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Research paper

Preparation and characterization of quaternized poly(vinyl alcohol)/chitosan/MoS_2 composite anion exchange membranes with high selectivity

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ABSTRACT

In this study, a series of novel quaternized poly(vinyl alcohol)/chitosan/molybdenum disulfide (QPVA/CS/MoS_2) anion exchange membranes (AEMs) were prepared for direct methanol alkaline fuel cell (DMAFC). The composite membrane was synthesized by adding different amounts of MoS_2 nanosheets (0, 0.1, 0.2, 0.5 and 1 wt %) into QPVA/CS mixture solution and using the solution casting method. The crystallinity, thermal and mechanical properties, ion conductivity and resistance to methanol of the QPVA/CS/MoS_2 membranes were characterized by X-ray diffraction, thermogravimetric analysis, tensile testing, ion exchange capacity, and methanol permeability measurements, respectively. The MoS_2 was homogeneously dispersed in the membranes. The mechanical strength of the composite membranes was enhanced with the addition of MoS_2. With the addition of 1.0 wt% MoS_2, the QPVA/CS/MoS_2 composite membrane has the lowest methanol permeability of 0.210×10^{-7} $cm^2 \cdot s^{-1}$. This study confirmed that the novel QPVA/CS/MoS_2 membrane would be a potential candidate for the application in DMAFCs.

1. Introduction

In recent years, the research of fuel cell has aroused more and more interest for the urgent desire for clean and renewable sources of electric power. Among these power sources, direct methanol alkaline fuel cells (DMAFCs), which are operated in the hydroxide-conduction mode, may be a promising alternative energy source. DMAFCs have attracted considerable attention as the power source for mobile and portable applications due to their advantages of low pollution emitting and high energy density (Yang, Wang, Ma, Jiang, & Sun, 2015). Moreover, compared to direct methanol fuel cells, DMAFCs have the fast methanol oxidation kinetics and the intrinsic reduction in methanol permeability due to the opposite direction of OH^- anion motion process and methanol flux (Li et al., 2016; Zhang et al., 2016). Consequently, many researchers have paid much attention to the development of DMAFCs.

Correspondingly, the main part of DMAFCs is the anion exchange membrane (AEM), which plays an important role in selectively conducting OH^- ions and hindering methanol penetration. Therefore, synthetic and natural polymers, such as poly(vinyl alcohol) (PVA) (Beydaghi, Javanbakht, & Kowsari, 2014), chitosan (CS) (Feketefoldi & Cermenek, 2016), and poly (phenylene oxide) (PPO) (Wu et al., 2010) have been used to prepare AEM. Among these materials, the inexpensive and semi-crystalline PVA has been extensively studied as an excellent film-forming material. CS, an abundant cationic polysaccharide, has been suggested as a good AEM material and has a low methanol permeability (Mukoma, Jooste, & Vosloo, 2004). Moreover, it has been reported that blending of CS with PVA can improve the ion conductivity and mechanical properties of the composite membrane (Smitha, Sridhar, & Khan, 2005). Although there have been so many studies on AEM, its stability, ion conductivity and methanol barrier property still need to be improved. Therefore, Xiong et al. (Xiong, Fang, Zeng, & Liu, 2008) and Zhang et al. (Zhang, Liu, Zhu, Xiong, & Ren, 2009) prepared the quaternized PVA (QPVA) which could well conduct OH^- ions by the grafted quaternary ammonium groups. At the same time, the crystallinity of the polymer membrane is also a considerable factor affecting the related performance of AEM. The high crystallinity of the polymer membrane will suppress the mobility of the polymer chain and lead to the low ion transport rate (Yang & Wang, 2015). In this regard, based on our previous study, $AlCl_3 \cdot 6H_2O$ aqueous solution was employed as a good solvent used to dissolve CS in preparation of CS/PVA membrane (Jiang, Zhao, & Hou, 2016).

In addition, many researchers have found that the incorporation of inorganic filler into polymer is another approach to improve the ion conductivity, thermal stability and methanol barrier property of the polymer membranes (Tripathi & Shahi, 2011). For example, the QPVA/Al_2O_3 (Yang, Chiu, Chien, & Chiu, 2010), CS/silica coated carbon nanotubes (Liu et al., 2016) and graphene-based PVA/CS (PCG) (Yang, Wang et al., 2015) composite membranes have been studied, and they

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all exhibit an excellent high performance in DMAFCs. Among these inorganic fillers two-dimensional (2D) layer nanomaterials graphene and graphene analogs have attracted a lot of attention as the filler for polymer composites (Potts, Dreyer, Bielawski, & Ruoff, 2011; Stankovich et al., 2006). Analogous to graphene, the molybdenum sulfide (MoS_2) nanomaterial also shows extensive attraction due to its 2D lamellar structure and advantageous to the proton transport (Li, Zhang, Zhang, & Huang, 2015). Besides these features, the barrier effect, good mechanical properties and thermal stability of MoS_2 nanosheets were also found (Lin, Ding, Xu, Chen, & Chen, 2009; Zhou et al., 2012). Herein, MoS_2 has been incorporated into many polymer matrices such as sodium alginate (Xuan, Zhou, Nie, & Chen, 2017), PVA (Zhang et al., 2015), and CS (Yang, Meng, Zhu, Zhou, Nie & Chen, 2015) to prepare polymer nanocomposites. Moreover, Tang et al. (Feng, Tang, & Wu, 2013) prepared the MoS_2/Nafion composite membrane for DMFCs, and the methanol permeability of MoS_2/Nafion membrane is much lower than Nafion. Zhang et al. (Li, Zhang, Zhang, & Huang, 2015) investigated the effect of MoS_2 on the proton conductivity of the sulfonated polyimide/s-MoS_2 (SPI/s-MoS_2) composite membrane, which could be applied for vanadium redox flow battery. These studies have revealed that suitable amount of MoS_2 would play an obviously positive role in improving the performance of polymer composite membrane for fuel cell.

The objective of this study is to improve the selectivity of AEM by improving the ion conductivity and resistance to methanol. In this study, we synthesized QPVA particles and MoS_2 nanosheets, and $AlCl_3{\cdot}6H_2O$ aqueous solution was used as the solvent for CS. Subsequently, the novel organic-inorganic composite QPVA/CS/MoS_2 membranes were prepared by casting the mixed solution with the addition of different amount of MoS_2. Then, the thermal stability, mechanical stability and crystalline properties of these membranes was investigated. For the application in DMAFCs, the QPVA/CS/MoS_2 membranes were immersed in 4 M KOH solution to form the alkaline polymer electrolyte membranes. The primary physical-chemical properties of these electrolyte membranes including ion-exchange capacity (IEC), ionic conductivity (σ) and methanol permeability were discussed. The positive effect of MoS_2 flakes on the polymer membrane was demonstrated by these characterization results.

2. Experimental

2.1. Materials

PVA was provided by Sichuan Vinylon Factory, SINOPEC (China). Degree of polymerization and hydrolysis of PVA were 1750 and 99%, respectively. (2, 3-epoxypropyl) trimethylammonium chloride (EPTMAC, purity ≥ 95%) and KOH were purchased from Tianjin Zhiyuan Chemistry Factory (China). CS (degree of deacetylation ≥ 95%, the viscosity of 100–200 mPa·s) and glutaraldehyde solution (GA, 50% aqueous solution) were purchased from Aladdin Reagent Co. (China). Ammonium molybdate ([$(NH_4)6Mo_7O_{24}{\cdot}4H_2O$]), elemental sulfur, and hydrazine monohydrate (86 wt% aqueous solution) were purchased from Aladdin Reagent Co. (China). All the other reagents of analytical grade were obtained from Sinopharm Chemical Reagent Co. Ltd (China). Distilled water was self-prepared in laboratory.

2.2. Preparation of MoS_2 and QPVA

The synthesis of the MoS_2 nanosheets was according to the process described in the literature by Peng et al. (Peng et al., 2001). Firstly, 2 g [$(NH_4)6Mo_7O_{24}{\cdot}4H_2O$] powder, 0.7 g elemental sulfur and 15 ml of hydrazine monohydrate were put into a 100 ml Teflon-lined stainless, which was filled with distilled water to the 70% total volume. Then the autoclave was maintained at 180 °C for 48 h, and then cooled to room temperature. The black precipitate was filtered from the solution, and washed with distilled water, diluted hydrochloric acid and ethanol solution, respectively. Finally, The dark-gray powder was dried under vacuum at 40 °C for 6 h. Due to the weak Van der Waals interactions between the bulk MoS_2 sheets, they can be exfoliated into 2D nanosheets by chemical and mechanical methods. 0.05 g MoS_2 powder was added into 100 ml 45% ethanol/water as the dispersion solvent mixture (Zhou, Mao, Wang, Peng, & Zhang, 2011). This mixed solution was sonicated for 8 h, and then the dispersion was centrifuged at 5000 rpm for 10 min to remove the aggregates. The suspension was collected for the experiment.

QPVA was prepared according to the following procedure. Firstly, 5 g PVA was dissolved in 90 ml distilled water to obtain a homogeneous viscous solution. Then 10 ml of KOH solution (2 M) and 10 g EPTMAC were added to the viscous solution under continuous stirring for 4 h at 65 °C for quaternization of PVA chains. The resulting viscous mixture was washed with anhydrous ethanol to obtain the precipitate and dried in a vacuum at 60 °C for 24 h. Finally, the white QPVA particles were obtained.

2.3. Preparation of the QPVA/CS/MoS_2 membranes

The QPVA/CS/MoS_2 membranes were prepared by solution casting method. 4 g QPVA was dissolved in 100 ml distilled water and 1 g CS was dissolved in 100 ml 1 wt% $AlCl_3{\cdot}6H_2O$ aqueous solution at 90 °C and with stirring, respectively. The QPVA and CS solutions were mixed together to obtain a mixture solution. Next, different volume of MoS_2 in 45% ethanol/water was poured into the mixture solution and stirred continuously. Afterwards, the QPVA/CS/MoS_2 mixture solution was cross-linked with 0.4 ml GA (10 wt%) for 1 h under continuous stirring. Finally, the resulting viscous solution was poured onto a round plate (with the diameter of 15 cm) and dried at 60 °C for 48 h to get the membrane with the thickness of about 150 μm. The final concentrations of MoS_2 in the prepared membranes were 0, 0.1, 0.2, 0.5 and 1.0 wt%, and named QPVA/CS, QPVA/CS/MoS_2-0.1, QPVA/CS/MoS_2-0.2, QPVA/CS/MoS_2-0.5 and QPVA/CS/MoS_2-1.0, respectively.

2.4. Characterization of the QPVA/CS/MoS_2 membranes

2.4.1. Scanning electron microscopy (SEM)

The cross-section morphology of the membrane were observed using a Quanta 250 (America). To view the cross section of the membranes, the samples were previously fractured by immersing in liquid nitrogen, and the cross section image was get. All of the samples were dried and sputtered with gold before the measurement.

2.4.2. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of the membrane samples were recorded using a Nicolet iS50 spectrometer (Thermo Fisher Scientific, USA). The dried membrane samples were recorded in the wavenumber range of 4000–500 cm^{-1}. All spectra were obtained with 32 scans at a nominal resolution of 4 cm^{-1}.

2.4.3. X-ray diffraction (XRD)

The XRD patterns of the samples were collected on an X' Pert PRO (Panalytical, Netherlands). The XRD radiation was generated using Cu Kα radiation at 40 kV and 40 mA. The scanning speed was 0.209°/s with the step size of 0.0167°, and recorded in the angle range of 5–65° at the ambient temperature.

2.4.4. Thermogravimetric analysis (TGA)

The TGA instrument STA449C (NETZSCH, Germany) was used to study the thermal properties of various samples. TGA was conducted from 50 °C to 800 °C at a heating rate of 10 °C/min under the nitrogen gas atmosphere. All the samples were dried at 60 °C in a vacuum oven and kept under vacuum until the measurement.