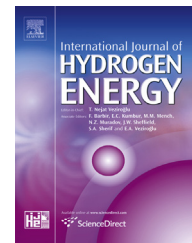




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Fabrication and properties of poly(vinyl alcohol)-based polymer electrolyte membranes for direct methanol fuel cell applications

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ABSTRACT

A series of poly(vinyl alcohol) (PVA)-based organic–inorganic crosslinked polymer electrolyte membranes with PVA and poly(methacrylic acid-2-acrylamido-2-methyl-1-propanesulfonic acid-vinyltriethoxysilicone) (PMAV) are prepared for direct methanol fuel cell applications. Fourier transform infrared (FTIR) spectroscopy measurements clearly reveal the existence of crosslinking reactions and molecular interactions in PVA–PMAV membranes. The results of TGA show that the PVA–PMAV membranes possess good thermal stability. The uptake behavior, methanol diffusion coefficient, proton conductivity and selectivity of membranes also are investigated as function of PMAV content. The results indicate that the PVA-based organic–inorganic crosslinked membranes are particularly promising to be used as polymer electrolyte membranes due to their excellent methanol barrier property, suitable proton conductivity and high selectivity.

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Introduction

Poly(vinyl alcohol) (PVA) has been extensively used in many fields, such as textile sizing, adhesives, desalination, food wrappings and fuel cells [1–6]. Particularly, PVA is very attractive for preparing polymer electrolyte membranes (PEMs) in direct methanol fuel cells (DMFCs) due to its good film-forming capacity, low cost, chemical stability, good mechanical property and excellent methanol barrier property [7–9]. However, PVA itself does not have fixed charges and swell easily in water, which make the conductivity and mechanical strength of PVA membrane unsatisfactory. Hence,

PVA needs to be modified to improve the proton conductivity and constrain swelling in aqueous solutions without destroying its other properties in order to enhance the applicability of PVA membrane in DMFCs. Blending, crosslinking and incorporating with inorganic fillers are commonly used to improve the properties of membranes [10–12]. Proton conduction of PVA is obtained possibly by combining it with other materials bearing acid groups, such as poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS) [8,13], poly(styrene sulfonic acid) [14], phosphor tungstic acid (PWA) [15,16] or by crosslinking it with poly(styrene sulfonic acid-co-maleic acid) [17,18], sulfosuccinic acid (SSA) [1], poly(acrylic acid) [19], etc. It is noted that the

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individual introduction of proton conductive materials seems be adverse to the swelling, methanol resistance and mechanical strength [20–22]. From the DMFC application point of view, the PVA-based PEMs with an IPN structure might obtain satisfied conductivity, long-term durability and low methanol crossover properties by modifying PVA with the materials containing acid groups and by further treatment with crosslinking. Mitsuru Higa et al. [23] described that one of the potential disadvantages of PEMs with a semi-interpenetrating network (IPN) structure was that they showed low long-term stability in aqueous solutions owing to the dissolution of the uncrosslinked water-soluble polyelectrolytes from the network into the solution. However, in PEMs with an IPN structure, the chains of PVA and PVA-based polyanion were crosslinked with each other, leading to the PEMs showed higher long-term stability in aqueous solution than PEMs with a semi-IPN structure.

Another approach to improve the properties of PVA membrane is to fabricate organic–inorganic composites [20,24,25]. Introducing inorganic particles (e.g. Al_2O_3 , SiO_2) into a polymer matrix can not only block methanol crossover, but also improve the conductivity and mechanical properties of membranes [26]. However, during the fabrication of organic–inorganic composites, it is difficult to ensure the homogeneous dispersion of inorganic particles in polymer matrix [27,28].

In this paper, we attempt to develop a novel organic–inorganic crosslinked membrane based on PVA and poly(methacrylic acid-2-acrylamido-2-methyl-1-propanesulfonic acid-vinyltriethoxysilicone) (PMAV). PMAV is used here as the donor of sulfonic acid groups, crosslinking agent and silica source. A significant feature of this technique is the successful combination of polymer with inorganic structure at the molecular level. Besides, the physical and chemical properties of PVA-based membranes could be improved to satisfy the need of DMFCs due to the addition of sulfonic acid group, multiple crosslinking and the existence of inorganic structure in membranes.

Experimental

Materials

Vinyltriethoxysilicone (VTES) was purchased from Shanghai Huarun Chemical Company and used as received. Methacrylic acid (MAA) and Ammonium persulfate (APS) were obtained from Shanghai Chemical Reagent Co. (China). 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) was used as received from Aldrich. All the other reagents and solvents were obtained commercially and used without further purification. The water used in this experiment was distilled followed by deionization.

Synthesis of the poly(methacrylic acid-2-acrylamido-2-methyl-1-propanesulfonic acid-vinyltriethoxysilicone) (PMAV)

The PMAV was synthesized via emulsion polymerization method. The polymerization was carried out in a 250 ml four-

neck flask that was nitrogen-purged, equipped with reflux condenser, mechanical stirrer, dropping funnel and nitrogen inlet. First, 6.21 g AMPS was introduced into the flask charged with 70 ml of deionized water, and the so-obtained solution was stirred until the AMPS completely dissolved. Then, the mixture of 1.72 g MAA, 0.61 g VTES and APS aqueous solution (0.05 g of APS was solved in 2.5 ml water) was added into the flask. The flask was placed in water bath and heated to 75 °C with a stirring rate of 300 rpm. After additional 30 min equilibration time, the mixture of 3.44 g MAA and 1.23 g VTES was dropped into the above flask in 2 h while APS aqueous solution (0.15 g of APS was solved in 7.5 ml water) was dropped into the above flask in 3 h. Subsequently, the temperature was raised to 80 °C and maintained at this temperature for 6 h to finish the reaction. The chemical structure of PMAV is shown in Fig. 1.

Membrane preparation

To prepare the PVA-based organic–inorganic crosslinked membranes (PVA–PMAV), a multistep protocol was required. First, PVA was fully dissolved in water at 90 °C and then cooled to room temperature. Subsequently, PMAV solution was added to PVA solution in proportions varying from 10% to 40%. After removing the air in a vacuum, the homogeneous solution was poured on a clean glass plate and heated at 60 °C for 24 h, and then at 120 °C for 2 h. In order to reduce swellability, the obtained membrane was immersed in glutaraldehyde (GA)/acetone/HCL mixture at 40 °C for 3 h. Among this process, the crosslinking took place between the –OH of PVA and the –CHO of glutaraldehyde in the membrane due to the acid-catalyzed reaction. Finally, the membrane was washed several times with distilled water to remove the residual solvent. For convenience, the membranes are designated as PVA–PMAV X, where X represents the weight percentage of PMAV in the membrane.

Measurements

The Fourier transform infrared (FTIR) spectra were measured using Nicolet Instruments Research Series 5PC Fourier

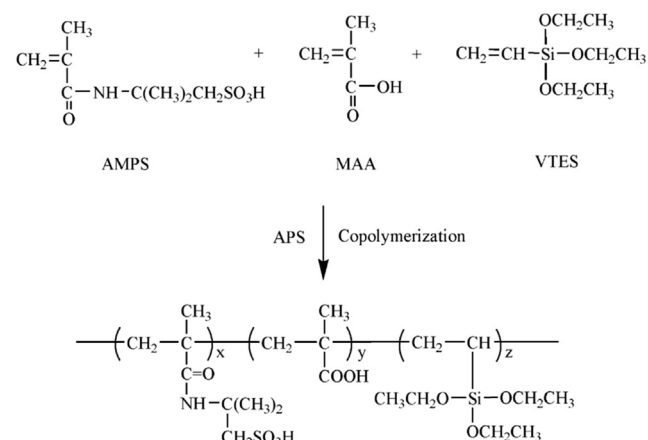


Fig. 1 – The chemical structure of PMAV.

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