

Development of high-temperature PEMFC based on heteropolyacids and polybenzimidazole

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Received: 14 July 2008 / Revised: 3 September 2008 / Accepted: 10 September 2008 / Published online: 30 September 2008
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Abstract Inorganic/organic composite membranes have been prepared from polybenzimidazole and two different heteropolyacids; namely phosphotungstic acid and silicotungstic acid. The membranes were characterized using SEM, XRD, and proton conductivity. The conductivity of the composite membrane was relatively high when compared to PBI membrane. The fuel cell performance with the composite membranes doped with phosphoric acid was investigated using hydrogen. It was found that pretreatment of PWA and SiWA influenced the fuel cell performance and that the performance was enhanced with the use of the composite membrane. However, from the electrode polarization and crossover current data it was revealed that the expected high performance of the fuel cell was not achieved because of voltage losses associated with contact resistance and poor ionic conductivity in the catalyst layer. The best performance of the fuel cell was achieved with a 40% SiWA/PBI composite membrane.

Keywords Fuel cell · Composite membrane · High-temperature proton-exchange membrane fuel cell · PBI · Phosphotungstic acid · Silicotungstic acid

Introduction

The development of high-temperature polymer electrolyte membrane fuel cells (HT-PEMFCs) is a recent research area. The interest in the development of HT-PEMFC is due to the numerous advantages of PEMFC technology operating above 100 °C [1–3]:

1. Kinetics of both the electrode reactions are enhanced
2. Tolerance of the Pt electrodes to carbon monoxide is increased
3. Non-noble metal catalysts may be used
4. The integration of reformer technology is simpler
5. The cooling system for facilitating heat dissipation is simplified

The proton-exchange membrane is the important step for the development of HT-PEMFC. Polymer electrolytes doped with inorganic proton donors have recently attracted much attention due to their high proton conductivity, chemical and electrochemical stability, and easier processing with polymer matrices [4]. As one of the most attractive inorganic proton donors, heteropolyacids (HPAs) have been shown to be highly conductive and have a stable structure [5, 6]. Heteropolyacids, known for over a century, exist in a series of hydrate phases. The basic structural unit of these acids is a special $[\text{PM}_{12}\text{O}_{40}]^{+3}$ cluster, the so-called Keggin unit. The typical compounds include $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$ —phosphotungstic acid (PWA), $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$ —polymolybdic acid (PMoA), and $\text{H}_3\text{SiW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$ —silicotungstic acid (SiWA). The crystalline structure of these heteropolyacids with 29 water molecules provides the high proton conductivity: the reported conductivity of PWA was 0.18 S cm^{-1} [7]. Staiti and Minutoli [8] tested the electrolyte in a PEMFC and achieved a power density of around 700 mW cm^{-2} at

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atmospheric pressure and room temperature. Unfortunately, during the cell operation, the electrolyte dissolved in the electrochemically produced water and flooded the electrodes, thus creating gas diffusion problems. During fuel cell tests they observed that the heteropolyacid electrolytes had a protective effect against CO poisoning of the Pt anode catalyst [9]. The heteropolyacid also had a beneficial effect on the electrochemical reduction of oxygen. These interesting aspects justify research into fixation of the heteropolyacids in stable structures so that they become water insoluble while retaining high proton conductivity. Therefore, heteropolyacids can be incorporated in a polymer matrix as inorganic–organic composites or hybrids [10].

PWA has been studied with organic polymers for the use in solar cells [4]. Zhang et al. [11] used a sulfonated poly(arylene ether nitrile ketone)–PWA as a potential proton-exchange membrane. The use of a thermally stable polymer like poly[2,2'-(*m*-phenylene)-5,5'-bibenzimidazole], commonly known as polybenzimidazole (PBI), is a potential candidate for composite membrane applications. He et al. [10] used PWA and SiWA to fabricate PBI composite membranes, whilst Staiti [12] used PWA/SiO₂, and Staiti and Minutoli [13] used SiWA/SiO₂ for PBI composite membranes. They reported that the SiO₂ support provided a stable structure for the heteropoly acid; making it insoluble in water.

Staiti et al. [13] successfully prepared composite PBI membranes with silica supported PWA, and SiWA. They reported that the membranes were thermally stable up to 400 °C. The reported conductivity at the operating condition was; however, low, i.e. around $1.5 \times 10^{-3} \text{ S cm}^{-1}$ at 150 °C for PWA/SiO₂/PBI and $2.23 \times 10^{-3} \text{ S cm}^{-1}$ at 160 °C for SiWA/SiO₂/PBI. He et al. [10] reported the conductivity of 30% PWA/PBI doped with phosphoric acid as 0.058 S cm^{-1} .

The available literature on heteropolyacid/PBI system reports various studies on the conductivity of the membrane. However, despite the good conductivity of the composite membrane, there is little data reported on fuel cell test. Hence this paper reports an attempt to develop a HT-PEMFC based on heteropolyacids and PBI polymer and the preliminary fuel cell data. The fuel cell was operated at different temperature using PBI in various ratios with PWA and SiWA.

Experimental

Composite membrane preparation

Phosphotungstic acid (PWA) and silicotungstic acid (SiWA) powders were procured from Sigma-Aldrich. PBI solution (5 wt.%) in *N,N*-dimethylacetamide (DMAc) was prepared

as described in a previous publication [2, 14]. Briefly, poly [2,2'-(*m*-phenylene)-5,5'-bibenzimidazole] was prepared from 3-3'-diaminobenzidine and isophthalic acid in polyphosphoric acid (PPA) by solution polycondensation at temperatures between 170–200 °C.

The inorganic proton conductor (PWA or SiWA) was pre-treated in the following way before synthesizing the composite membrane. PWA or SiWA was dispersed in a smaller amount of water and neutralized by addition of 1 mol dm⁻³ (M) NaOH solution. Then the suspension was dried by evaporating the solvent and the remaining powder was ground to produce a fine powder.

To synthesize the composite membrane the pre-treated PWA or SiWA was dispersed in a PBI solution in DMAc, to produce a casting liquid. The solution was then poured onto an optical glass and kept in an oven at a temperature of 90 to 110 °C for 12 h to produce a thin membrane. The membrane was then treated with HCl solution to reinforce the protons instead of sodium ions [15]. Furthermore, the membrane was boiled in distilled water and then dried in a vacuum oven at 120 °C overnight to remove any residual solvent. Finally, the membrane was immersed in phosphoric acid solution (85%) for acid doping. Composite membranes were prepared with different loadings of PWA or SiWA. The thickness of the membranes was 30 μm. The phosphoric acid doping level of all the membranes was kept constant at five molecules of acid per repeating unit of PBI polymer. Pre-treated heteropolyacids were used in all experiments unless otherwise stated.

Inorganic proton conductor and membrane characterization

The morphology of the PWA and SiWA powders was characterized using SEM. X-ray diffractograms were scanned on PBI, PWA/PBI, and SiWA/PBI composite membranes. Analysis was carried out with a diffractometer using Cu-Kα radiation operated at 40 kV and 40 mA. The XRD patterns were collected with a scan rate of 0.5°/min.

The surface conductivities of the membranes were measured in a conductivity cell in which a strip of the membrane was placed over two platinum strips separated 0.5 cm apart. The bulk conductivity of the membrane was measured using a frequency response analyzer as shown in Fig. 1. AC impedance measurements were carried out between frequencies of 100 Hz and 30 kHz. The membrane was held in the conductivity cell at the desired temperature to reach the steady state before every measurement.

Membrane electrode assemblies (MEA)

To prepare the membrane electrode assembly, the catalyst ink was prepared with carbon supported catalysts (anode,

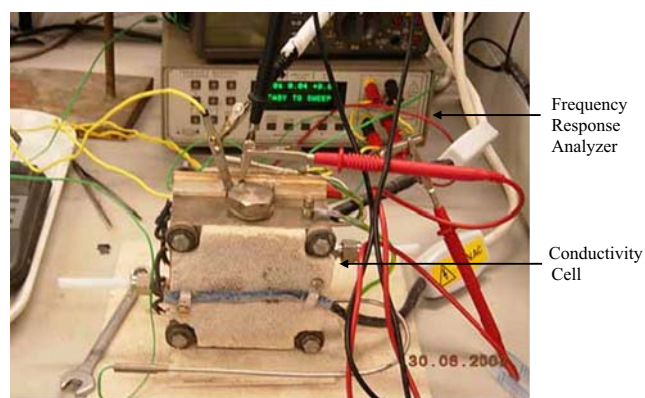


Fig. 1 Experimental set-up for conductivity measurement

20% HP Pt on Vulcan XC-72, Etec Inc.; cathode: 40% HP Pt on Vulcan XC-72, Etec Inc.), PBI solution (5 wt.% in *N,N*-dimethylacetamide (DMAc) and DMAc as solvent. The ink was sprayed by an airbrush onto a carbon cloth gas diffusion layer (Etec Inc.). Catalyst loadings at the anode and cathode were 0.2 and 0.4 mg cm⁻², respectively. After airbrushing, the electrodes were dried and sintered at 190 °C overnight. Membrane electrode assemblies were made by hot pressing the phosphoric-acid-doped membrane in between anode and cathode electrodes at 110 °C and 0.4 ton cm⁻² pressure for 10 min. Once the MEA was ready, it was inserted into the cell. The active area of the electrodes was 1 cm².

Fuel cell tests

To perform cell tests the MEA was in contact with high-density graphite blocks, impregnated with phenolic resin, into which parallel gas flow channels were machined. The total machined cross sectional area (1 cm²) was considered as the active cell area. Electrical 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 cell and controlled with temperature controllers. Gold-plated steel bolts were screwed into the blocks to act as electrical contacts. The outer body of the fuel cell, shown in the Fig. 2, was made of aluminum. Hydrogen and oxygen (dry gases) were supplied at atmospheric pressure to the fuel cell as reactant and oxidant. The flow rates of both gases were in excess of stoichiometric requirements.

Crossover current of the fuel cell was measured by operating the fuel cell with hydrogen on one side and argon gas on the other side. A potential was applied across the cell, so that the hydrogen permeating through the membrane was oxidized electrochemically and the anode polarization and crossover current was measured.

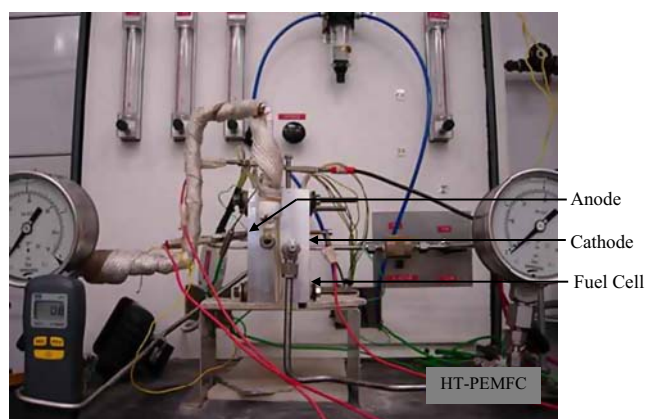


Fig. 2 Photograph of the fuel cell experiment set-up

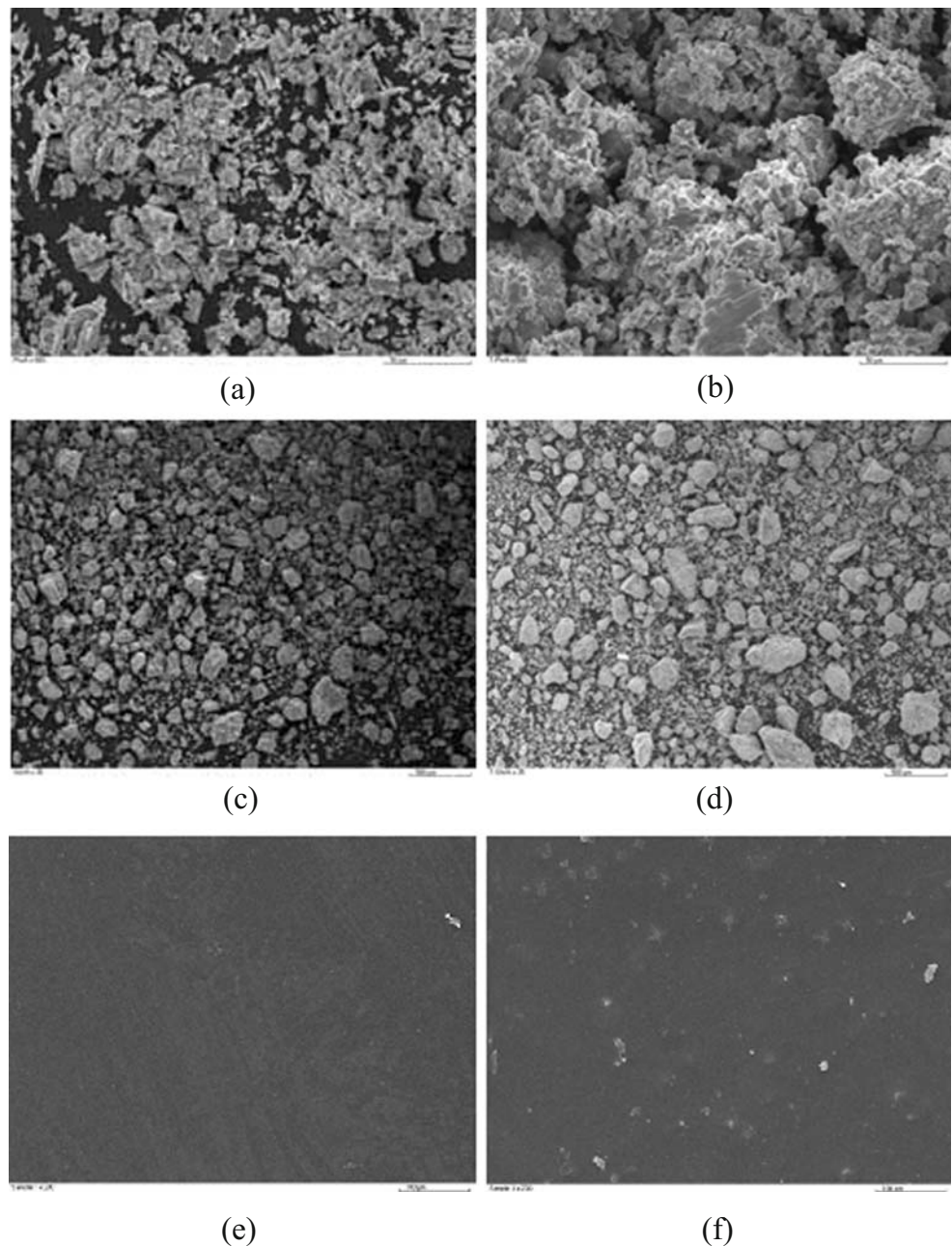
Results and discussion

Figure 3 shows SEM images of PWA, treated PWA, SiWA, treated SiWA particles, 20%PWA/PBI membrane using untreated PWA, and 20%PWA/PBI membrane using treated PWA. It can be seen from the images that the morphological properties do not change with the treatment of PWA and SiWA particles. The SEM images of the solid powder show agglomerates of particles but the SEM images of a representative composite membrane (Fig. 2e) 20%PWA/PBI; using treated PWA, show a dense structure, because the powder was well dispersed in the PBI solution using ultrasonication. Whereas, Fig. 2f shows the SEM image of an agglomerated form of PBI and PWA in 20%PWA/PBI composite membrane using un-treated PWA powder.

Figure 4 shows the XRD image of PBI membrane and representative XRD images of 40%PWA/PBI, and 20% SiWA/PBI composite membranes. The PBI membrane showed a broad peak at $2\theta=22^\circ$ associated with the convolution of an amorphous region and a crystalline region [12]. The XRD patterns of different composite membranes present very broad peak in the region of 2θ from 15 to 40°, which denotes that the materials were mainly amorphous. The XRD does not show the characteristic peaks of PWA and SiWA and it is clear that the heteropolyacids were uniformly distributed in the PBI membrane [12] during the preparation of membrane and no agglomeration process occurred. Jang and Yamazaki [16] have also found the only peak overlaid by the broad polymer reflection in the region of 2θ from 15 to 35 in the X-ray spectra of a PBI membrane modified with zirconia tricarboxylphosphonate.

Figure 5 shows conductivities of the PBI, PWA/PBI, and SiWA/PBI membranes, doped with H₃PO₄. From Fig. 5a, it is clear that the composite membranes had higher conductivities than that of the PBI membrane. This behavior can be attributed to a combination of conductivities of PWA or

Fig. 3 SEM images of **a** PWA, **b** treated PWA, **c** SiWA, **d** treated SiWA, **e** 20% PWA/PBI membrane using treated PWA, and **f** 20% PWA/PBI membrane using un-treated PWA



SiWA and phosphoric acid as well as the characteristic of heteropolyacids to hold water at higher temperature. At 150 °C, the SiWA/PBI composite membrane, containing 40% SiWA, exhibited the highest conductivity of 0.177 S cm⁻¹ under the present experimental conditions. The conductivity values for 40%PWA/PBI and 20%SiWA/PBI were in the same range of approximately 0.12 S cm⁻¹. However, the conductivity of 20%PWA/PBI was only slightly greater than the PBI membrane ca. 0.003–0.013 S cm⁻¹. The conductivity curves for the membranes show maxima at about 150 °C. The reason for the maxima may be because the membranes were doped with phosphoric acid. The phosphoric acid becomes pyrophosphate [17], a

less conductive chemical, in a condensation reaction of two molecules of phosphoric acids, by losing a water molecule at above 150 °C. Figure 5b shows the conductivity of the composite membranes using treated and un-treated heteropolyacids. The effect of HPA treatment is discussed in the subsequent section.

The effect of the use of pre-treated PWA in the composite membrane (20%PWA/PBI) on fuel cell performance is shown in Fig. 6. The performance of the fuel cell with the un-treated PWA in the membrane was much poorer than that with the membrane prepared from the pre-treated PWA. In the case of the data with the un-treated powder, the fuel cell performance was best at between temperatures

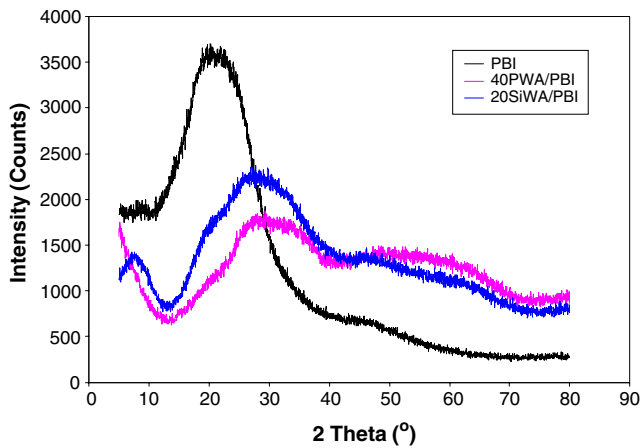


Fig. 4 XRD images of PBI membrane, 40%PWA/PBI, and 20% SiWA/PBI

of 80 to 100 °C and was low at both 60 and 120 °C. Note that the fuel cell performance is generally quite low in comparison to previous published data [2], which is a result of not doping the electrode layers with phosphoric acid.

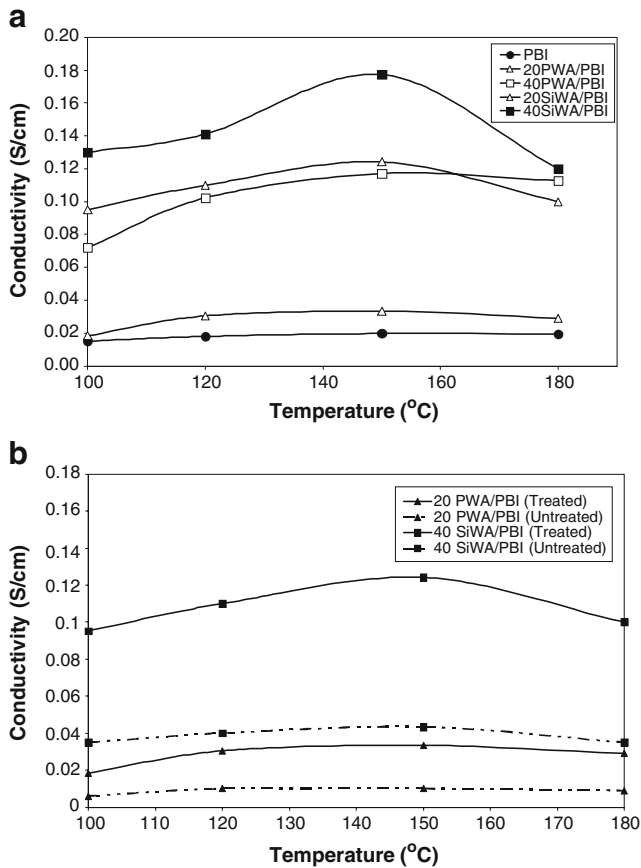


Fig. 5 Conductivity of the composite membranes at **a** different loading of heteropolyacids in PBI as a function of temperature; **b** different loading of heteropolyacids, treated and un-treated: phosphoric acid doping level: five molecules per repeat unit of PBI

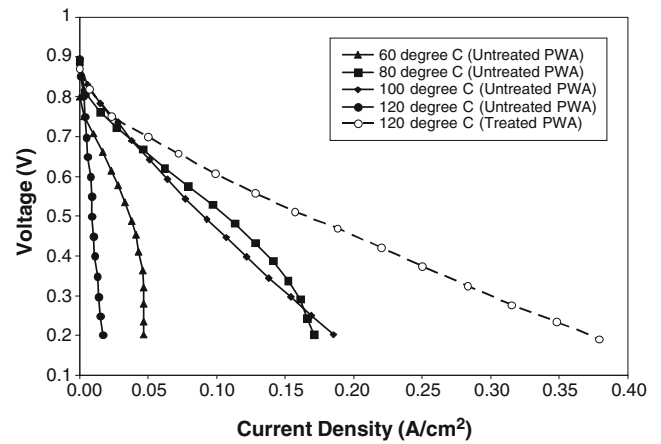


Fig. 6 Performance curves of a HT-PEMFC operated at different temperatures and 20% PWA/PBI composite membrane with and without pre-treatment of PWA. Phosphoric acid doping level: five molecules per repeat unit of PBI

The reason for the difference in performance may be that the mixture of heteropolyacids (acidic in nature) and PBI solution (basic in nature) caused precipitation of the polymer from the solution [7, 16]. Therefore, the membrane prepared with the dispersion had agglomeration of the particles and thus the cast film did not have a good network of the heteropolyacid; as can be seen from SEM picture (Fig. 3e). The doped phosphoric acid may thus mainly surround the heteropolyacids and accordingly the hydrogen permeability increased. Therefore, once the operating temperature of the fuel cell was reduced, the performance was enhanced due to slower cross-over and the maximum performance was achieved at 80 °C. In the case of the pre-treated powder (by neutralization with NaOH solution), it was more easily dispersed in the PBI/DMAc solution and thus an enhanced fuel cell performance was achieved. The fuel cell performance of 20%SiWA/PBI using un-treated SiWA was also expected to be very low, as the conductivity of the membrane was around 30% of that of the membrane using treated SiWA (Fig. 5b).

Figure 7 shows the typical performance of H₂/O₂ fuel cell at the temperature of 120 °C (a), 150 °C (b), and 180 °C (c) with the PBI, PWA/PBI, and SiWA/PBI composite membranes using the pre-treated HPA powders. Open circuit voltages (OCV) for the fuel cells, operated with PBI membranes, were nearly 0.92 V at all three temperatures. However, the OCV of the fuel cells operated with composite membranes were less than 0.9 V for all three operating temperatures. This result may have been due to of fuel crossover from the composite membranes. Electrode polarization studies were performed to investigate the effect of fuel crossover and are discussed in the subsequent section. At 120 °C (Fig. 7a), the fuel cell with 40% SiWA composite membrane showed the best performance. The

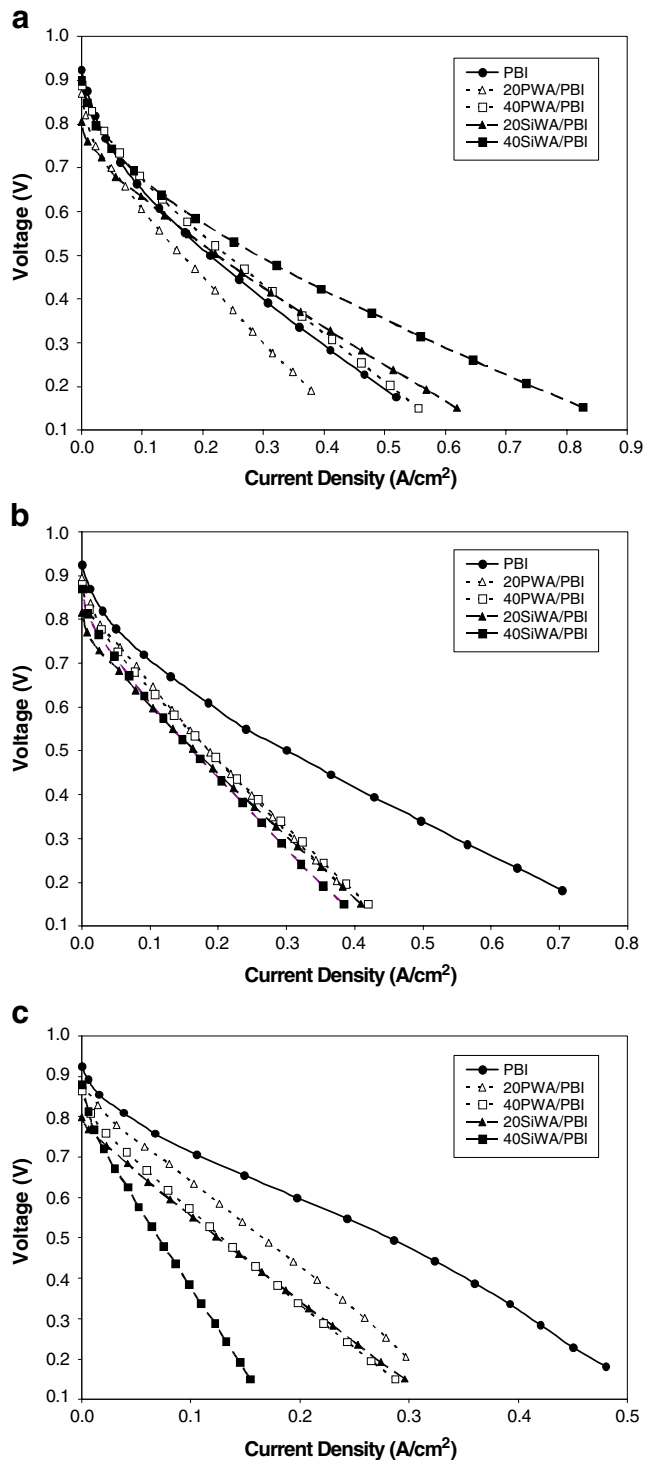


Fig. 7 Fuel cell performance curves of a HT-PEMFC operated at a 120 °C, **b** 150 °C, and **c** 180 °C

performance of the fuel cell with different membranes followed the trend found in the conductivity data. The relative performance of fuel cells at different operating temperatures followed the trend in the variation in conductivity with different HPA (and content). However,

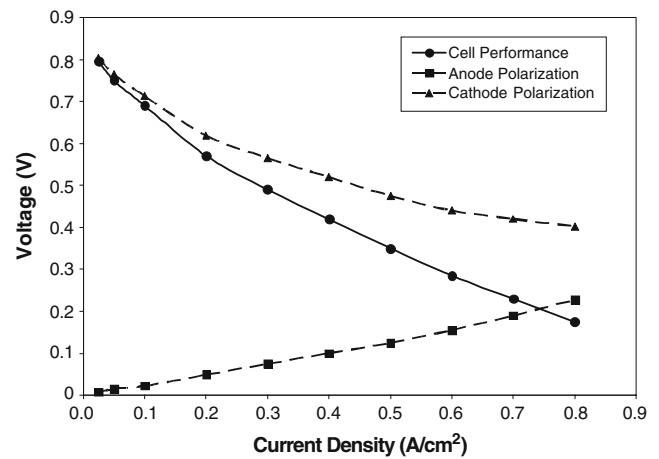


Fig. 8 Polarization curves of 40%SiWA/PBI composite membrane at operating temperature of 120 °C

the best performance shown by the fuel cell was with the PBI membrane. One of the probable reasons may have been fuel crossover as the thickness of the membranes was only 30 μm . Another reason may be associated with phosphoric acid doping; the heteropolyacids particles may be surrounded by an excess of phosphoric acid molecules and permeability of the hydrogen gas increases. The temperature greatly influences the cell performance by the reduced electrolyte conductivity and by reduced hydration level of the membrane or by the self-dehydration of the phosphoric acid at high temperature [17]. That is why the performance of the SiWA/PBI membrane based fuel cell fell to a significant level (Fig. 7c). However, the conductivity of the composite membrane was significantly higher than the other membranes used in the experiments.

Based on the measured conductivities (for example 40% PWA/PBI and 20%SiWA/PBI), the composite membranes should exhibit only around 10–15 mV loss in cell potential due to IR drop. In the case of PBI, this potential loss would be around 75 mV at 500 mA cm^{-2} . Clearly the fuel cell data indicate that the loss in power was due to other factors, which may in part be associated with contact resistance and poor ionic conductivity in the catalyst layers. For example, from the data of Fig. 7b, if we simply assign the slope of the linear curves to resistance, this gives a conductivity for the PBI membrane fuel cell of approximately 0.003 S cm^{-1} and for the composites, approximately 0.0015 S cm^{-1} . These values are clearly an order of magnitude or more lower than those of the membranes alone. Thus it would appear that with the fuel cells used, large potential losses occurred from the electrode polarization and/or hydrogen crossover to the cathode. The former may, in part, be due to the lack of acid in the catalyst layer which would promote ionic conductivity and also create a greater “3-phase reaction zone” between Pt, gas, and the electrolyte. PBI, when undoped, has a relatively low conductivity. In the

case of the PBI membrane, the absence of HPA may have enabled phosphoric acid to move into the catalyst layer and enhance electrode performance; thus, providing the best performance obtained in this study. Such effects of mobile phosphoric acid behavior and its role in PBI fuel cell performance is the subject of work to be reported [work in preparation, 18].

Composite membranes typically exhibit a smaller crossover of un-reacted hydrogen gas from the anode to cathode. In this work, permeability of the membrane to hydrogen was measured electrochemically and quantified as an equivalent crossover current. The measured crossover current was relatively high, e.g., the crossover current was 12 mA cm^{-2} using the 40%SiWA/PBI composite membrane at 120°C . The crossover of reactants lowers the open circuit voltage of the fuel cell and also affects the cell voltage. Typically at 150°C , the OCV of PBI was 0.925 V whereas the OCVs of 20%PWA/PBI and 40%PWA/PBI membrane based fuel cell were 0.895 V and 0.880 V , respectively.

Figure 8 shows typical anode and cathode potentials of a fuel cell using the 40% SiWA/PBI composite membrane. The anode polarization contributed more than 35% of the losses and remaining 65% was from the cathode polarization.

Conclusions

A high conductive composite proton-exchange membrane was prepared using PWA/PBI or SiWA/PBI doped with phosphoric acid for use in high-temperature PEMFC. The composite membrane showed high conductivity compared to PBI membranes. At 150°C , the conductivity of the 40% SiWA/PBI composite membrane was 0.1774 S cm^{-1} at the prevailing experimental conditions. Pre-treatment of the PWA and SiWA was found to be an important factor in achieving reasonable fuel cell performance. The best fuel cell performance was achieved with a 40% SiWA/PBI composite membrane at 120°C . However, at higher temperatures the performance of the composite membrane fell, contrary to that of the PBI membrane based fuel cell. The results showed that the PBI composite membranes with PWA and SiWA, doped with phosphoric acid may become

potential membranes for high-temperature polymer electrolyte membrane fuel cell because of its high conductivity and fuel cell performance. However, at the prevailing experimental conditions, it was found that the PWA/PBI composite membranes were suitable for the temperature limit of 120°C .

Acknowledgment The authors gratefully acknowledge the British Council for the UK India Education and Research Initiative (UKIERI) Research Fellowship to Dr. Anil Verma (IIT Guwahati) for carrying the research work at Newcastle University, UK and Dr. M Mamlouk for useful technical discussion.

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