



A polytetrafluoroethylene porous membrane and dimethylhexadecylamine quaternized poly (vinyl benzyl chloride) composite membrane for intermediate temperature fuel cells



Yuan-Cheng Cao^{a, b, *, 1}, Chenxi Xu^{c, 1}, Linling Zou^{a, b}, Keith Scott^d, Jiyang Liu^{a, b}

^a Key Laboratory of Optoelectronic Chemical Materials and Devices of Ministry of Education, Jiangnan University, Wuhan 430056, China

^b Flexible Display Materials and Technology Co-Innovation Centre of Hubei Province, Jiangnan University, Wuhan 430056, China

^c School of Materials Science and Engineering, Hefei University of Technology, Hefei, Anhui, China

^d School of Chemical Engineering and Advanced Materials, University of Newcastle, NE1 7RU, UK

H I G H L I G H T S

- Polytetrafluoroethylene can effectively reinforce phosphoric acid (PA) doped membrane for fuel cells.
- The conductivity of the composite membrane showed not too much different from the neat membranes.
- The thickness of the composite membrane can be as thin as 2 μm to keep necessary mechanical strength.
- The fuel cell peak power density of the H_2/O_2 at 175 °C was 360 mW cm^{-2} .

A R T I C L E I N F O

Article history:

Received 3 October 2014

Received in revised form

3 June 2015

Accepted 24 June 2015

Available online xxx

Keywords:

H_3PO_4 membrane

Ionomer

Quaternary ammonium

PTFE porous membrane

Fuel cells

A B S T R A C T

A composite material for phosphoric acid (PA) loaded membrane was prepared using a porous polytetrafluoroethylene (PTFE) thin film. N, N-Dimethylhexadecylamine partially quaternized poly (vinyl benzyl chloride) (qPVBzCl⁻) was synthesized as the substrate for the phosphoric acid loaded polymer membrane. SEM observation indicated that the pores were filled with the qPVBzCl⁻. The maximum PA loading level was calculated to be 4.67–5.12 per repeat unit on average. TGA results showed that resultant composite membrane was stable in the intermediate temperature from 100 °C to 200 °C. The composite membrane tensile stress was 56.23 MPa, and the Young's Modulus was 0.25 GPa, and the fractured elongation was 23%. The conductivity of the composite membrane after the PA addition (H_3PO_4 @PTFE/qPVBzCl⁻) increased from 0.085 S cm^{-1} to 0.11 S cm^{-1} from 105 °C to 180 °C. The peak power density of the H_2/O_2 at 175 °C under low humidity condition (<1%) for H_3PO_4 @PTFE/qPVBzCl⁻ membranes was 360 mW cm^{-2} .

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) play an important role among fuel cells which are considered as potential power source for future pollution-free applications. In recent years, considerable efforts have been made to develop intermediate temperature (100–200 °C) PEMFC [1,2]. This temperature range offers advantages of: (1) high CO tolerance, (2) enhancement in

efficiency, (3) avoidance of flooding, (4) system simplification and (5) more potential to use non-noble metal catalyst [3–7].

Solid state electrolytes loaded with phosphoric acid can provide less corrosion and more immobilization compared to aqueous phosphoric acid fuel cell (PAFCs). Quaternized polymers are considered as promising membrane materials for intermediate temperature PEMFC. Li et al. reported a poly (R1R2R3)-N⁺/H₃PO₄ which showed high proton conductivity (0.12 S cm^{-1}) at 160 °C and greater than 0.7 W cm^{-2} at 150 °C with dry H_2/O_2 [3]. Wang et al. showed that quaternary diazabicyclo-octane polysulfone/H₃PO₄ providing acceptable performance for intermediate temperature fuel cells (400 mW cm^{-2} at 150 °C and atmospheric pressure) [8]. Although a number of novel materials have been developed, there

* Corresponding author. Key Laboratory of Optoelectronic Chemical Materials and Devices of Ministry of Education, Jiangnan University, Wuhan 430056, China.

E-mail address: yuancheng.cao@jhu.edu.cn (Y.-C. Cao).

¹ These authors contributed equally to this work.

are still some challenges in the exploration of membrane with high ion conductivity and good fuel cell performance [3–8].

The quaternary ammonium (QA) groups in the modified polymer materials significantly affect the resultant polymer physico-chemical properties due to the reasons such as polymer chain rearrangements and crystal structure changes [8–10]. Therefore, beside the ion conductivity, the stability and tensile strength are the key factors for considering them as polymer electrolyte membranes in PAFCs. Good mechanical strength is an important property for membrane, which benefits the working life in the fuel cells. Polytetrafluoroethylene (PTFE) is a material that can increase the mechanical strength of the membrane as reported by Li et al. [11]. Xing et al. reported a montmorillonite/sulfonated poly (phenylether sulfone)/PTFE composite membrane that provided good stability and strength at high temperature and low swelling ratio [12]. A polytetrafluoroethylene (PTFE)/quaternized polysulfone (QNPSU) composite membrane has been fabricated for a hydrogen fuel cell and gave a power density of 400 mWcm⁻² using oxygen at 175 °C [8,13]; Also a proton-conducting composite membrane was fabricated by blending Sn_{0.95}Al_{0.05}P₂O₇, PBI and polytetrafluoroethylene (PTFE), which is to increase the tensile strength of the resulting composite membrane. A fuel cell made with this composite membrane yielded a power density exceeded 200 mW cm⁻² at above 100 °C [14]; Another Polybenzimidazole based PTFE composite membrane for acid doping fuel cells gave a power density of 200–300 mW, OCV 0.80–0.95 V at 180 °C [15].

Here in this work, a porous PTFE fibre film was used as the support to provide good mechanical strength based on synthesized qPVB/Cl⁻ ionomer which was immobilised in the pores. This composite membrane has good mechanical strength and good proton conductivity after being treated with H₃PO₄.

2. Experimental

2.1. Chemicals and reagents

Mw 55 kDa of Poly (vinyl benzyl chloride) (60/40 mixture of m- and p-isomers) and N,N-Dimethylhexadecylamine were purchased from Sigma; Porous Polytetrafluoroethylene (PTFE) film was purchased from Sterlitech Co. (QM712, Hydrophilic Microporous Membrane, 2 µm in thickness, 80% porosity); PVDF colloidal, Microscope glass slides (76 mm × 26 mm), Toluene, iso-propanol, Tetrahydrofuran and other inorganic chemicals such as KOH were purchased from Fisher Scientific (UK). 60% Pt/C Catalyst was purchased from Alfa Aesar (UK, catalogue no. 44171) and carbon paper with gas diffusion layers were purchased from Freudenberg Inc (Germany, catalogue no. H2315 T10A C1). All other chemicals were used as received and the water used in this work was distilled water.

2.2. The quaternary ammonium ionomer synthesis and PTFE membrane preparation

First, in a conical flask equipped with the reverse condenser, Poly vinyl benzyl chloride 10 g was dissolved in 100 mL toluene at 70 °C under the stirring to obtain the polymer solution. Then 20 mmol of N,N-Dimethylhexadecylamine amination reagent was added to the flask which followed by the 24 h reaction at 70 °C, and then precipitation and purification procedures were taken to harvest the as-synthesized quaternary ammonium modified PVBCl (qPVB/Cl⁻) (Fig. 1(a)). Then 5 mL of qPVB/Cl⁻ polymer was diluted to 20 mL with toluene to make the 300 mg/mL final diluted ionomer for the membranes cast and MEA preparation.

PTFE films were treated in ethanol first under sonication for 1 h and then treated with acetone. Then these films were dried in air

till the weights kept constant. The treated PTFE films were cut into the size of 10 cm × 10 cm and weighted individually before being immersed into the above prepared diluted qPVB/Cl⁻ ionomer solution for 30 min and then dried in air. Then these films were immersed in the ionomer again before drying in the air; these procedures were repeated for several times until the pores were filled with ionomer by observation in microscopy. The resultant films were weighted and calculated to be the 71% of ionomer percentages by the weight differences.

Then 11 mol dm⁻³ (M) H₃PO₄ solution was used to treat the ionomer filled PTFE membranes for 2 days to have the maximum doping lever. The samples were subjected to acid loading measurement, TGA, mechanical strength, conductivity and fuel cell tests.

The acid loading was calculated by:

$$\text{PA doping level} = \frac{(\text{Molar}_{\text{PA}})}{(\text{Molar}_{\text{ionomer}})}$$

where Molar_{PA} is the molarity of PA in the membrane, $\text{Molar}_{\text{ionomer}}$ is the molarity of quaternary ammonium groups in the qPVB/Cl⁻ ionomer that filled in the PTFE film.

2.3. Conductivity measurement

Four-point probe was used to measure the membrane conductivity with a Frequency Response Analyser (Voltech TF2000, UK). On the four platinum foils (probes), the membrane samples (1 cm by 5 cm) were placed with equal spacing of 5 mm. In the range of the 1 and 20 kHz, AC impedance measurements were applied under different cell temperatures which were held for 2 h. During the tests, the whole test system was supplied with N₂ gas flow to obtain the desired humidity from the humidifier. All the samples were kept in the same conditions. The measurements were taken at 30 min intervals. The setup system information can be found in the [Support information](#).

2.4. Membrane electrode assemblies and fuel cell tests

In brief, catalyst inks prepared in THF for the Membrane Electrode Assemblies (MEA) were made with the Pt/C catalyst, qPVB/Cl⁻ ionomer and 5% PVDF. This mixture was prepared under ultrasonic disperse for 60 min before the spray. Carbon-supporting electrodes with gas diffusion layer were prepared under 80 °C with pressure N₂ flow. These electrodes were then dried at 80 °C to remove any solvent and traces. The Pt loading on the electrodes were calculated to be 0.5 mg cm⁻². By pressing the anode and cathode onto the membranes to make the MEAs at room temperature for 2 min and the pressure was 50 kg cm⁻². The operation cell was made of two high-density graphite blocks that implanted with phenolic resin in the central. The active electrode area was 1 cm² with the parallel gas flow channels area. Four cartridge heaters were applied at the sides of graphite blocks for the desired temperature. Metal bolts which screwed into the blocks were used for the electrical contact and current collection. Fuel gas H₂ was fed to the cell at flow rates of 0.4 dm³ min⁻¹ and O₂ was fed with the rate of 0.7 dm³ min⁻¹. These gases were used at the atmospheric pressure. The scan rate was 5 mV s⁻¹.

3. Results and discussion

Quaternary ammonium (QA) containing polymer membranes are reported to show promising performance in the phosphoric acid fuel cells (PAFCs) at intermediate temperatures [3–8]. However, good mechanical properties and thermal stability are still the

Download English Version:

<https://daneshyari.com/en/article/7730924>

Download Persian Version:

<https://daneshyari.com/article/7730924>

[Daneshyari.com](https://daneshyari.com)