



Short communication

# A polytetrafluoroethylene/quaternized polysulfone membrane for high temperature polymer electrolyte membrane fuel cells

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## ABSTRACT

A polytetrafluoroethylene (PTFE)/quaternized polysulfone (QNPSU) composite membrane has been fabricated for use in proton exchange membrane fuel cells (PEMFCs). The composite membrane is made by immobilizing a QNPSU solution into a hydrophobic porous PTFE membrane. The structure of the composite membrane is examined by SEM and EDX. The ionic conductivity of the PTFE/QNPSU membrane, at a relative humidity lower than 0.5% and a temperature of 180 °C, is greater than 0.3 S cm<sup>-1</sup>, when loaded with 400% H<sub>3</sub>PO<sub>4</sub>. A hydrogen fuel cell with this membrane operating at 2.0 atmosphere absolute (atma) pressure and 175 °C gives voltages >0.4 V at current densities of 1.0 A cm<sup>-2</sup> using oxygen.

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## 1. Introduction

Recently, high temperature PEMFCs (120–200 °C) have been proposed, as alternatives to low temperature PEMFCs, to solve such problems as catalyst poisoning by CO and fuel cell electrode flooding by liquid water, as well as to improve fuel cell efficiency, to reduce the amount of noble metal catalyst and to avoid reactant gas humidification [1–3].

A key material for high temperature PEMFCs is the proton conducting membranes. The requirements of a proton conducting membrane for high temperature PEMFCs are chemical, mechanical and thermal stability, gas impermeability (H<sub>2</sub> and O<sub>2</sub>) high proton conductivity at 120–200 °C and low cost. It is well known that the phosphoric acid fuel cell (PAFC) operates in the intermediate temperature range around 200 °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 bind the phosphoric acid to certain stable polymer groups through chemical bonding [4–7]. Thus previous work has focused on phosphoric

acid loaded/absorbed polybenzimidazole (PBI), in which phosphoric acid was connected to the polymer unit by hydrogen bonding [8–12]. However, so far few membranes have been developed that meet such requirements [13,14].

In this work, we used a porous polytetrafluoroethylene (PTFE) membrane as the mechanical supporting structure and the quaternized polysulfone (QNPSU) loaded with H<sub>3</sub>PO<sub>4</sub> as proton conductor to fabricate the membrane, which, to our knowledge, has not been reported previously. The PTFE/QNPSU composite membranes loaded with H<sub>3</sub>PO<sub>4</sub> were fabricated to provide good mechanical strength and low cost.

## 2. Experimental

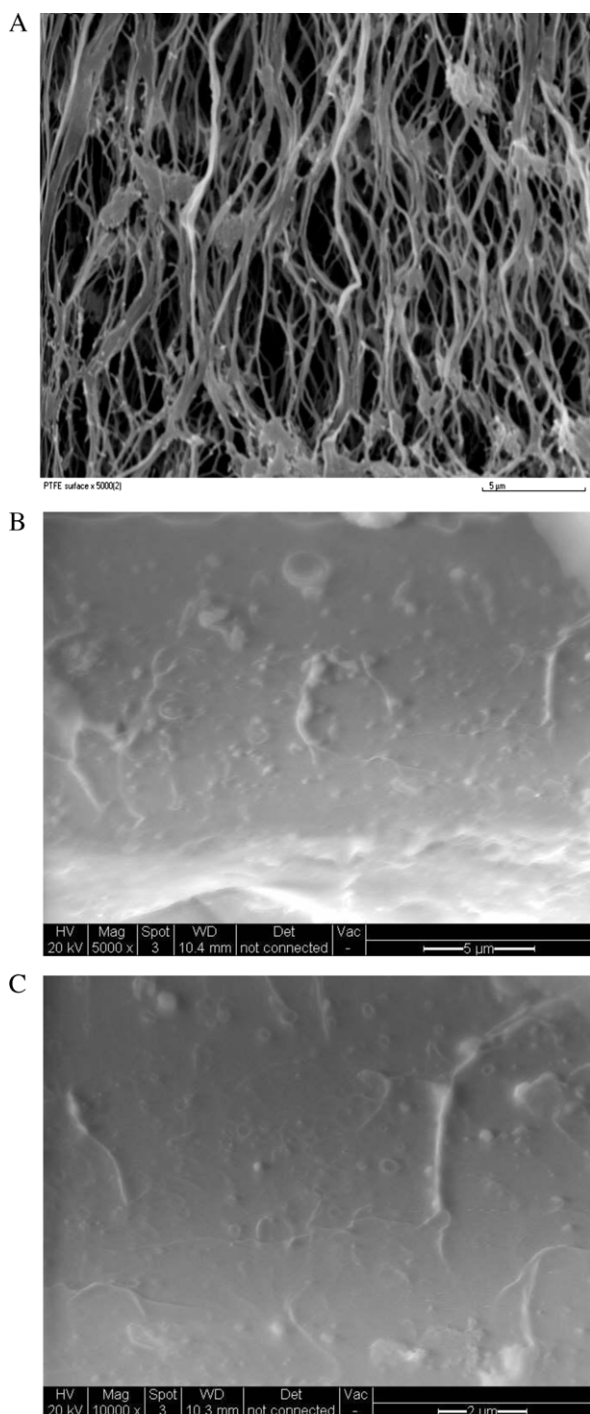
### 2.1. Polytetrafluoroethylene-QNPSU membrane preparation

The procedure for membrane preparation was as follows. The porous PTFE membrane (30 μm), obtained from Shanghai DaGong New Materials Co., Shanghai, China, was first surfaced activated by immersion in a solution containing 7 parts H<sub>2</sub>SO<sub>4</sub> (98 wt.% aqueous solution) and 3 parts H<sub>2</sub>O<sub>2</sub> (30 wt.% aqueous solution) at 80 °C for 1 h. An SEM image (Fig. 1) of the PTFE membrane shows its highly porous structure. The porous PTFE was then rinsed with copious amounts of water and further treated by immersion in a solution containing 1 part aqueous 1.0 mol dm<sup>-3</sup> (M) NaOH solution, 1 part H<sub>2</sub>O<sub>2</sub> (30 wt.% aqueous solution), and 5 parts de-ionised

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**Fig. 1.** SEM of PTFE membrane and PTFE/Cl-PSU composite membrane: (A) surface of the porous PTFE membrane and (B and C) the cross section of Cl-PSU composite membrane.

ionised water at 70 °C for 30 min, followed by rinsing with copious amounts of water. The activated porous PTFE was then immersed in 50 ml of ethanol for 30 min, followed by immersions in 50 ml of a dimethylacetamide (DMAC) for 30 min at 50 °C.

Composite membranes (PTFE/QNPSU) were prepared using the procedure previously reported by us [15] as shown in Scheme 1. The activated porous PTFE was exposed to a solution of 1 mg cm<sup>-3</sup> of chlorinated PSU (Cl-PSU) in DMAC, for 30 min at 50 °C and then dried at 100 °C. The Cl-PSU membranes were then immersed into trimethylamine solution at 25 °C for 7 days to form the QNPSU membrane [16]. Finally, the QNPSU membranes were immersed in

phosphoric acid at 150 °C to make the QNPSU/H<sub>3</sub>PO<sub>4</sub> membrane. The loading of phosphoric acid was calculated according to the molar ratio between phosphoric acid and the QNPSU repeat units after heating the membrane at 150 °C for 2 h to remove water.

## 2.2. Conductivity measurement

Membrane conductivity was measured using a four-point probe and frequency response analyser (Voltech TF2000, Voltech Instruments Ltd, Didcot, Oxfordshire, UK.). The relative humidity was obtained from an intrinsically safe humidity sensor (Vaisala HUMICAP®, Helsinki, Finland).

The membranes were cut into 1 cm × 5 cm strips and placed across four platinum foils with equal spacing of 0.5 cm. AC impedance measurements were carried out at frequencies between 1 and 20 kHz. The polymer membranes were held at the desired temperature and humidity for 0.5 h, to ensure steady state was achieved, and measurements were taken at 1 min intervals.

## 2.3. Membrane electrode assemblies

Membrane electrode assemblies (MEA) were prepared by hot pressing the anode and cathode onto opposite sides of the membranes at 150 °C and 0.1 t cm<sup>-2</sup> pressure for 10 min. The anode and cathode catalyst layers were prepared from inks formed by blending carbon supported catalysts (60% Pt on Vulcan XC-72) supplied by E-TEK Division De Nora North America, Inc., Somerset, NJ and DMAC solution of 5% (wt/wt) with polybenzimidazole (PBI) and 1% (wt/wt) polyvinylidene fluoride (PVDF). The ink was cast onto a carbon paper support covered with a carbon gas diffusion layer (E-TEK) to form an electrode. The Pt loadings of both electrodes were 0.58 mg<sub>Pt</sub> cm<sup>-2</sup>.

## 2.4. Fuel cell tests

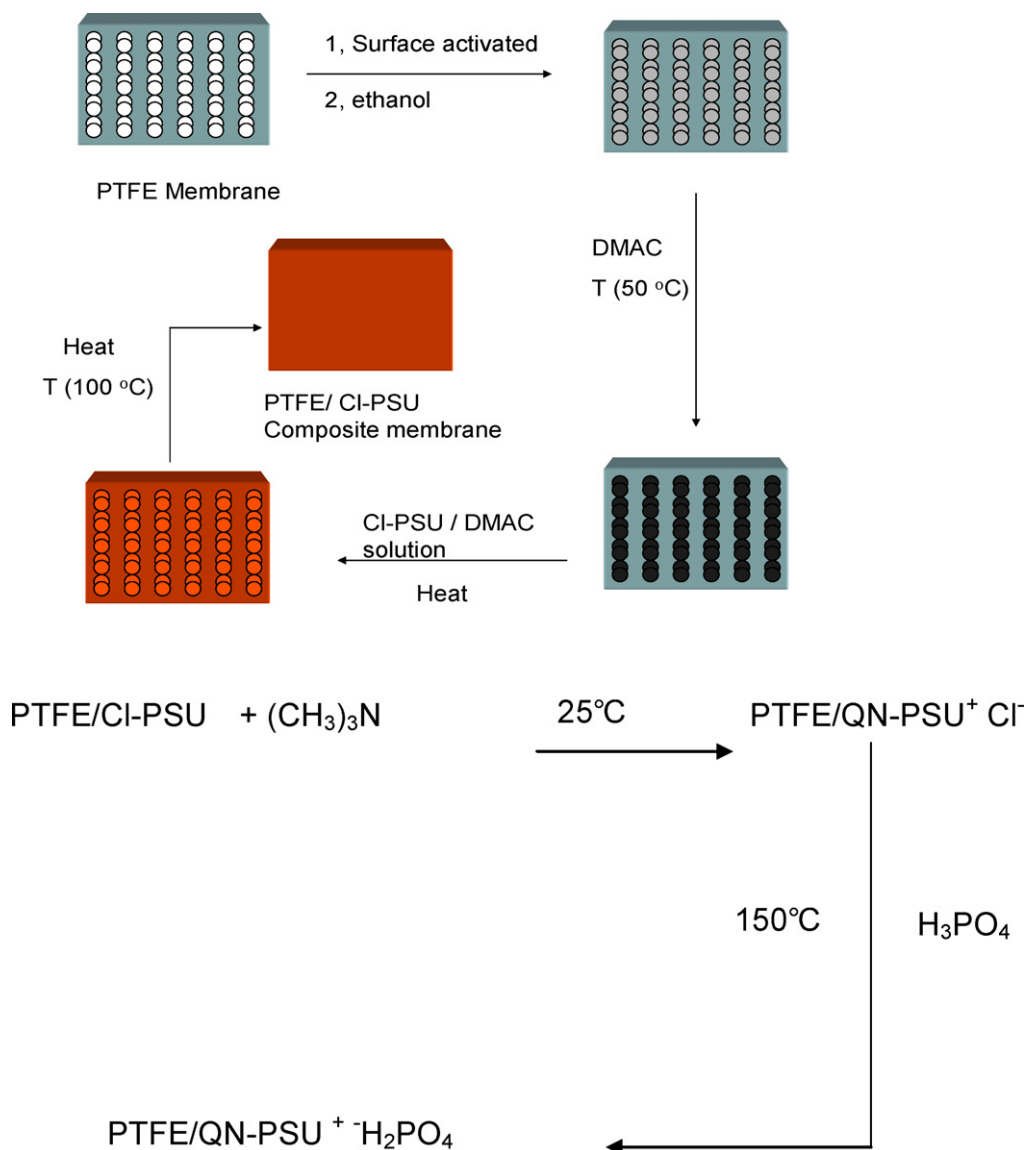
To perform cell tests an MEA was sandwiched between two high-density graphite blocks, impregnated with phenolic resin, into which were machined parallel gas flow channels. The active cross section area of the membrane was 1.0 cm<sup>2</sup>. The ridges between the channels provided electrical contact to the carbon electrodes and the total cross sectional 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 the desired cell temperature, which was monitored by thermocouples embedded in the graphite blocks and controlled with a temperature controller. Gold-plated steel bolts were screwed into the blocks to allow electrical contact. Hydrogen, oxygen and air were supplied (BOC Ltd, Worsley, Manchester, UK) as dry gases from cylinders at flow rates of 0.2, 0.45 and 0.45 dm<sup>3</sup> min<sup>-1</sup> respectively. These flow rates were some 40 times excess of stoichiometric requirements at the maximum current obtained from the cell tests.

## 3. Results and discussion

### 3.1. SEM and EDX

The structure of the composite membrane was examined by SEM and EDX. The membrane was put into liquid N<sub>2</sub> for 10 min; then broken so that the cross section could be investigated using SEM and EDX.

Fig. 1 shows the SEM of the cross section of the PTFE/Cl-PSU composite membrane. The PTFE membrane surface was dense and quite uniformly filled with Cl-PSU. Thus the membranes were essentially non-porous which should minimize hydrogen or oxygen gas cross-over during fuel cell operation.



Scheme 1. Preparation of the QNPSU/PTFE membrane.

Fig. 2 shows the EDX results of the cross-section of the PTFE/CI-PSU composite membrane. It can be seen that the C, F, Cl and O elements were dispersed homogeneously through the cross-section of the membrane and thus the PTFE/CI-PSU composite membranes had a uniform CI-PSU distribution.

Fig. 3 shows the variation in conductivity of the PTFE/QNPSU/H<sub>3</sub>PO<sub>4</sub> composite membrane, with temperature at a doping level of 400 wt.% phosphoric acid and a RH below 0.5%. In this membrane, the molar ratio between phosphoric acid and the QNPSU repeat units is approximately 32:1. The membrane conductivity with 400% high phosphoric acid loading varied from 0.1 S cm<sup>-1</sup> at 100 °C, to more than 0.3 S cm<sup>-1</sup> at a temperature of 180 °C. Such high conductivity has not, to our knowledge, been reported for a PEM, although clearly arises from the high doping level of phosphoric acid. Moreover, the proton conductivity of PTFE/QNPSU membrane without phosphoric acid at 180 °C was lower than 10<sup>-4</sup> S cm<sup>-1</sup>. Hence, the ionic conductivity of the membrane was largely that of the phosphoric acid immobilized in it.

### 3.2. Fuel cell performance

Fig. 4 shows polarization curves of the fuel cell with PTFE/QNPSU/H<sub>3</sub>PO<sub>4</sub> composite membranes at different temperatures and with different oxidants and pressures. From the data we see that the fuel cell performance increased with increased temperature and oxygen partial pressure. 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. The open circuit potentials for the fuel cell were somewhat low (around 0.85 V with oxygen), which was possibly a result of relatively high gas cross-over. This indicates that there was still a small degree of porosity in the membrane. This factor would need to be investigated in more detail in subsequent development of the membrane for fuel cell applications.

As expected the decline in fuel cell voltage with increasing current density was greater with air at low pressure and at lower temperatures. For example, at 175 °C, at a cell voltage of 0.4 V a current density of 0.4 A cm<sup>-2</sup> was obtained with air and 0.7 A cm<sup>-2</sup>

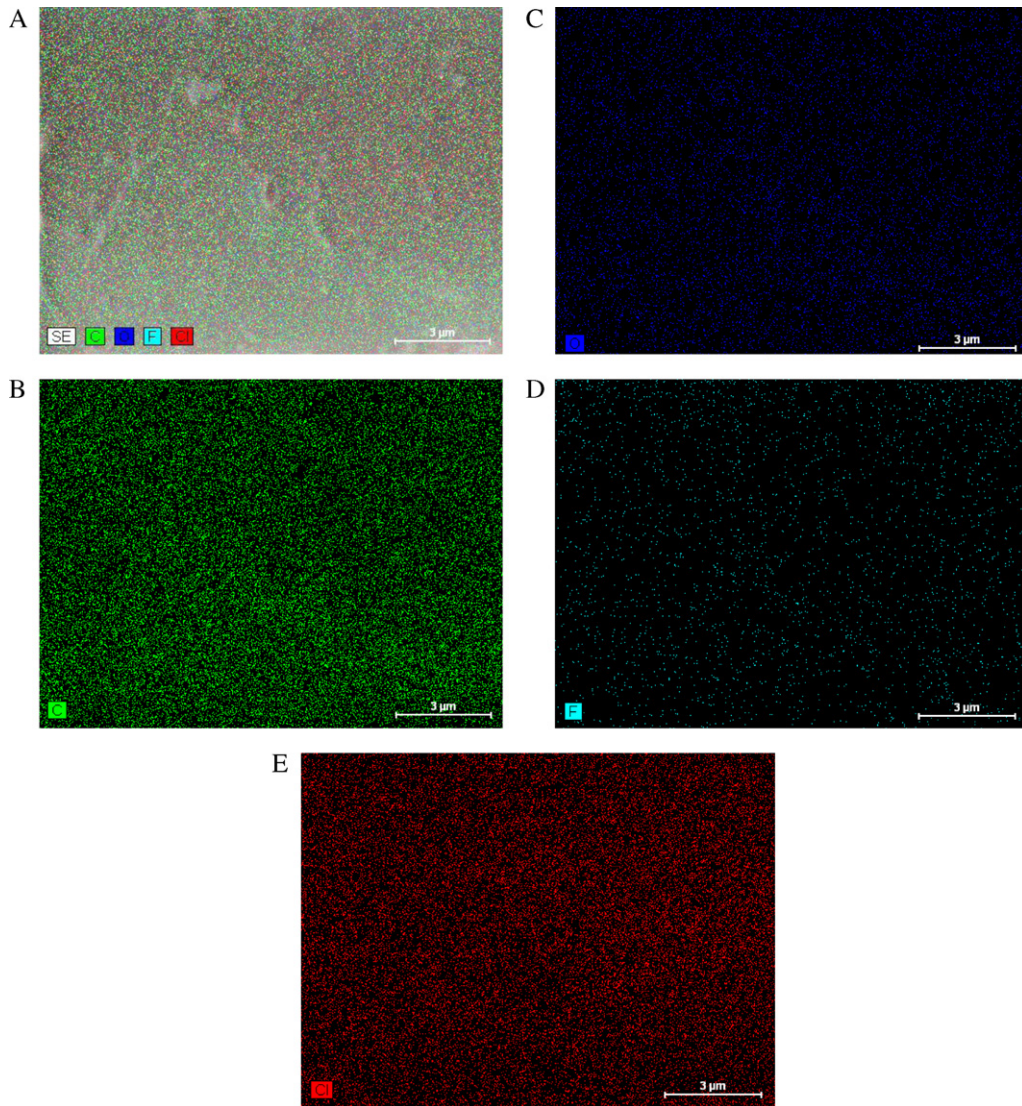


Fig. 2. EDX of the cross section of the PTFE/CI-PSU composite membrane. (A) Map of the elements; (B) C; (C) O; (D) F; (E) Cl.

with oxygen at 1.0 atmosphere absolute (atma) pressure. The peak power density with air was around  $160 \text{ mW cm}^{-2}$ . The relatively good performance was mainly attributed to the high proton conductivity of the composite membrane. However, apart from hydrogen crossover, the major cause of voltage loss in the fuel cell

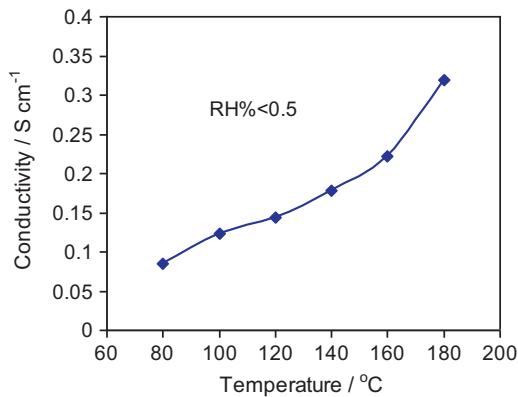


Fig. 3. Proton conductivity of the PTFE/QNPSU/H<sub>3</sub>PO<sub>4</sub> composite membrane. Phosphoric acid doping 400 wt.%. Thickness: 40 μm.

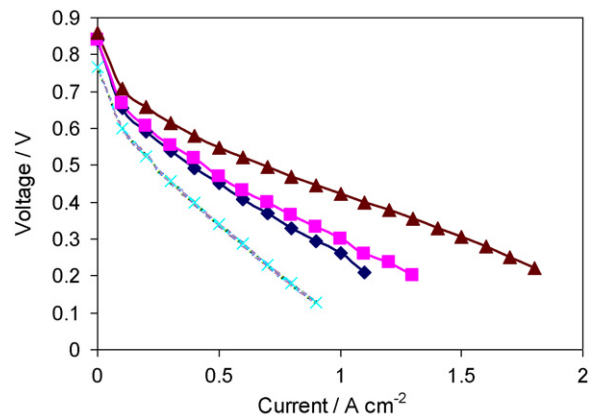


Fig. 4. Polarization curves of a hydrogen PEMFC with a PTFE/QNPSU/H<sub>3</sub>PO<sub>4</sub> composite membrane. Electrode Pt loading:  $0.58 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$  (60 wt.% on carbon):PVDF:PBI = 130:7:15. Membrane thickness = 40 μm. H<sub>3</sub>PO<sub>4</sub> doping level: 180% (weight) ♦: 150 °C, oxygen, 1.0 atmosphere absolute (atma) pressure. ■: 175 °C, oxygen 1.0 atmosphere absolute (atma) pressure. ▲: 175 °C, oxygen, 2.0 atma pressure. X: 175 °C, air, 1.0 atmosphere absolute (atma) pressure.

was associated with the activity and performance of the electrode layers. The decline in voltage in the linear region of the polarization curve was equivalent to a cell conductivity of  $10^{-2} \text{ S cm}^{-1}$  which was an order of magnitude lower than the conductivity of the membrane alone. This indicates that improvement in the fuel cell performance can be made through further development of the electrocatalyst layers.

#### 4. Conclusions

PTFE/QNPSU composite membranes were fabricated by immobilizing QNPSU solution into a hydrophobic porous PTFE membrane. The PTFE/QNPSU membrane conductivity was greater than  $0.3 \text{ S cm}^{-1}$  at a relative humidity lower than 0.5% and a temperature of  $180^\circ\text{C}$  with a 400%  $\text{H}_3\text{PO}_4$  loading level. A hydrogen fuel cell using this membrane with oxygen, at 2.0 atmosphere absolute (atma) pressure gave cell voltages  $>0.4 \text{ V}$  at current densities of  $1.0 \text{ A cm}^{-2}$ . These results indicate that the composite membrane is a promising material for a high temperature phosphoric acid based polymer fuel cell.

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