized according to the literature method (Ma, Hua, Ren, He, & Gao, 2003). In a typical synthesis process, an aqueous solution of Cs_2CO_3 (0.1 mol/l) was added drop wise to an aqueous solution of $H_3PW_{12}O_{40}$ (PTA, Aldrich) (0.08 mol/l) with Cs/P molar ratios of 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0, respectively, at room temperature under vigorous stirring. The resulting white colloidal solution was aged overnight at ambient temperature and then evaporated at 50 °C till it was dry. The obtained samples were denoted as Cs_x-PTA.

The Cs_2-PTA powders with 1, 5 and 10 wt% proportions were added to a 2% (w/v) chitosan–acetic acid solution. After complete dispersion, the solution was cast on a glass plate and dried at 333 K for 24 h. The dry membranes on the plates were striped from the plate and then immersed in the absolute methanol (Sigma–Aldrich) for 2 h to remove the acetic acid. Finally, the prepared membranes were used for analysis without further treatment. CTS with 1, 5 and 10 wt% Cs_2-PTA was denoted as CTS/Cs_2-PTA-1 wt%, CTS/Cs_2-PTA-5 wt%, CTS/Cs_2-PTA-10 wt%, respectively.

2.2. Characterization of CTS/Cs_2-PTA membranes

Both the surface and cross section morphology of CTS/Cs_2-PTA membranes were examined under a scanning electron microscope equipped with energy dispersive X-ray spectrometer (EDS) detector (SEM, Oxford, Camscan3400; Oxford Instruments). Elemental mapping analysis was used to study the distribution of typical elements tungsten (W) of PTA in the structure of composite membrane.

Fourier transform infrared (FT-IR) spectroscopy of the membranes was recorded with a Nicolet (Madison, WI, USA) AVATAR 470 Fourier transform infrared spectrometer in the wavelength range from 4000 to 500 cm^{-1}. X-ray diffraction (XRD) patterns for polymeric membrane and Cs_x-PTA powder were obtained on a D/max 2200PC X-ray diffract meter using Cu Kα radiation source operating at 40 kV and 30 mA. The scanning rate was 4°/min in the angular range of 5–60°.

Thermal stability of the polymer electrolyte membranes was tested by TG analysis. Membrane samples for TG analysis were cut to small pieces before the test. Then the samples were encapsulated in hermetically sealed aluminum pans. The thermal analysis was performed by Shimadzu TGA-50 thermal analysis system with heating rate of 10 °C/min under N_2 atmosphere.

To investigate the swelling behaviors of the composite electrolyte membrane, the membrane samples were cut and stored in a hydration-controlled container. To determine the water uptake (WU) at each state of hydration, the membranes were removed from the container using a filter paper to remove excess surface water, and quickly weighed to give the initial wet weight, $M_{wet.}$ The dry weight of the membrane samples, M_{dry} was obtained after drying at oven. Meanwhile, the areas, S of wet and dry samples was measured. The changes in water uptake and areas were calculated with the following equations (Tang, Wang, Pan, & Wang, 2007).

$$\text{Wateruptake}\,(\%) = \frac{M_{wet} - M_{dry}}{M_{dry}} \times 100 \quad (1)$$

$$\Delta S\,(\%) = \frac{S_{wet} - S_{dry}}{S_{dry}} \times 100 \quad (2)$$

where S_{wet} is the area of wet membrane sample, and S_{dry} is the area of the dry membrane sample.

The tensile strength and elongation of the composite membranes were evaluated by a tensile test instrument (INSTRON 3365). The test was carried out at a strain rate of 5 mm/min at 293 K and a relative humidity of ∼10%. The membrane samples were prepared in rectangular shape with a gauge length of 40 mm and a width of 8 mm. The data of tensile strength elongation were determined according to the stress–strain curve. Each data was the average of at least three parallel experiments.