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Inorganic–organic hybrid membranes with anhydrous proton conduction prepared from tetraethoxysilane, 3-glycidyloxypropyltrimethoxysilane, trimethyl phosphate and diethylethylammonium trifluoromethanesulfonate

Wen-hao Luo, Lian-hua Zhao*

Department of Chemistry, College of Science, Yanbian University, Yanji 133002, Jilin, China

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ABSTRACT

New silicon source (3-glycidyloxypropyltrimethoxysilane (GPTMS)) was used to make non-glass inorganic–organic hybrid membranes with diethylethylammonium trifluoromethanesulfonate ([dema][TfO]) by the sol–gel method. The hybrid membranes were studied with respect to their structural, thermal, proton conductivity and pores properties. The Fourier transform infrared spectroscopy (FT-IR) results showed that there was intermolecular interaction between ionic liquid and Si–O–Si skeleton structure in the inorganic–organic hybrid membranes. The thermogravimetric (TG) and differential scanning calorimetry (DSC) analysis showed that the hybrid membranes displayed good chemical stability and were thermally stable up to more than 200 °C in air. The N₂ adsorption test showed the hybrid membranes had good pore property and ionic liquid influenced the structure of hybrid membrane. Proton conductivity was measured from 20 °C to 220 °C and high conductivity of 1.2×10^{-2} S/cm was obtained for a 60 wt% [dema][TfO] doped hybrid membrane (ionogel) at 220 °C under anhydrous conditions. This method for the preparation of hybrid membranes is promising and may be used for the proton exchange membrane in fuel cells.

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1. Introduction

A fuel cell is an energy-conversion device that can directly convert chemical energy into electrical energy. It has many advantages such as high efficiency, easy cleaning, no charging requirement, high energy density and high power density, etc. [1–3]. Compared with other types of fuel cells, the electrolyte of a proton exchange membrane fuel cell (PEMFC) is solid and thus has a more compact structure and can achieve a higher energy density. In addition, it is portable and showcases a broad range of prospective applications [4–6]. The proton exchange membrane is the core component of the PEMFC. It is required to conduct protons and block electrons. Until now, both H₂/O₂ PEMFC and direct alcohol fuel cells use Nafion® family of films produced by DuPont. Although the Nafion® perfluorosulfonated film has high proton conductivity (humidification), good chemical stability and high mechanical strength [7,8], these features are limited by the strict temperature (< 100 °C) requirement. It also has the disadvantages of high cost, difficulties in water management and a high

ratio of methanol permeability [9–11], which pose limitations in the usage of PEMFC application. Therefore, it is essential to develop film material with good electrical conductivity and high thermal stability at a relatively high temperature (> 100 °C) that is not restricted by humid conditions. Noto et al. [12,13] modified Nafion membranes with ionic liquids (ILs), which improved the thermal stability of the membranes and it could work below 150 °C. However, the proton conductivity and thermal stability still need to be improved.

H₃PO₄, NH₄SCN and ILs are proton-conducting electrolytes in mid-temperature range under non-humidifying conditions [14–16]. However, they are liquid electrolytes, and therefore it is inconvenient for their storage and transportation. It needs a supporter to contain the liquid electrolyte in PEMFC. Nogami et al. [17] has used SiO₂ as a supporter, which was modified with phosphotungstic acid for use in PEMFC. Based on his group's research, SiO₂ is found to support the ionic liquid in making hybrid membranes [18–21]. These membranes show high conductivity and thermal stability, but they are glass membranes. Tetraethyl orthosilicate (TEOS), tetramethoxysilane, and methyltrimethoxysilane were used as the silicon sources, and trimethyl phosphate (PO(OCH₃)₃) was usually added, which can increase the proton-conductivity [22].

* Corresponding author. Tel./fax: +86 433 2732292.

E-mail address: zhaolianhua@ybu.edu.cn (L.-h. Zhao).

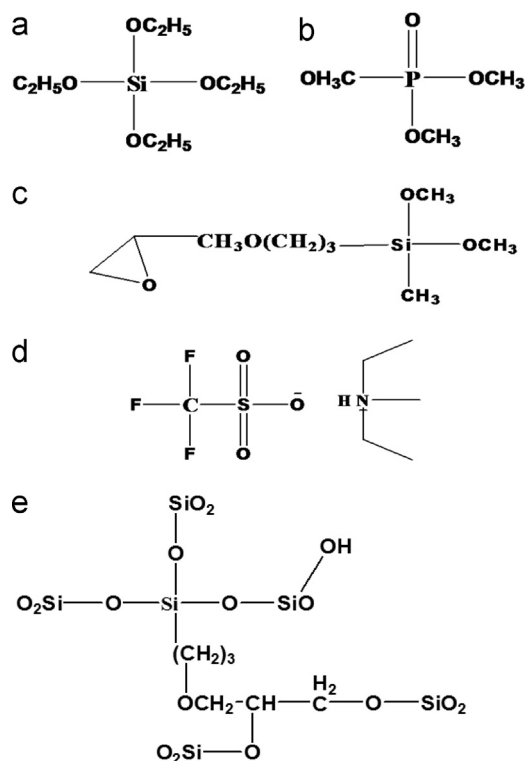


Fig. 1. Schemes of the basic chemical structure of (a) TEOS, (b) PO(OCH₃)₃, (c) GPTMS, (d) [dema][TfO] and (e) the possible siloxane net skeleton structure.

In order to improve the tenacity of hybrid membrane, we added new silicon source GPTMS into TEOS and PO(OCH₃)₃ precursor when preparing the hybrid membrane. The ratio of GPTMS and TEOS was varied until the optimal ratio was achieved for the pristine membrane (hybrid membrane without ionic liquid). We chose ILs ([dema][TfO]) as the organic component, because it shows high conductivity at room temperature. The amount of [dema][TfO] was also modulated to increase the conductivity of the hybrid membranes. And the ionogel was obtained when we added the IL into the pristine membrane. The structure of TEOS, GPTMS, PO(OCH₃)₃, [dema][TfO] and the possible siloxane net structure of hybrid membrane are shown in Fig. 1.

2. Experimental

2.1. Reagents and instruments

N,N-dimethyl-ethylamine ([dema], Aldrich, 97%), trifluoromethyl sulfonic acid ([TfO], Alfa, 98%), anhydrous ethanol (AR), 3-glycidyloxypropyltrimethoxysilane (GPTMS, Aladdin, 97%), trimethyl phosphate (PO(OCH₃)₃, Aladdin, 98%), tetraethyl orthosilicate (TEOS, Aladdin, 98%), toluene (AR), ethyl acetate (AR), dichloromethane (AR), acetone (AR), n-ethyl silicate (AR), and formamide (AR) were purchased and used without further purification.

An infrared spectrometer (Prestige-21), a vacuum drying oven (DZF-6020), a thermal analyzer (STA-449F3), an isothermal magnetic stirrer (85-2), an ultrasonic oscillator (KQ2200), an electric hot plate (DB-3A) and an electrochemical workstation (CHI-660D) were all used in this study.

2.2. Preparation of ionic liquid and hybrid membrane

2.2.1. Preparation of [dema][TfO]

A given amount of N,N-dimethyl-ethylamine was dissolved in 100 ml anhydrous ethanol as solution A. The equal molar amount

of trifluoromethyl sulfonic acid was dissolved in 100 ml anhydrous ethanol as solution B. The B solution was then slowly added drop-wise to the solution A under magnetic stirring and was kept stirring for 6 h at room temperature. The solvent was then removed by distillation at 80 °C. Finally, the solution was vacuum dried at 120 °C for 24 h. The yield of the [dema][TfO] is 96.7%.

2.2.2. Preparation of inorganic–organic ionogel

The ionogel was prepared using tetraethyl orthosilicate, 3-glycidyloxypropyltrimethoxysilane, trimethyl phosphate, and [dema][TfO]. All synthesis processes were fabricated at room temperature under atmospheric pressure by the sol–gel process. Several compositions of TEOS-GPTMS-PO(OCH₃)₃+IL were selected for optimization. Here, it should be noted that we added ionic liquid content in excess of wt% to the pristine membranes which was TEOS-GPTMS-PO(OCH₃)₃.

Initially, the calculated amount of TEOS was hydrolyzed with water (0.15 N-HCl aq) and ethanol under stirring for 60 min. The molar ratio of TEOS/EtOH/H₂O/HCl was 1/4/4/0.004. Then, GPTMS, which was pre-hydrolyzed with water (as 0.15 N-HCl aq) and ethanol, was added to the TEOS solution under constant stirring for 1 h. The molar ratio of GPTMS/EtOH/H₂O/HCl was 1/4/4/0.004. Approximately 1 h later, when the above mixed solution became transparent, trimethyl phosphate dissolved in C₂H₅OH (molar ratio of trimethyl phosphate and C₂H₅OH is 1:5) was added drop-wise under a magnetic stirring for a time period of 1 h. After this reaction proceeded for 1 h, [dema][TfO] was separately added drop-wise to the hydrolyzed solution. It was kept under continuous stirring for 3 h until a homogeneous solution phase was formed. CH₃CONH₂ (1–3 ml) was also added to the standard solution followed by 60 min stirring. Then, the solution was treated with ultrasonic vibration for 30 min. This resulting clear transparent solution was called sol. The sol was cast onto a PTFE plate and gelled for 10 days. The obtained gel films were dried at 100 °C for 12 h. The whole synthetic process is shown in Fig. 2. The thickness of hybrid membranes is about 1 mm.

2.3. Characterization method

Structures of the synthesized IL monomer and PIL were confirmed by ¹H NMR spectroscopy (Bruker 3000 Hz) using DMSO-d₆ as the solvent. Infrared spectra of the compounds were recorded with a FT-IR spectrometer (Prestige-21) between 4000 cm⁻¹ and 400 cm⁻¹ using the KBr pellet. The N₂ gas adsorption–desorption isotherms were measured using a Quantachrome-Nova-1000 nitrogen gas sorption analyzer. Heat treatment was used to remove ionic liquids by a three-step procedure before measurement occurred. The first step involved keeping the sample at 150 °C for 40 min, the sample was kept at 300 °C for 60 min in the

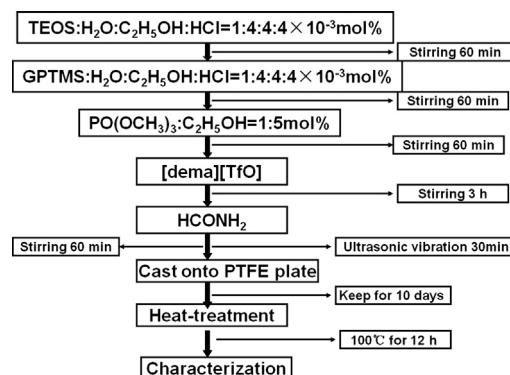


Fig. 2. Flow chart for the preparation of hybrid membranes.

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