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

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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 H₂/O₂ at 175 °C was 360 mW cm⁻².

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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 (H₃PO₄@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 H₂/O₂ at 175 °C under low humidity condition (<1%) for H₃PO₄@PTFE/qPVBzCl⁻ membranes was 360 mW cm⁻².

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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 H₂/O₂ [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

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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

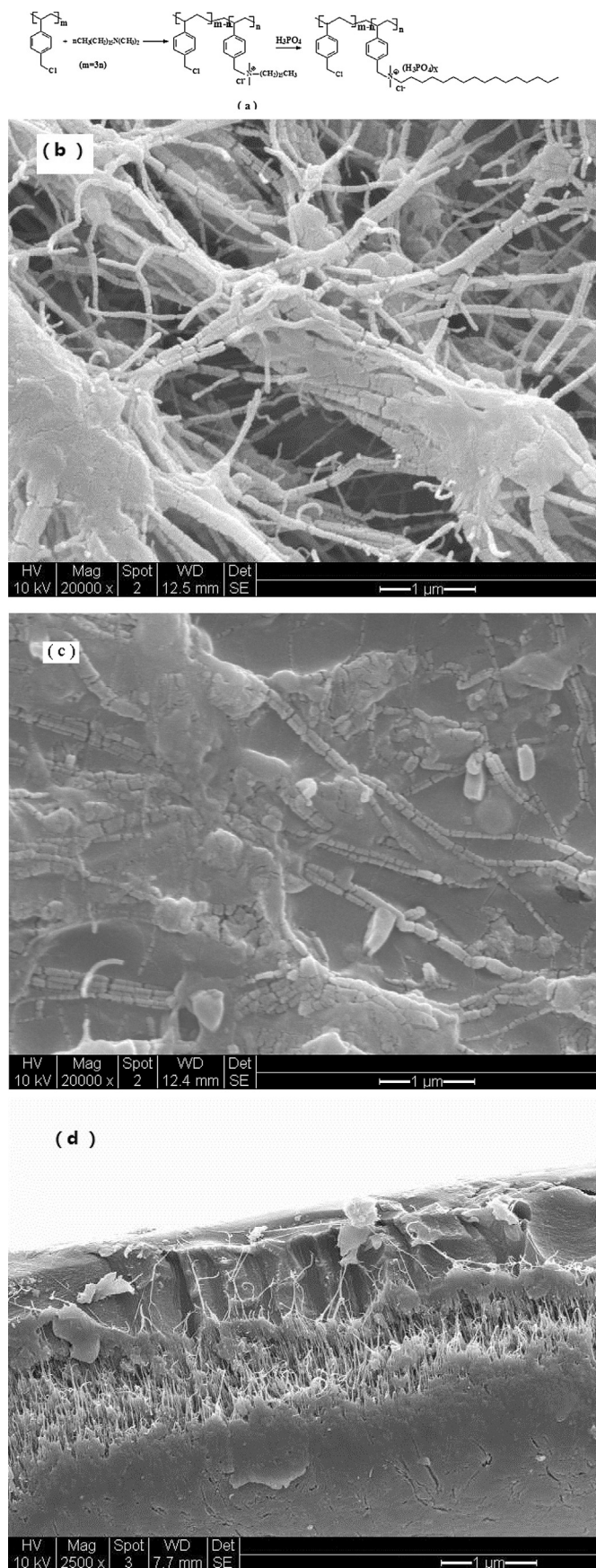
Four-point probe was used to measure the membrane conductivity with a Frequency Response Analyser (Voltech TF2000, UK). On the four platinum foils (probes), the membrane samples (1 cm by 5 cm) were placed with equal spacing of 5 mm. In the range of the 1 and 20 kHz, AC impedance measurements were applied 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



challenges in these membranes. *N,N*-Dimethylhexadecylamine partially quaternized poly (vinyl benzyl chloride) (qPVBzCl⁻) was synthesized as the ionomer for phosphoric acid loaded membrane. The ionomer synthesis route and molecule structure are shown in Fig. 1(a). High porosity hydrophilic modified polytetrafluoroethylene (PTFE) is an ideal polymer material to overcome these challenges by filling the interconnected pores with the QA ionomers. As showed in Fig. 1(b), SEM observation show the PTFE thin film porous structure, while after filling with qPVBzCl⁻; the pores were blocked with the QA ionomer (Fig. 1(c)) and the cross-section was uniform with that filled ionomer (Fig. 1(d)). The weight of the qPVBzCl⁻ ionomer in the PTFE was calculated to be 71% of the overall membrane weight. The PA maximum doping level was calculated to be 4.67–5.12. In such a PTFE/qPVBzCl⁻ composite membrane, the PTFE interlinked network provides the mechanical strength while the QA grafted ionomer contributes to the proton conductivity after the PA doping.

Following thermogravimetric analysis (TGA) of the H₃PO₄ doped PTFE/qPVBzCl⁻ composite membrane was carried out and the results are showed in Fig. 2. From the curve we can see that there were mainly three steps for the weight loss: first step, between the temperatures 30 °C–100 °C, was the dehydrate process of the composite membrane. The weight loss in this step was 10% which was mainly contributed by the free absorbed water in the membrane; second step, from the temperatures 250 °C–450 °C, was the degradation of the ionomer and PTFE; third step, from the temperatures 550 °C–600 °C, was the carbonization process. From the curve we can see that the resultant composite membrane was stable in the intermediate temperature from 100 °C to 200 °C, which is in the fuel cell operation range.

Further tensile test results for the neat PTFE film, H₃PO₄ doped PTFE/qPVBzCl⁻ composite membrane (H₃PO₄@PTFE/qPVBzCl⁻) and H₃PO₄ doped PVBzCl⁻ (H₃PO₄@qPVBzCl⁻) membranes are showed in Fig. 3. From the results we can see that the H₃PO₄@qPVBzCl⁻ membrane tensile strength was 9.55 MPa and Young's modulus was 0.1 GPa. For the H₃PO₄@PTFE/qPVBzCl⁻ membrane, the tensile stress was 56.23 MPa, and the Young's Modulus was 0.25 GPa, and the fractured elongation was 23%. The PTFE, tensile strength was 51.20 MPa and Young's modulus was 0.131 GPa. The H₃PO₄ doped PTFE/qPVBzCl⁻ composite membrane have a better tensile strength than the PTFE thin film, which is the contribution of the filled polymer qPVBzCl⁻. However, the strain of the H₃PO₄@PTFE/qPVBzCl⁻ was lower than that of the original PTFE film. We hypothesize that the qPVBzCl⁻ filled in the PTFE changes the mechanical property of the composite membranes, and the interconnected fibres of the PTFE film (Fig. 1(b)) have better elongation than that of the filled membranes. From the results we can see that the composite membrane is a promising electrolyte material after the application of the PTFE thin film.

Through-plate conductivity tests showed that the conductivity data of the H₃PO₄@PTFE/qPVBzCl⁻ membrane loaded with phosphoric acid maximum doping level of 5 under relative humidity <1% (Fig. 4(a)). Both the conductivity of the PTFE composite membrane and H₃PO₄@qPVBzCl⁻ membrane increased with increased temperature indicating that good stability at intermediate temperature. Although the neat H₃PO₄@qPVBzCl⁻ membrane showed higher conductivity in the range of 105 °C–165 °C than PTFE composite membrane, it lost enough mechanical strength to hold at 180 °C to complete the test. The peak conductivity for the neat H₃PO₄@qPVBzCl⁻ membrane was 0.97 S cm⁻¹ at 165 °C. While for

Fig. 1. qPVBzCl⁻ synthesis route (a), and SEM images of PTFE porous membrane (b) and PTFE/qPVBzCl⁻ composite membrane (c) and the cross-section of the composite membrane (d).

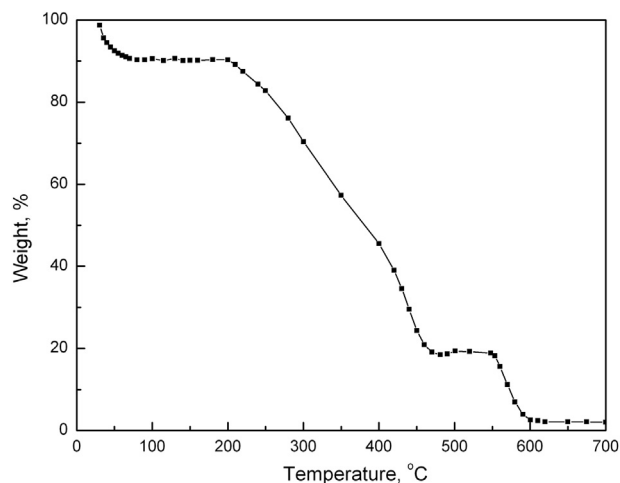


Fig. 2. TGA analysis of the H_3PO_4 doped PTFE/qPVBzCl⁻ composite membrane.

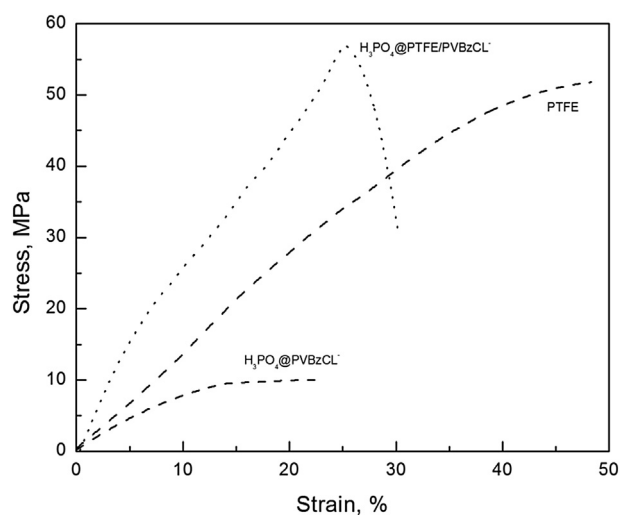


Fig. 3. Stress–strain curves of the PTFE porous membrane, H_3PO_4 doped PTFE/qPVBzCl⁻ composite membrane and H_3PO_4 doped qPVBzCl⁻.

PTFE composite membrane, the peak conductivity was 0.11 S cm^{-1} at 180°C . Furthermore, long term stability test at 180°C under the conductivity operation conditions showed that the membrane was stable during the 36 h test period (Fig. 4(b)). Combination of hydrophobic (PTFE substrate) and hydrophilic (qPVBzCl⁻) structure might affect the water retention inside the composite membrane, while the water retention benefits to the conductivity [3,8].

The polarization and power density curves are shown in Fig. 5. The fuel cell tests were performed with the increasing temperature which showed agreement with the conductivity results. When the operation temperature increased from 120°C to 175°C , the Open Cycle Voltage (OCV) increased from 0.71 V to 0.85 V, which is in the typical range of OCV for the acids doping membrane fuel cells [3–13,16]. The voltage increasing may be the filler qPVBzCl⁻ became softer when the temperature rising, and that the composite membrane in MEA might become denser under the cell system pressure, thus reduce the gas permeable. At 0.6 V, the fuel cell provided with 200 mA cm^{-2} current density at 175°C , which is a promising candidate for fuel cell applications. A power density of 360 mW cm^{-2} was achieved at 175°C , although the OCV was 0.85 V in this fuel cell operation. The better performances were mainly

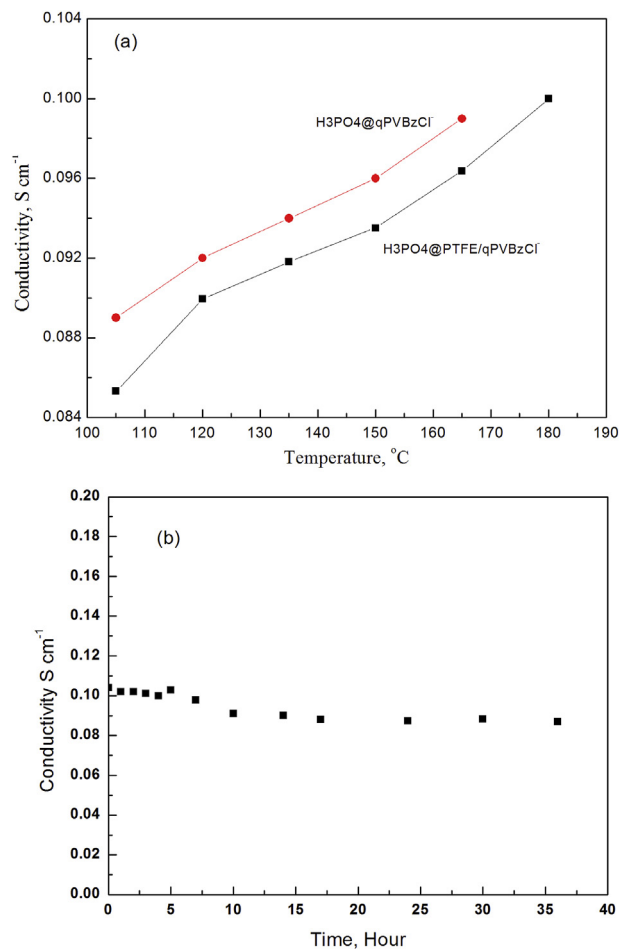


Fig. 4. Ion conductivity–temperature relation curve for the H_3PO_4 @PTFE/qPVBzCl⁻ and H_3PO_4 @qPVBzCl⁻ membrane (a) and long term stability test at 180°C under the conductivity operation conditions for the H_3PO_4 @PTFE/qPVBzCl⁻ (b).

contributed by the strong acid and water retention properties of the composite membrane.

Fig. 6(a) shows the IR corrected V–I polarization curves for the different operation temperatures of 125°C , 150°C and 175°C . And Fig. 6(b) shows the Tafel plot of the IR corrected V–I curves. These results show that the voltage loss was 68 mV, 65 mV and 58 mV per decade of current and the effective exchange current density was $2.04 \times 10^{-10} \text{ A cm}^{-2}$, $1.20 \times 10^{-9} \text{ A cm}^{-2}$ and $5.75 \times 10^{-9} \text{ A cm}^{-2}$ for the temperature 125°C , 150°C and 175°C respectively. The internal resistance, as estimated from the voltage drop in the intermediate voltage range, gave a cell conductivity of 0.018 S cm^{-1} at 175°C . This conductivity is much less than that of the membrane itself and indicates significant voltage loss in the electrode layers (and other cell components). And this loss might be partly contributed from three-phase boundary. The low Tafel slope values may be caused by the poor three phase boundary between the electrode and electrolyte. The interconnected PTFE fibres in the composite membrane might increase the ions transport resistance after the MEA preparation. Other possibility is that the membrane may be degraded under the high temperature over 150°C and it is suitable for the intermediate temperature fuel cells. As this report here is a feasibility study of the porous PTFE related composite membrane for acid loaded fuel cells, the catalyst compositions in the MEA were not “optimal” in the these fuel cell tests.

Overall, although the H_3PO_4 @PTFE/qPVBzCl⁻ is a potential membrane for polymer phosphoric acid electrolyte membrane fuel

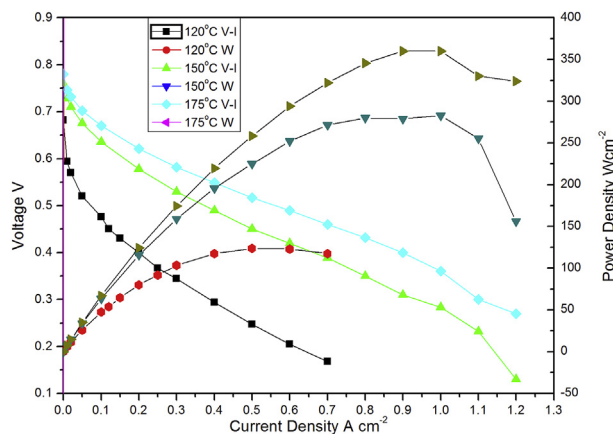


Fig. 5. Polarization curves of $\text{H}_3\text{PO}_4@PTFE/qPVBzCl^-$ membrane for the H_3PO_4 doping fuel cell test. H_2/O_2 was used without back pressure; Pt/C (0.5 mg cm^{-2}).

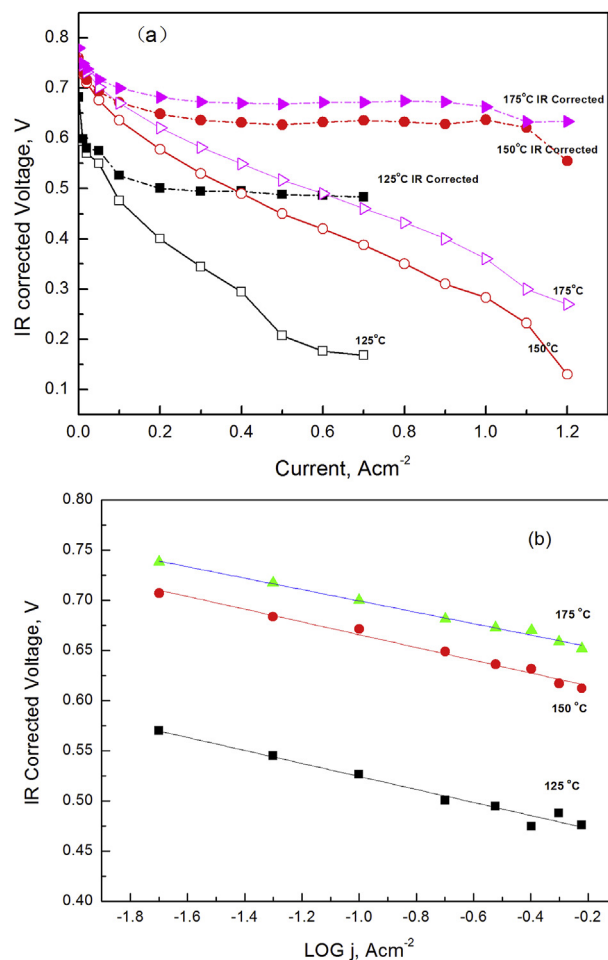


Fig. 6. IR corrected V–I polarization curves (a) and Tafel slopes (b) for different operation temperatures.

cells in intermediate temperature range, more studies such as OCV improvement and conductivity enhance are required to optimize this composite membrane fuel cell. And the composition of electrode catalyst layer with different ionomer ratios and preparation of suitable MEA, are the also the key subjects of on-going research.

4. Conclusions

N,N-Dimethylhexadecylamine partially quaternized poly (vinyl benzyl chloride) ($qPVBzCl^-$) can be synthesized as the substrate for the phosphoric acid doping membrane through porous polytetrafluoroethylene (PTFE) thin film. $qPVBzCl^-$ was successfully filled into the interconnected pores of the PTFE film to prepare the solid PTFE/ $qPVBzCl^-$ membranes. The $\text{H}_3\text{PO}_4@PTFE/qPVBzCl^-$ composite membrane tensile strength was greatly improved after the applications of the PTFE thin film and the membrane was stable in the intermediate fuel cell operation temperature. This study provides a new approach for the development of phosphoric acid doping membrane.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jpowsour.2015.06.113>.

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