



Short communication

A poly($R_1R_2R_3$)- N^+ /H₃PO₄ composite membrane for phosphoric acid polymer electrolyte membrane fuel cells

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ABSTRACT

A poly($R_1R_2R_3$)- N^+ /H₃PO₄ composite membrane has been developed for use in a polymer electrolyte fuel cell (PEMFC). The quaternized polysulfone (QNPSU) membrane doped with H₃PO₄ showed high proton conductivity (0.12 S cm⁻¹) at 160 °C and gave good performance in a single fuel cell tests. The peak power density with the QNPSU/H₃PO₄ composite membrane (at 150 °C, with dry H₂/O₂) was greater than 0.7 W cm⁻². The effect of the phosphoric acid doping level on fuel cell performances with the QNPSU membrane was investigated. The data show that the QNPSU/H₃PO₄ composite membrane is promising for higher temperature PEMFC applications. The study demonstrated that the poly($R_1R_2R_3$)- N^+ /H₃PO₄ composite system produced an effective method to connect phosphoric acid to a non-conducting polymer structure, to produce a promising membrane for phosphoric acid polymer electrolyte membrane fuel cells.

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1. Introduction

Recently, intermediate-temperature fuel cells (ITFCs) have attracted wide interest [1,2]. Such fuel cells have operating temperatures (e.g. 150–400 °C) in a range, much lower than that of solid oxide fuel cells (SOFCs) and higher than that of low temperature, proton-exchange membrane fuel cells (PEMFCs). Compared with low temperature PEMFC, the ITFC offers some significant advantages; such as reduced anode catalyst poisoning by CO and avoiding fuel cell flooding by the product water. Moreover, in ITFC system it is feasible to, remove the reactant gases humidification, to decrease the catalyst loading and to increase the efficiency of the fuel cell [3].

It is well known that the phosphoric acid fuel cell (PAFC) operates in the intermediate temperature range (150–220 °C). However, the conventional phosphoric acid fuel cell has certain disadvantages, e.g. the phosphoric acid electrolyte can have limited immobilization in certain matrices. So, several attempts have been made to connect the phosphoric acid with certain elements through chemical bonding [4–6]. Thus previous work has focused on phosphoric acid doped polybenzimidazole (PBI), in which phosphoric acid is connected to the polymer unit by hydrogen bonding [7,8].

In our work, composite membranes of phosphoric acid and polymers, with a general structural formula poly($R_1R_2R_3$)- N^+ have been developed to meet the requirement of ITFCs. The poly($R_1R_2R_3$)- N^+ is reasonably stable in the temperature range of phosphoric acid

fuel cells because of the poly($R_1R_2R_3$)- skeleton. The repeat unit $-(R_1R_2R_3)-$ could also provide good mechanical and chemical stability for the membrane, as well as greater structural diversity than poly(R_1R_2)- N membranes (like PBI). After quaternization, the $-N^+$ group would increase the connection between phosphoric acid and the polymer, which results in good proton conduction in poly($R_1R_2R_3$)- N^+ /H₃PO₄ membranes, such as QAPPESK/H₃PO₄ [9].

In this work, a poly($R_1R_2R_3$)- N^+ , quaternized polysulfone (QNPSU), was synthesized and the QNPSU/H₃PO₄ composite membrane developed and investigated in terms of its fuel cell performance. Compared with QAPPESK, the QNPSU is a general and cheap polymer, applied in many areas and widely available. Moreover, QNPSU only has the $-N^+$ group and no $-N$ group, compared with QAPPESK which has two such groups. This will benefit the conductivity of the poly($R_1R_2R_3$)- N^+ /H₃PO₄ structure.

2. Experimental

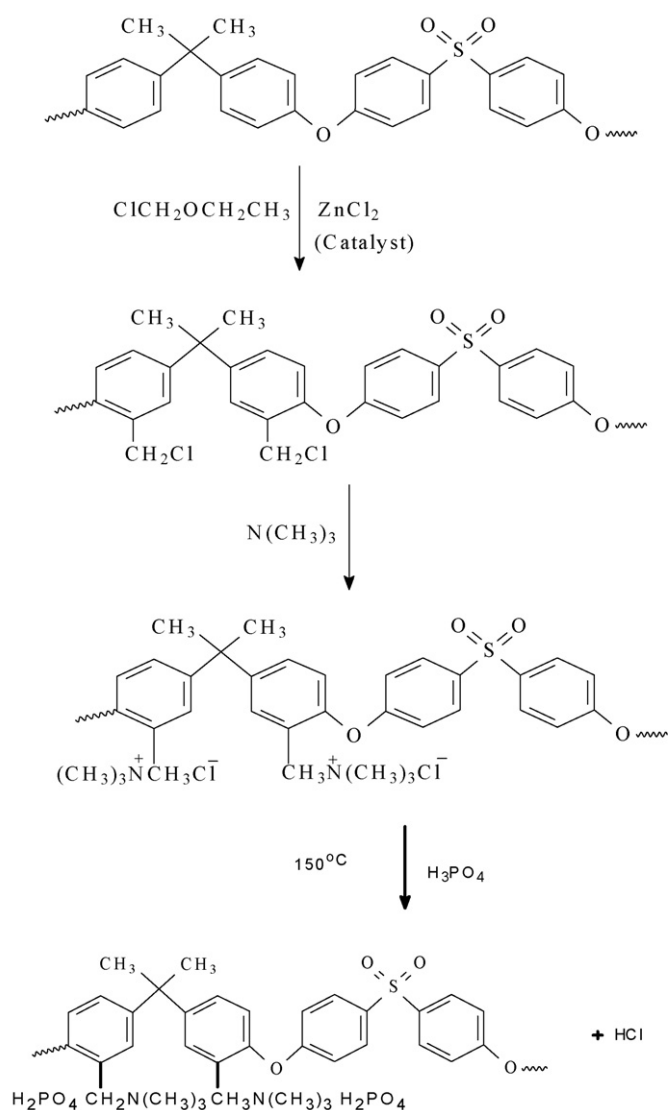
2.1. Membrane preparation

The QNPSU was prepared from the reaction of polysulfone (PSU) and ClCH₂OCH₂CH₃ catalyzed by ZnCl₂ at temperatures between 60 and 70 °C, according to the reaction shown in Scheme 1.

Chloromethylated PSU was prepared from the PSU polymer according to a modification of a published procedure [10]. First, ZnCl₂ (0.5 g) was added to ClCH₂OCH₂CH₃ (15 ml) and the mixture stirred until it formed a solution. Then the PSU (10 g) was added to this solution. At the end of the reaction between PSU and ClCH₂OCH₂Cl (8 h), the reaction solution was placed into hot water

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Scheme 1. Preparation of the QAPSU/ H_3PO_4 membrane.

(70 °C) to precipitate the product. The product, Chloro Methyl PSU (CMPSU), was filtered and purified by washing with $\text{ClCH}_2\text{CH}_2\text{Cl}$ (100 ml). Afterwards, the CMPSU was dissolved into dimethylacetamide (DMAC) and cast onto a glass plate to form membranes. The CMPSU membranes were then immersed into trimethylamine solution to form the QNPSU membrane. Finally, the QNPSU membranes were immersed in phosphoric acid to make the QNPSU/ H_3PO_4 membrane. The doping level of phosphoric acid was calculated after heating the membrane at 150 °C for 2 h to remove the water.

2.2. Membrane characterisation

The membrane conductivity was measured with the four-probe AC impedance method with a Frequency Response Analyzer (Voltech TF2000, UK). The membranes were cut into 1 cm × 5 cm strips and placed across the four probes (platinum foil) with equal spacing of 0.5 cm. AC impedance measurements were carried out at frequencies between 1 and 20 kHz. The conductivity cell was held at a desired temperature and humidity for 30 min until a steady state was achieved, before the measurements were taken at 10 min intervals [11].

2.3. Membrane electrode assemblies (MEAs)

MEAs were prepared as follows. First, catalyst inks were prepared by blending carbon supported catalysts (60% Pt on Vulcan XC-72, Etek) and the DMAC solution of 5% (wt/wt) polybenzimidazole (PBI) and 1% (wt/wt) polyvinylidene fluoride (PVDF) for 12 h. The inks were cast onto a carbon support layer covered with a gas diffusion layer (ETek). After 10 h at room temperature, the electrodes were heated at 150 °C for 1 h. Membrane electrode assemblies were made by hot pressing the anode and cathode onto the phosphoric acid doped membranes at 150 °C and 0.1 ton cm^{-2} pressure for 10 min.

2.4. Fuel cell tests

The MEA was sandwiched between two high-density graphite blocks impregnated with phenolic resin, on which parallel gas flow channels were machined. The active cross section area of the membrane was 1.0 cm^2 . The ridges between gas flow channels provided electrical contact with the carbon layers of the MEA and the area exposed to the MEA was taken as the active cell area. Electric cartridge heaters were mounted at the rear of the graphite blocks to maintain desired cell temperatures using associated temperature controllers. Temperature was monitored by thermocouples imbedded in the graphite blocks. Gold-plated steel bolts were screwed into the blocks as current collectors. Hydrogen and air were fed to each side of the cell, at flow rates of 0.2 and 0.45 $\text{dm}^3 \text{min}^{-1}$, respectively. These flow rates were some 40 times more than stoichiometric requirements corresponding to the maximum current obtained from the cell tests.

3. Results and discussion

3.1. Membrane preparation

Several sheets of CMPSU membranes were obtained by casting, from the polymer/DMAC solutions onto a glass plate at 60 °C and then dried at 100 °C until the membranes formed. The CMPSU membranes were then immersed in trimethylamine solution, of a certain concentration, at a specified temperature for given time, and then immersed into 20 ml 5 wt.% HCl. The concentration of the trimethylamine would influence the mechanical strength of the membrane. Investigations of trimethylamine aqueous solution showed that the most suitable concentration that leads to a mechanically strong membrane was 20%. As shown in Table 1, if the membrane was immersed at a high reaction temperature for a short time, it did not react sufficiently and, if the reaction time was longer the membrane cracked. Hence for effective membrane preparation immersing the membrane in trimethylamine solution for more than 4 days at room temperature was used.

3.2. FTIR measurement

The infrared spectra of QNPSU-Cl and QNPSU/ H_3PO_4 membranes are shown in Fig. 1. The major vibration associated with QNPSU membrane structures were found in the two samples. The

Table 1
QNPSU membranes prepared from Chloro Methyl PSU reaction with $(\text{CH}_3)_3\text{N}$.

	Reaction time	Reaction temperature	Membrane condition
Membrane sheet 1	1 h	45 °C	Not swollen
Membrane sheet 2	4 days	Room temperature	Swollen
Membrane sheet 3	2 h	45 °C	Small swelling but cracked

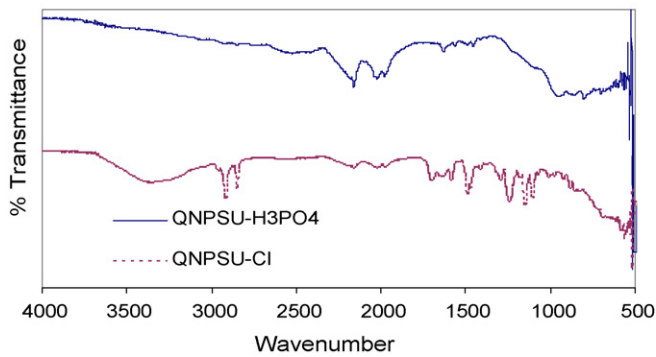


Fig. 1. The infrared spectra of QNPSU-Cl and QNPSU/H₃PO₄ membranes.

peak at 1149 cm^{-1} is attributed to the stretching vibration of C–O–C. The peaks at 1631 and 1490 are attributed to the stretching vibration of the Ar–S=O [12]. For QNPSU/H₃PO₄ membrane, the intense peaks at 998 cm^{-1} and small peak at 802 cm^{-1} are due to the stretching vibrations of P=O for H₃PO₄ and $\nu\text{P}(\text{OH})_2$ for H₂PO₄[−], respectively. This data indicate that H₃PO₄ can be combined with QNPSU to form QNPSU/H₃PO₄ composite membranes.

3.3. The variation of the proton conductivity of QNPSU/H₃PO₄ membrane with temperature

The variation of the proton conductivity of QNPSU/H₃PO₄ membrane with temperature, under dry conditions, is shown in Fig. 2. The proton conductivity increased from approximately 0.035 S cm^{-1} at 80°C , to 0.12 S cm^{-1} at 160°C , which is as high as that of Nafion membranes [13]. This suggests that QNPSU/H₃PO₄ membrane is a potential candidate for proton exchange membrane fuel cells.

3.4. Fuel cell test of QNPSU/H₃PO₄ membranes

Fig. 3 shows the effect of temperature on the cell polarization behavior with a $120\text{ }\mu\text{m}$ thick membrane doped with 180% phosphoric acid. The fuel cell power performance clearly improved with an increase in temperature. This can be attributed to the improved conductivity of the membrane at higher temperatures. Also, as shown in Fig. 3, higher gas pressure improved cell power performance.

Fig. 4 shows the typical fuel cells performance of a thin QNPSU/H₃PO₄ membrane with a high phosphoric acid doping level

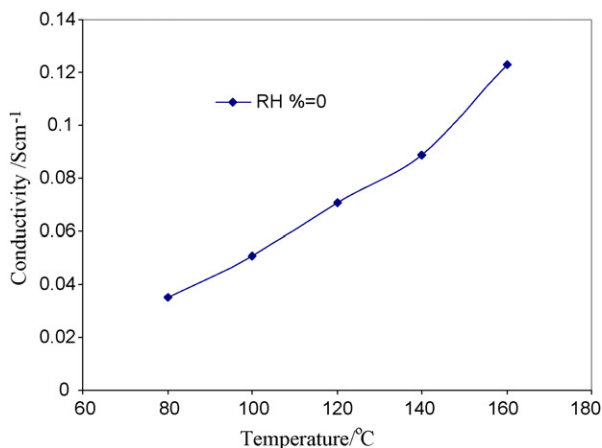


Fig. 2. Ionic conductivity of QNPSU/H₃PO₄ composite membrane (4-point AC impedance method; membrane thickness is $70\text{ }\mu\text{m}$; H₃PO₄ doping level is 300%).

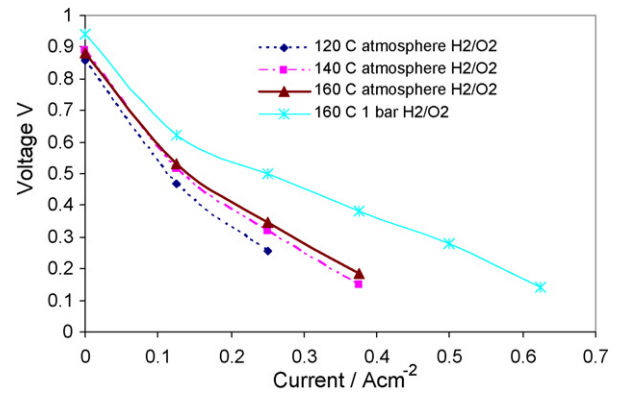


Fig. 3. Polarization curves of a PEMFC with QNPSU/H₃PO₄ composite membranes at different temperature. RH% = 0; doping level of phosphoric acid = 180%; thickness: $120\text{ }\mu\text{m}$; Pt loading: 0.79 mg cm^{-2} .

(doping level = 400%, thickness = $20\text{ }\mu\text{m}$) at 150°C . Open circuit potentials were some 100 mV lower than that with the membrane used for Fig. 3 (doping level = 180%, thickness = $120\text{ }\mu\text{m}$). This indicates a greater effect of gas crossover on the cell behavior with a thinner membrane. However, the cell performance was much better than that achieved with a lower acid doping of the membrane. The good performance was mainly attributed to the superior proton conduction of the membrane with high phosphoric acid doping. It can be estimated that for a $20\text{-}\mu\text{m}$ thick membrane, at 1 A cm^{-2} there would be an approximate 0.125 V larger voltage due to the higher conductivity, which is in approximate agreement with the observed cell polarization behavior. In addition, assuming that the linear regions of the cell voltage vs. current density curves were only associated with the membrane resistance, the slope agrees reasonably well with the value estimated from the QNPSU/H₃PO₄ membrane conductivity (approximately 0.016 S cm^{-1}).

Fig. 4 also shows the influence of increased oxygen pressure on the fuel cell voltage and power density performance at 150°C . Cell voltages were much greater at the higher pressure of 1 bar at high current densities. At 150°C the power density was above 0.7 W cm^{-2} .

Fig. 5 shows fuel cell performance results obtained with a high acid doping membrane at lower temperatures and with H₂/air. Compared with performance obtained with the low acid dop-

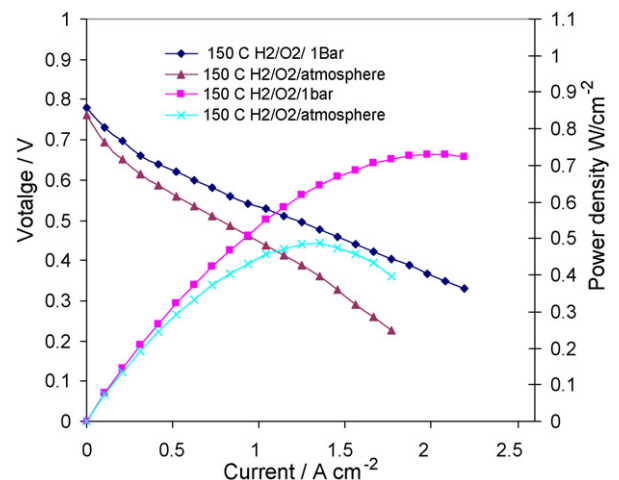


Fig. 4. Polarization and power density curves of a PEMFC with QNPSU/H₃PO₄ composite membranes with 400% phosphoric acid doping level at 150°C . RH% = 0; membrane thickness: $20\text{ }\mu\text{m}$; Pt loading: cathode 0.81 mg cm^{-2} , anode 0.81 mg cm^{-2} ; Pt/C (60%):PVDF:PBI = 230:7:15.

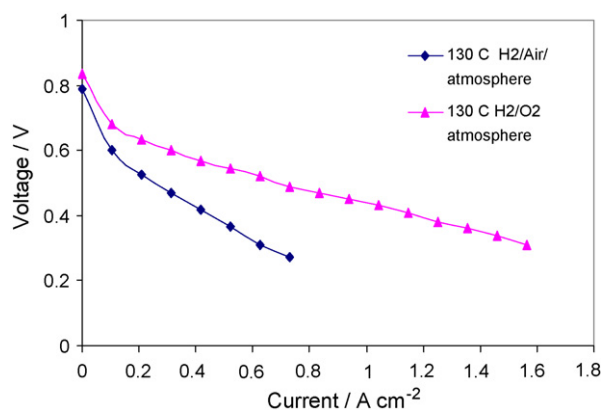


Fig. 5. Polarization curves of a PEMFC with QNPSU/H₃PO₄ composite membranes with 400% phosphoric acid doping level at 130 °C with air and oxygen. RH%=0; membrane thickness: 20 μm; electrode: Pt loading: cathode 0.81 mg cm⁻², anode 0.81 mg cm⁻²; Pt/C (60%):PVDF:PBI=230:7:15.

ing level in the membrane (Fig. 4), the open circuit potentials at the lower temperatures were approximately 100 mV higher with the greater acid doping level, because of reduced gas crossover. Obviously, using air instead of O₂ would significantly reduce the performance, although power densities at lower temperatures were not dramatically smaller than at higher temperatures.

The QNPSU membrane is a suitable polymer material for phosphoric acid polymer electrolyte membrane fuel cells, though more studies are still required to optimize the electrode catalyst layer composition and to establish suitable MEA stability in long-term tests.

However we have measured the 40 h fuel cell life performance of the fuel cell with a 120-μm thick membrane doped with 180% phosphoric acid (at 160 °C with O₂ under the atmospheric pressure condition) for 40 h. The performance of fuel cell with the QNPSU/H₃PO₄ composite membrane at a current density of 0.2 A cm⁻² did not exhibit any noticeable degradation after 40 h

operation at 160 °C. Longer fuel cell tests still need to be carried out for future development.

4. Conclusion

A new phosphoric acid polymer electrolyte membrane system, poly(R₁R₂R₃)-N⁺/H₃PO₄ was proposed and a quaternized polysulfone (QNPSU) and phosphoric acid composite membrane was synthesized and applied in single polymer electrolyte fuel cell tests at intermediate temperatures (120–200 °C). The QNPSU membrane, complexed with H₃PO₄, showed high proton conductivity (0.12 S cm⁻¹ at 160 °C) and good fuel cell performance (greater than 0.7 W cm⁻² at 160 °C). It was observed that membrane, phosphoric acid doping level had a significant effect on the cell performance. Increasing temperature and gas pressure, and using of oxygen rather than air improved the fuel cell performance. The experimental results showed that the QNPSU/H₃PO₄ composite membrane is suitable for intermediate-temperature utilization. With this system, an effective method to connect phosphoric acid to non-conducting polymer membranes was designed, which brings the intermediate-temperature fuel cell a promising future.

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