



A fuel cell operating between room temperature and 250 °C based on a new phosphoric acid based composite electrolyte

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ABSTRACT

A phosphoric acid based composite material with core-shell microstructure has been developed to be used as a new electrolyte for fuel cells. A fuel cell based on this electrolyte can operate at room temperature indicating leaching of H₃PO₄ with liquid water is insignificant at room temperature. This will help to improve the thermal cyclability of phosphoric acid based electrolyte to make it easier for practical use. The conductivity of this H₃PO₄-based electrolyte is stable at 250 °C with addition of the hydrophilic inorganic compound BPO₄ forming a core-shell microstructure which makes it possible to run a PAFC at a temperature above 200 °C. The core-shell microstructure retains after the fuel cell measurements. A power density of 350 mW/cm² for a H₂/O₂ fuel cell has been achieved at 200 °C. The increase in operating temperature does not have significant benefit to the performance of a H₂/O₂ fuel cell. For the first time, a composite electrolyte material for phosphoric acid fuel cells which can operate in a wide range of temperature has been evaluated but certainly further investigation is required.

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1. Introduction

Fuel cells are electrochemical devices which can directly convert chemical energy into electricity with high efficiency [1–3]. Progressive efforts have been devoted to developing fuel cells that operate at intermediate temperature (150–300 °C) which gives considerable advantages: increasing the tolerance of Pt catalysts towards CO [4], reducing the loading of Pt catalyst or even replacing Pt by other non-noble metal catalysts, boosting the energy efficiency [5], simplifying the water management and fuel cell infrastructure [5,6]. In other words, the increased temperatures from low to medium level is expected to cut down the capital and operational costs of the fuel cells into the ballpark of other prevailing power generation systems [7,8]. This gives us some alternatives to the power suppliers such as combustion engines for vehicles [9]. To develop new H₃PO₄-based electrolyte which can retain H₃PO₄ at lower temperature will improve thermal cyclability, making PAFCs easy to operate and extend the applications from stationary to portable and transport.

Phosphoric acid fuel cells (PAFCs) were the first fuel cells to cross the commercial threshold. Around 300 of these power units were placed in operation in stationary power applications in the United

States and overseas. United Technologies Corporation has installed over 75 MW of PAFC systems, operating for over 8 million hours, in 85 cities and 19 countries [10]. At the moment, conventional PAFCs are mainly developed for stationary power generation because they are based on H₃PO₄ electrolyte and are not suitable for portable and transport applications due to limited thermal cyclability and life issues related to the leaching of the acid [11] which could be related to the interaction of H₃PO₄ and liquid water produced during cell operation, too high the operating temperature or, high mechanical pressure on membrane electrolyte assembly (MEA) due to material choice or stack design. The leaching of H₃PO₄ with liquid water at a temperature below 100 °C cause decrease of proton conductivity thus the degradation of the cell. On the other hand, the existing H₃PO₄-based composite electrolytes can only work at a temperature below 200 °C. The CO tolerance of PAFC is much higher than conventional proton exchange membrane fuel cells (PEMFCs) due to the higher operating temperature. It is expected that CO tolerance of PAFCs will be further improved if the operating temperature can be further increased.

The conventional electrolyte materials for PAFCs are PTFE–SiC–H₃PO₄ or PTFE–PEO–SiC–H₃PO₄ matrices [12,13]. The operating temperature of a PAFC is normally below 200 °C because phosphoric acid may react to form polyphosphoric acid which causes decrease in conductivity [14,15].

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However, in the presence of steam, reaction (1) will shift to left therefore the polymerisation temperature for H_3PO_4 will increase. This makes it possible to run PAFCs at higher temperatures. BPO_4 is a hydrophilic inorganic compound which is in favour of proton conduction. BPO_4 was reported to hold water up to 300°C [16]. It has been found that the conductivities of the sulfonated poly(ether ether ketone) (SPEEK)/boron phosphate (BPO_4) composite are approximately six times higher than that of the SPEEK plain membrane [17]. In a previous report, the conductivity of $\text{Al}(\text{H}_2\text{PO}_4)_3\text{-H}_3\text{PO}_4$ composite has been investigated and it was found that the proton conductivity is stable at 175°C [18]. The core-shell microstructure will help to retain H_3PO_4 . However, in our experiments, it was found that the proton conductivity of $\text{BPO}_4\text{-H}_3\text{PO}_4$ composite is stable at a higher temperature, say 250°C which makes it possible to run a PAFC at a temperature above 200°C . In addition, it was found that fuel cells based on $\text{BPO}_3\text{-H}_3\text{PO}_4\text{-PTFE}$ electrolyte can be operated at room temperature for a long time indicating that leaching of H_3PO_4 with liquid water was insignificant in the presence of hydrophilic BPO_4 . The performance of the new phosphoric acid fuel cell based on $\text{BPO}_4\text{-H}_3\text{PO}_4\text{-PTFE}$ composite electrolyte is presented.

2. Experimental

BPO_4 -based proton conductors were prepared from H_3BO_3 and P_2O_5 . A calculated amount of boron acid was mixed with phosphorus pentoxide according to different molar ratios: B:P = 1:1.3, 1:1.4, 1:1.5 and 1:1.7 without adding any solutions. The mixtures were ball milled and transferred into alumina crucibles for heat treatment. After heat treatment at 300°C for 2 h, the powders were ground again and collected for the preparation of organic-inorganic composites.

The as prepared $\text{BPO}_4\text{-H}_3\text{PO}_4$ composite were dispersed in deionized water and were stirred until a homogeneous paste was produced. Then a calculated amount of PTFE solution (60 wt% dispersed in water from Aldrich) was adding according to weight ratio $\text{BPO}_4\text{:PTFE} = 1:1$. The dispersion obtained was then heated at 200°C with continuous stirring in order to get rid of water until it became solid. The solid obtained was then heated at 300°C for further polymerisation and was labelled according to the B:P ratios (1:1.3, 1:1.4, 1:1.5 and 1:1.7) as BPP1, BPP2, BPP3 and BPP4, respectively. Samples BPP1, BPP2, BPP3 and BPP4 was mixed with 40 wt% PTFE to form $\text{BPO}_4\text{-H}_3\text{PO}_4\text{-PTFE}$ composites which were labelled as BP1.3P, BP1.4P, BP1.5P and BP1.7P, respectively. The $\text{SiC-H}_3\text{PO}_4\text{-PTFE}$ composite for conventional PAFCs was prepared

according to Ref. [12]. The weight ratio of each component was $\text{SiC:H}_3\text{PO}_4\text{:PTFE} = 65:33:2$.

Crystal structure and phase purity were examined by X-ray diffraction (XRD) analysis of powders on a Stoe STADI/P powder diffractometer. Incident radiation was generated using a $\text{CuK}\alpha_1$ source ($\lambda = 1.54056 \text{ \AA}$). The microstructures were examined by a transmission electron microscope (TEM) JEOL JEM-2011.

The conductivity measurements were carried out by the a.c. impedance method over the frequency range from 1 MHz to 10 mHz at 100 mV bias on a Solartron 1287/1255 controlled by software Z-Plot/Z-view. Pellets were used for measurements and were obtained by pressing powders under a pressure of $5 \times 10^3 \text{ kg cm}^{-2}$. Both sides of the pellets are dabbed with PTFE bonded carbon which serves as electrodes. Carbon paper was subsequently pressed on as current collector. The pellets were mounted into the tube furnace for impedance measurements. Data were collected from the highest temperature to the lowest after holding at least 1 h at each temperature to reach equilibrium. Different atmospheres were applied to simulate fuel cell conditions.

Sample BP1.5P with B:P ratio 1:1.5 was chosen as the key part of the composite electrolyte since it exhibits higher and more stable conductivity. The electrolyte for fuel cell tests was $\text{BPO}_4\text{-H}_3\text{PO}_4\text{-PTFE}$ with 40 wt% PTFE in order to achieve the highest conductivity. The mechanical strength of the composite membrane is not good enough when PTFE content is less than 40 wt%. The $\text{BPO}_4\text{-H}_3\text{PO}_4\text{-PTFE}$ membrane was hot pressed at 120°C . Pt/C (E-TEK, 30 wt% Pt) was used for both sides with a loading of 0.6 mg/cm^2 for both electrodes for the hydrogen fuel cells. Wet hydrogen (passed through room temperature water) and wet oxygen were used for the H_2/O_2 fuel cell. Carbon paper (Toray-090) was used as current collector. The cell area was 1 cm^2 . The fuel cell performance was measured by a Solartron 1287 Electrochemical Interface coupled with a Solartron 1250 controlled by electrochemical software CorrWare/CorrView and Z-Plot/Z-view. The a.c. impedance was measured in the frequency range between 65 kHz and 0.01 Hz at the amplitude of the a.c. signal 20 mV. The hydrogen and oxygen were bubbled through room temperature water respectively before feeding to the fuel cell.

3. Results and discussion

X-ray powder diffraction patterns (not displayed) confirmed the existence of crystalline BPO_4 for all samples with lattice parameters consistent with reported ones [19]. The microstructure of the $\text{BPO}_4\text{-H}_3\text{PO}_4\text{-PTFE}$ composite with B:P ratio 1:1.5 before fuel cell

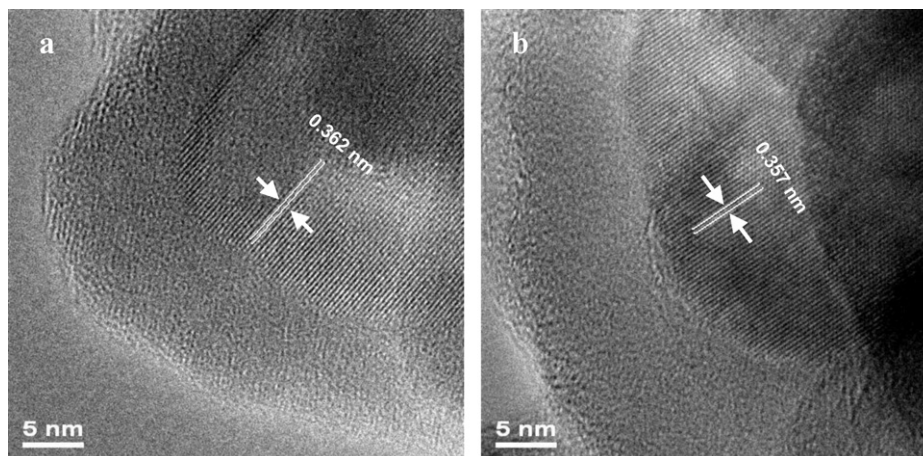


Fig. 1. HR-TEM images of the $\text{BPO}_4\text{-H}_3\text{PO}_4\text{-PTFE}$ composite electrolyte before (a) and after (b) fuel cell measurements. The d-spacing of 0.362 nm and 0.357 nm, both belong to (1 0 1) plane of BPO_4 .

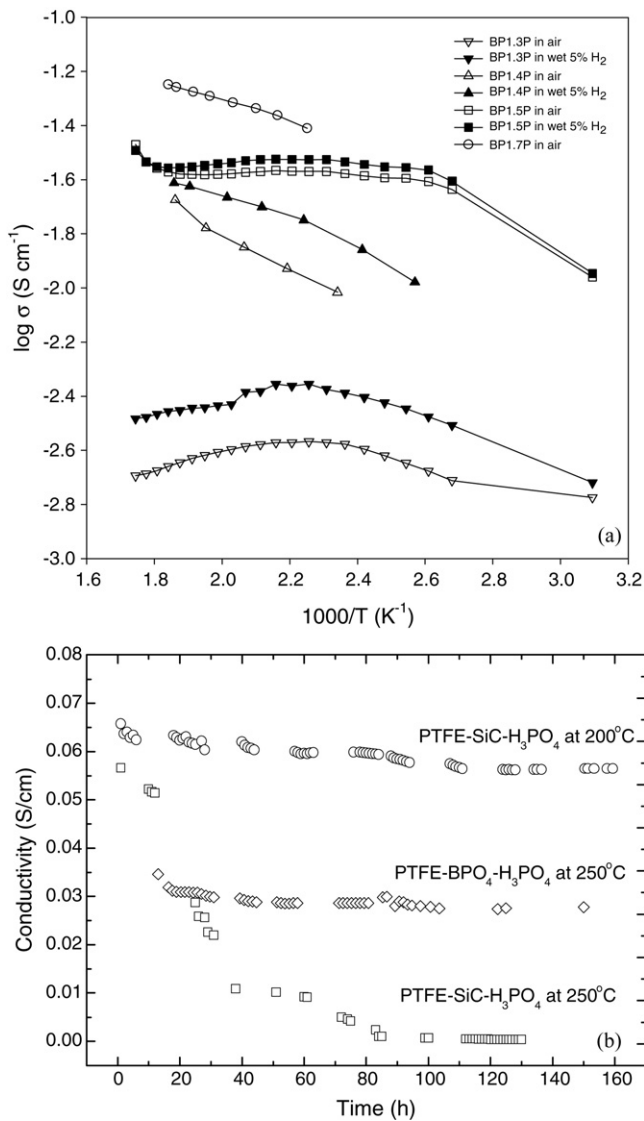


Fig. 2. Conductivity of BPO₄-H₃PO₄-PTFE composites in different atmospheres (a) and stability of conductivity of the materials in air at different temperatures (b).

measurements is shown in Fig. 1a. Under high resolution TEM pictures, an amorphous layer was observed in addition to the BPO₄ crystals and was well distributed on the surface of BPO₄ implying good interface contact. The amorphous layer was believed to be H_{3n-2x}P_nO_{4n-x} and was acting as a functional part for proton conduction. Thus, a core shell structure has been observed in the BPO₄-H₃PO₄-PTFE composite. A similar phenomenon was observed in the Al(H₂PO₄)₃-H₃PO₄ composite [18]. It was difficult to put the PTFE polymer on the copper grid when preparing the sample for TEM therefore PTFE was observed.

The conductivities of the samples as functions of temperature and atmosphere are shown in Fig. 2a. A systematic increase in conductivity was observed from samples BPP1-BPP4 which is due to the enhanced phosphorous loading. Like other proton conductors, a wetter atmosphere (humidified at 20°C) leads to an increase in conductivity indicating that the presence of water promotes conduction. The temperature dependence of the conductivity deviated significantly from a linear relationship which probably implies changing composition with temperature, so the determination of activation energy for proton transport is not reasonable since the state of the systems (i.e. water content, H_{3n-2x}P_nO_{4n-x} composition) strongly depends on temperature. Sample BPP1 shows a

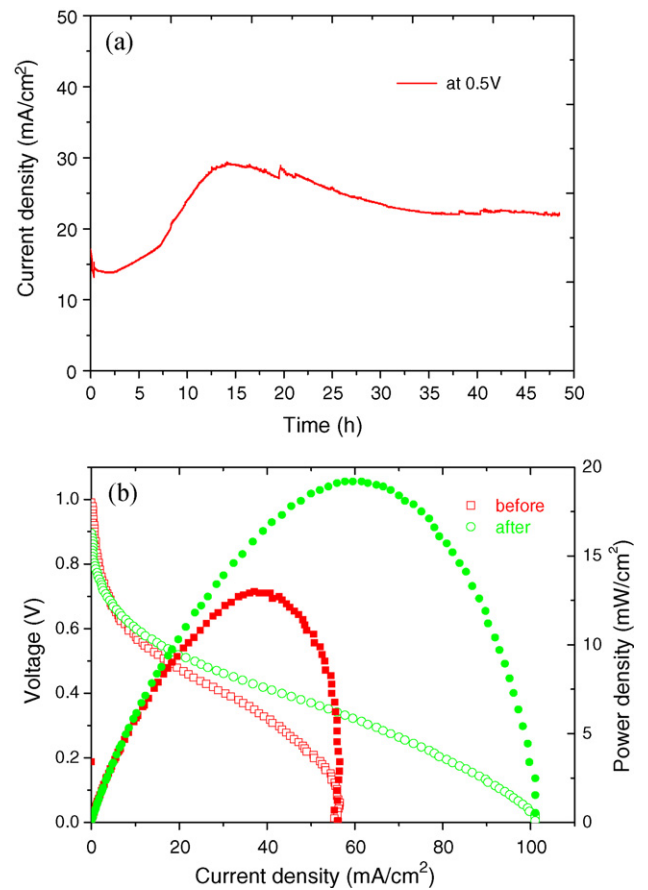


Fig. 3. Long time performance of the cell at room temperature under a voltage of 0.5 V (a); the I - V curves of the H₂/O₂ fuel cell at room temperature before and after the long term stability tests (b).

maximum conductivity at 180°C; Sample BPP3 has “plateau” conductivity from 110°C to 280°C and then gradual increase at higher temperature.

The stability of conductivity is another crucial factor in evaluation of a conductor for practical use. This was examined by measuring the conductivity against time at 250°C. It was found that the conductivity is stable for samples with and without impregnating PTFE at a B:P ratio of less than 1.5. Sample BPP4 has a high phosphorous loading (B:P=1:1.7) but the long term stability of the conductivity value is unsatisfactory. One possible explanation is the leakage or evaporation of phosphoric acid at high H₃PO₄ loading which is a common problem encountered by phosphoric acid fuel cells (PAFCs) [20,21]. Since we maintained the sample at 250°C which is much higher than the operating temperature of conventional PAFCs (200°C), it is more likely for the phosphorous to “escape” from the systems at a large B:P loading. Over loading of H₃PO₄ may form a thick shell thus cause leaching of H₃PO₄. However, after slightly decreasing the phosphorous loading (B:P=1:1.5), the samples exhibit good stability on conductivity in both air and wet 5% H₂ (humidified at 20°C). The conductivity of sample BPP3 is about 0.03 S/cm at 250°C. The unusual stability was attributed to the favourable interface contact between hydrophilic phosphates and amorphous layers which makes reaction (1) shifts to the left. For comparison, the conductivity stability of a SiC-H₃PO₄-PTFE electrolyte for conventional PAFCs is also shown in Fig. 2b. Obviously, the conductivity is stable at 200°C but unstable at 250°C. On the contrary, the stability of BPO₄-H₃PO₄-PTFE composite is good apart from an initial decrease. The conductivity stabilised at 0.03 S/cm during the mea-

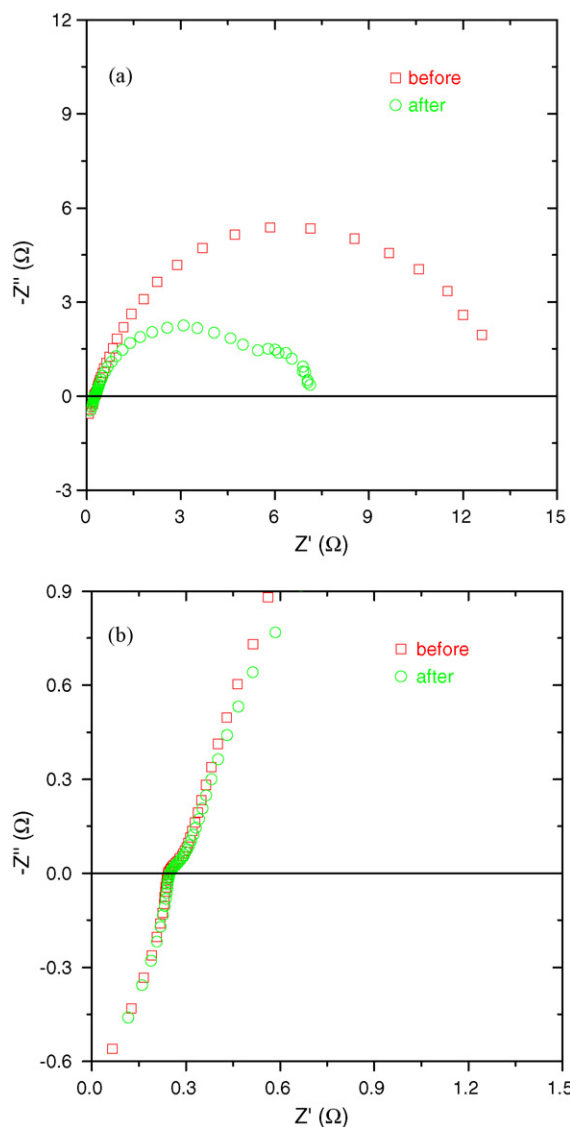


Fig. 4. A.c. impedance spectra of the cell before and after performance stability test at room temperature (a) and enlarged area (b).

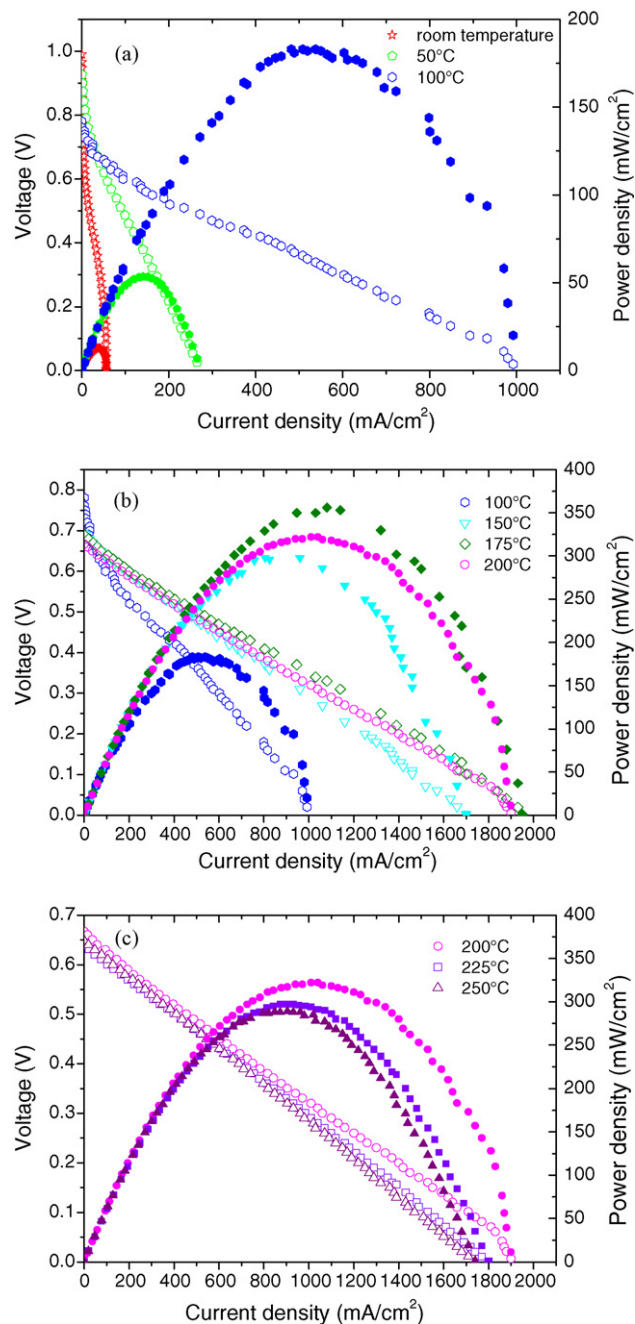


Fig. 6. Performance of the H₂/O₂ fuel cell from room temperature to 250 °C.

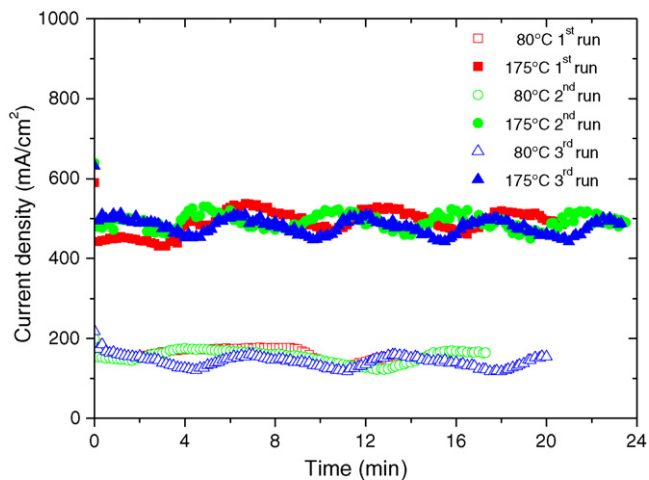


Fig. 5. Performance stability of the cell at 80 °C and 175 °C, respectively, when the working temperature switched between 80 °C and 175 °C.

sured 150 h which is high enough to be used as electrolyte for a fuel cell. This makes it possible to evaluate the performance of a high temperature phosphoric acid fuel cell with a working temperature above 200 °C.

As the first step, the H₂/O₂ fuel cell tests were conducted at room temperature. An open circuit voltage (OCV) of 1 V was observed at room temperature indicating that the membrane electrolyte is quite dense. A maximum current density of 50 mA/cm² has been achieved (Fig. 3a). From impedance analysis, the series resistance was only 0.245 Ω which is quite small at room temperature (Fig. 4). The low performance is due to the large electrode polarisation resistance. The hydrophilic nature of BPO₄ will make the composite electrolyte to hold more water. In order to test the possible leaching of H₃PO₄ with liquid water, a long term stability test of the H₂/O₂ fuel cell at room temperature was carried out for two days. It was

found that the performance was improved during this test apart from an initial decrease. Both current and power densities increase after the stability test (Fig. 3b). A.c. impedance measurement indicates that the increase is due to improved electrode process (Fig. 4). The series resistance mainly due to the ohmic resistance of electrolyte increased from 0.245 to 0.249 Ω after exposing for two days in continuously generated liquid water from the cell. The leaching of H_3PO_4 is insignificant during the process otherwise larger series resistance would have been observed. This implies that fuel cells based on $BPO_4-H_3PO_4-PTFE$ electrolyte may frequently start up at room temperature. Performance of three thermal cycling between 80 °C and 175 °C has been carried out and it was found that the cell is quite stable during the cycling (Fig. 5).

Fig. 6 shows the fuel cell performance of a H_2/O_2 fuel cell from room temperature to 250 °C. The OCV is lower at high temperature which can be explained by the presence of short circuits in the electrode [22] and/or the presence of gas crossover [23]. An OCV of 0.7 V at 180 °C was also observed in a conventional PAFC [13]. The sharp initial cell voltage drop (from 0.95 V to 0.7 V) under loading for fuel cells using H_3PO_4 -based electrolytes indicates that high OCV did not benefit high power density [24]. The current density kept increasing between room temperature and 200 °C and a maximum current density of 1.9 A/cm² was observed at 200 °C. The maximum power density was 320 mW/cm² at a voltage of 0.31 V which is comparable to that for conventional PAFCs [13]. When the operating temperature increased to 225 and 250 °C, the maximum power density is slightly lower compared to that at 200 °C. The catalytic activity of Pt/C electrodes may enhance at higher temperature but the coarsening, agglomerating and dissolving of Pt catalyst also become serious. In our experiments, no obvious benefit was achieved on the H_2/O_2 fuel cell when the operating temperature of a PAFC was above 200 °C. Better CO tolerance is expected at higher temperatures however, which needs further investigation. The microstructure of the $BPO_4-H_3PO_4-PTFE$ composite after the fuel cell measurements is shown in Fig. 1b. It was found that the core-shell microstructure retained after the fuel cell tests indicating that the composite is relatively stable under the fuel cell operating condition.

4. Conclusion

In conclusion, a fuel cell based on H_3PO_4 -based electrolyte can run at room temperature indicating leaching of H_3PO_4 with liquid water is insignificant indicating this type of PAFC has the potential to start up at room temperature. This will help to improve the

thermal cyclability of PAFCs, to make it easier for practical use and to extend the application of PAFCs to portable and transport while frequent start-up is required. The conductivity of this H_3PO_4 -based electrolyte is stable at 250 °C with addition of the hydrophilic inorganic compound BPO_4 forming a core-shell microstructure which makes it possible to run a PAFC at a temperature above 200 °C. The core-shell microstructure retains after the fuel cell measurements. The increase operating temperature above 200 °C does not have significant effects on the performance of a H_2/O_2 fuel cell. For the first time, a composite electrolyte material for phosphoric acid fuel cells which can operate in a wide range of temperatures has been evaluated but certainly further investigation is required.

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