



Phosphoric acid doped polybenzimidazole membranes: Physicochemical characterization and fuel cell applications[†]

LI QINGFENG, H.A. HJULER and N.J. BJERRUM*

Materials Science Group, Department of Chemistry, Technical University of Denmark, DK-2800 Lyngby, Denmark
(*author for correspondence)

Received 19 January 2000; accepted in revised form 27 September 2000

Key words: electrolyte, fuel cell, polybenzimidazole (PBI), polymer membrane

Abstract

A polymer electrolyte membrane fuel cell operational at temperatures around 150–200 °C is desirable for fast electrode kinetics and high tolerance to fuel impurities. For this purpose polybenzimidazole (PBI) membranes have been prepared and H₃PO₄-doped in a doping range from 300 to 1600 mol %. Physicochemical properties of the membrane electrolyte have been investigated by measurements of water uptake, acid doping level, electric conductivity, mechanical strength and water drag coefficient. Electrical conductivity is found to be insensitive to humidity but dependent on the acid doping level. At 160 °C a conductivity as high as 0.13 S cm⁻¹ is obtained for membranes of high doping levels. Mechanical strength measurements show, however, that a high acid doping level results in poor mechanical properties. At operational temperatures up to 190 °C, fuel cells based on this polymer membrane have been tested with both hydrogen and hydrogen containing carbon monoxide.

1. Introduction

As a clean and efficient technology, fuel cells are expected to provide a practical form of power generation. Among others, polymer electrolyte membrane fuel cells (PEMFC) are receiving increasing attention due to their abilities as power generators for both stationary and transportation applications. The main features of the PEMFC are high power density, low operational temperature, pollution free operation and all-solid construction and therefore less corrosion.

The currently well developed technology is based on perfluorosulfonic acid (PFSA) polymer membranes (e.g., Nafion[®]) as electrolyte [1]. The conductivity of this polymer membrane is dependent on the presence of water to solvate the protons from the sulfonic acid groups. Consequently, the operational temperature is limited to be below 100 °C, typically 60–95 °C, at atmospheric pressure. This is unfortunate because the use of a polymer membrane electrolyte at temperatures higher than 100 °C is desirable in several ways. The reaction kinetics will be enhanced and the catalytic activity increased at higher temperatures for both electrodes. Another benefit is the reduced poisoning effect of the catalysts by fuel impurities, for example, carbon monoxide. This poisoning effect has been shown

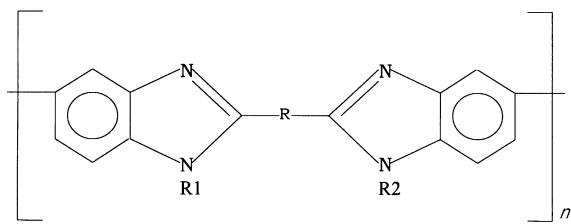
to be very temperature-dependent, that is, CO adsorption is less pronounced with increasing temperature [2]. At 80 °C, the typical operational temperature of a Nafion[®]-based polymer membrane electrolyte fuel cell, for example, a CO content as low as 20–50 ppm in the fuel stream will result in a significant loss in the cell performance [3]. Since the reformat gas of methanol and natural gas always contains a certain amount of carbon monoxide [4], further purification is necessary.

Direct usage of methanol will be the ultimate option, since the dispensation with the complicated gas processors for reforming and CO removal is very much desired, especially for automobile applications. However, the technology is far from satisfactory. One of the major challenges is the anode catalyst, which is not sufficiently active, resulting in high anodic overpotential loss (~350 mV compared to ~50 mV for hydrogen) and high catalyst loading of electrode (3.0–8.0 mg cm⁻²) [5]. The low activity of the anode catalyst is due to the slow kinetics of methanol oxidation and the strong poisoning effect of the intermediate species (CO) from methanol oxidation. Both are expected to be considerably improved by increasing the operational temperature of the DMFC.

The newest technology in the field of PEMFC is based on polybenzimidazole (PBI) membranes [6]. PBI is an amorphous thermoplastic polymer (chemical structure shown in Scheme 1). It forms excellent textile fibres. In the form of a membrane PBI has received much attention in recent years, mainly for use in blood-related

[†]Paper presented at the workshop on "Electrocatalysis in direct and indirect methanol fuel cells" held at Portoroz, Slovenia, September 1999.

dialysis and reverse osmosis at high temperature and harsh environments.



Scheme 1. Polybenzimidazoles.

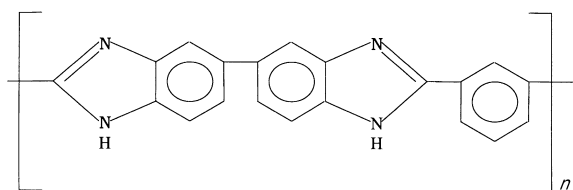
It is well known that polymers containing basic groups can form complexes with stable acid or polymers containing acidic groups. This provides an alternative to the polymer membrane electrolytes for PEMFC and other electrochemical applications. Polybenzimidazoles, with various functional groups such as alkane chains, fluoro alkane chains and other chains, are one of these basic polymer families. Being sulfonated [7], phosphonated or doped with an acid [6], the polymer membrane becomes a proton conductor at temperatures up to 200 °C. It has been shown that this polymer membrane electrolyte exhibits high electrical conductivity [6], low methanol crossover rate [8], excellent thermal stability [9], nearly zero water drag coefficient [10] and enhanced activity for oxygen reduction [11, 12].

It has been suggested that this polymer membrane be used as electrolyte for fuel cells with various types of fuels such as hydrogen [13], methanol [14], trimethoxymethane [15] and formic acid [16]. Besides these, this polymer membrane electrolyte has also been used for other electrochemical applications [17]. The present paper reports the recent development and characterization of this polymer electrolyte for PEMFC.

2. Experimental details

2.1. Preparation of polymer membranes

The polybenzimidazole used (PBI, Celazole[®]) is a poly(2,2'-(*m*-phenylene)-5,5'-bibenzimidazole) product, provided by Celanese Acetate (Scheme 2). The polymer powder (100 mesh) was first mixed with dimethylacetamide (DMAc) and contained in a stainless steel bomb reactor. 2 wt % LiCl was added as a stabilizer. Oxygen was excluded from the bomb by bubbling argon through



Scheme 2. Poly(2,2'-*m*-(phenylene)-5,5''-bibenzimidazole).

the mixture solution for 2 h. The bomb reactor was then closed and placed in a rotating oven at 250 °C for 3 h.

The solution was filtered and diluted for membrane casting.

Membranes were cast using Petri dishes. The thickness and size of the membranes were varied by controlling the volume of solution and the diameter of the dishes. The majority of the solvent was evaporated in a ventilated oven in a temperature range from 80 to 120 °C. The membranes were then washed with distilled water at 80 °C in order to remove the stabilizer and solvent. Traces of the solvent were removed by drying at 190 °C. As a comparison, Nafion[®] 117 membranes were used. These were first boiled in 6 wt % H₂O₂ aqueous solution, rinsed with distilled water and dilute sulfuric acid, and finally washed and kept in distilled water until use.

2.2. Characterization of polymer membranes

Water uptake of PBI and Nafion[®] membranes from liquid water was determined by immersing the samples in distilled water for at least 48 h. The membrane samples were then taken out of the water, blotted with filter paper and weighed. After weighing, the PBI and Nafion[®] membranes were dried at 165 °C and 125 °C, respectively, for about 10 h in order to obtain the dry weight of the membranes. To determine the water uptake of the membranes from the vapour phase the samples were exposed to nitrogen with 100% relative humidity for several days. The samples were weighed during the experiment and the weight gain was obtained.

Membranes were doped by immersing in acid solutions of different concentrations at room temperature for 4–5 days. The doping level of the membranes was determined by comparing the weight changes before and after doping. Thus the weight gain was due to both water and phosphoric acid. However, no effort was made to separate their contributions, and the acid-doping level was determined by assuming that the water uptake remained unchanged in the presence and absence of phosphoric acid, though it may be dependent on the doping level.

Conductivity measurements were carried out by means of a four-probe cell. The cell was placed in an oven. Humidified nitrogen at different temperatures was passed through the cell. Temperature and humidity inside the cell were monitored by a humidity meter (Testo 635).

The mechanical properties of the membranes were measured by means of tensile strength, i.e., the ultimate tensile stress when the sample broke. The sample had an original cross-section of 1 × 0.08 cm² and was tested in a glass furnace, where the temperature was controlled. The tensile strength was measured as a function of doping level at different temperatures.

The electroosmotic drag coefficient of water in the membrane was measured by operating a PEMFC fuel cell under a hydrogen oxidation–reduction mode. When well humidified hydrogen is supplied to the anode side, the membrane conductivity and therefore the cell potential remain unchanged under constant applied current. After the anode gas is switched to dry hydrogen under

constant current, the membrane conductivity will decrease if the passage of protons carries water molecules through the membrane, and therefore the cell voltage increases dramatically after a period of time, indicating drying out of the membrane. The time interval from the dry hydrogen switch to the extrapolated drying out point of the membrane was determined, while the amount of passed charge was measured by means of the applied constant current. Using the predetermined water content of the membrane, the water-osmotic drag coefficient of the membrane was calculated.

2.3. Fuel cell tests

Platinum catalysts (20% Pt) supported on carbon black (Vulcan XC-72R, Cabot) were prepared by chemical reduction of platinum chloroacid (H_2PtCl_6). The catalysts were applied onto wet-proofed carbon paper (Toray TGP-H-120) by a tape-casting technique. The gas diffusion electrodes obtained were then impregnated with the polymer solution used for membrane casting by means of brushing. The loading of the polymer in the catalyst layer was controlled in a range from 0.6 to 0.8 mg cm^{-2} . The Nafion[®]-impregnated electrodes were directly used for preparing the membrane-electrode assemblies (MEAs) by hot pressing at 128 °C for 10 min. The PBI-impregnated electrodes were first doped with phosphoric acid and then used for preparing MEAs by hot pressing at 150 °C for 10 min.

A single test cell (5 cm^2) was made of graphite plates with gas channels. Two aluminium end plates with attached heaters were used to clamp the graphite plates. Fuel and oxidant gases were supplied by means of mass flow controllers. Performance curves were obtained by a current step potentiometry. Potential values at various current densities were then taken from chronopotentiometric curves when a steady state was reached.

For evaluating the tolerance of the technology to fuel impurities, a mixture of 97 vol % hydrogen and 3 vol % carbon monoxide was prepared beforehand. Mixed gases of other compositions were obtained by means of mass flow meters and controllers (Bronkhorst, HI-TEC E-5514).

3. Results and discussion

3.1. Casting and doping of membranes

In the present study, the PBI membrane was prepared from a PBI containing solution. Very few solvents are able to dissolve PBI and *N,N'*-dimethyl acetamide (DMAc) is one of them. It is believed that polar groups in PBI interact strongly with the DMAc molecules [18]. This makes it difficult to remove traces of solvent during the membrane casting. A series of studies show that a final drying temperature of up to 190 °C for hours is necessary.

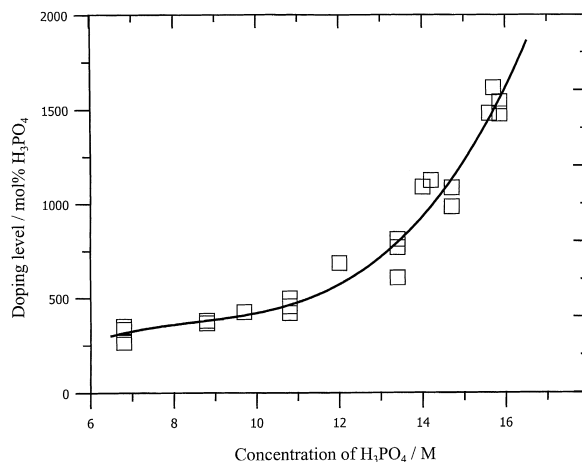


Fig. 1. Doping levels of PBI membranes, in molar percent of H_3PO_4 per repeat unit of the PBI polymer, as a function of concentration of the doping acid.

Chemically, PBI possesses both donor and acceptor hydrogen-bonding sites which are capable of participating in specific interactions. In the presence of acids or bases, a PBI polycation can be formed resulting in acid or base neutralization and formation of a salt with the imidazole ring structure. An electrolyte active species dispersed within the polymer structure is a necessity for proton conduction. The proton conducting active species can either be an acid or a base. In the present study the membranes were doped with phosphoric acid.

The doping level of the membranes is defined as the molar percentage of the acid (mol % H_3PO_4) per repeat unit of the PBI polymer. Figure 1 shows the acid-doping results of the membranes as a function of acid concentration. As can be seen from the figure, a doping level between 450 and 500 mol % H_3PO_4 can be achieved by using a 9–11 M H_3PO_4 solution, which is in good agreement with other work [6, 10, 13, 24]. A doping level as high as 1600 mol % H_3PO_4 can be obtained by using concentrated acid.

3.2. Water uptake

The water uptake of polymer membranes from both liquid and vapour phase is of high importance, since water is involved in the electrode reactions and proton conduction through the membrane. This phenomenon has been investigated by a number of investigators for perfluorosulfonic acid (PFSA) polymer membranes [19–22]. By using the hydration number of the membranes, that is, molar ratio of water to sulfonic acid group (i.e., mol $\text{H}_2\text{O}/\text{mol SO}_3\text{H}$), the water uptake by PFSA membrane is reported to be about 22 from the liquid phase and about 16 from the vapour phase at room temperature. At high temperature or after thermal treatment, this value decreases. The lower water uptake

from the vapour phase [20], as well as at high temperature [22], can be attributed to the difficulty in condensing water vapour within the pores in the membrane.

In the present work, Nafion[®] 117 membrane (equivalent weight 1100) was used for water uptake measurements. With the dry polymer membrane as a basis, the results are 32.8 and 24.9 wt % water uptake from liquid and saturated vapour phase, corresponding to 20.0 and 15.2 mol H₂O/mol SO₃H, respectively. The value for the water uptake from the vapour phase is used in calculation of the water drag coefficient.

It is well known that PBI has a high affinity for moisture and is hydrophilic. This is possibly due to an intermolecular hydrogen bonding between N and N–H groups in PBI and water [23]. By immersing PBI membranes in distilled water for several days at room temperature, it was found that up to 20–21 wt % (with dry polymer as basis) water can be absorbed by pristine PBI membranes, corresponding to 3.4 to 3.6 water molecules per repeat unit of PBI. The same amount of water uptake from the vapour phase was obtained after the PBI membranes were exposed to nitrogen at 100% relative humidity for 10 days.

3.3. Conductivity

The conductivity of acid doped PBI electrolyte was measured as a function of temperature and acid doping level at relative humidity between 80 and 85%. For the purpose of comparison, the conductivity of Nafion[®] membranes (117) was also measured but at relative humidity between 92 and 98%. The conductivity of Nafion[®] membranes was found to increase from 0.02 to 0.1 S cm⁻¹ as temperature increased from 25 to 85 °C. This conductivity is very much influenced by the water activity in the atmosphere. In contrast, the conductivity of PBI membranes is not sensitive to humidity.

It is found that the membrane conductivity is very much dependent on the doping level and also the temperature. At a doping level of 450 mol % H₃PO₄, the measured conductivity is 4.5 × 10⁻³ at room temperature and 4.6 × 10⁻² S cm⁻¹ at 165 °C. At high doping levels between 1300 and 1600 mol % H₃PO₄, the conductivity of PBI membranes is in the same range as Nafion[®] at temperatures from 25 to 85 °C. At high temperatures around 160 °C the membrane exhibits a conductivity as high as 0.13 S cm⁻¹.

The conductivity values reported in the literature vary a great deal. Considering the various experimental conditions, comparison cannot be straightforward. For example, Wainright et al. [6] reported a conductivity value of 2.5 × 10⁻³ S cm⁻¹ at 130 °C in a dry atmosphere for a PBI membrane doped with 338 mol % H₃PO₄. Fontanella et al. [24] obtained a conductivity of 4.5 × 10⁻⁵ S cm⁻¹ for dry PBI doped with 600 mol % H₃PO₄ at room temperature. Using anhydrous mixture of PBI and H₃PO₄, Bouchet et al. [25] reported an

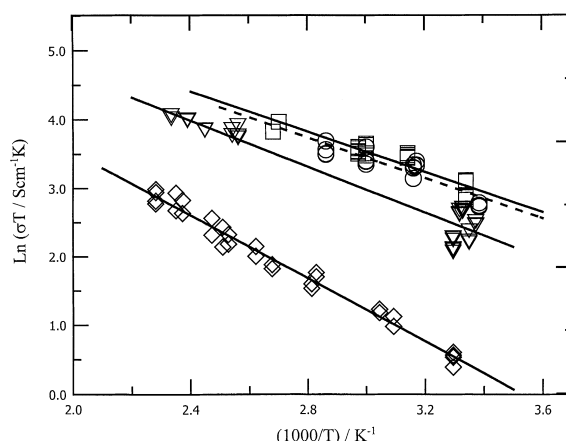


Fig. 2. Arrhenius plots of conductivity of phosphoric acid doped PBI membranes (—) and Nafion[®] (- - -). Doping levels of PBI membranes: (□) 1600%, (▽) 1300% and (◇) 450%. Relative humidity was 92–98% for Nafion[®] and 80–85% for PBI membranes.

anhydrous conductivity of 7 × 10⁻⁶ S cm⁻¹ at temperature of 30 °C and doping level of 305 mol % H₃PO₄.

As expected, the conductivity follows the Arrhenius law:

$$\sigma = \sigma^0 \exp\left(\frac{-E_a}{RT}\right) = \frac{A}{T} \exp\left(\frac{-E_a}{RT}\right) \quad (1)$$

where σ^0 and A are preexponential factors and E_a is the activation energy. Figure 2 shows log(σT) against $1/T$ curves for PBI membranes at different doping levels. It is found that the activation energy decreases as the acid doping level increases, for example, 19.1 kJ mol⁻¹ for doping level of 450 mol % H₃PO₄, 13.9 kJ mol⁻¹ for doping level of 1300 mol % H₃PO₄, and 12.1 kJ mol⁻¹ for doping level of 1600 mol % H₃PO₄. On the contrary, Bouchet et al. [25] found that the activation energy was approximately constant, regardless of the acid doping level. They found that the anion associated to the polymer was H₂PO₄⁻ in a more limited range of the acid doping level (from 20 to 305 mol % H₃PO₄) and a correlation between the conductivity and the nature of the predominant anion associated to the polymer was suggested. Compared with the poor conductivity for PBI–HBr and PBI–H₂SO₄ at low doping levels, it was proposed that the conductivity is governed by a hopping mechanism and may result from proton migration along the anionic chain rather than from proton exchange along the polymer chain between the protonated and non-protonated nitrogen. It was therefore concluded that a high conductivity can be obtained with amphoteric acids as the active dopant. The amphoteric acids give associated anions, which are able to act both as donors and acceptors in proton transfer [25].

This anion-chain proton transfer assumption suggests the significance of the acid doping level to the proton conducting mechanism. For example, at low acid doping level the P–P distance could be too large so that a cooperative motion of two protons along the polymer-

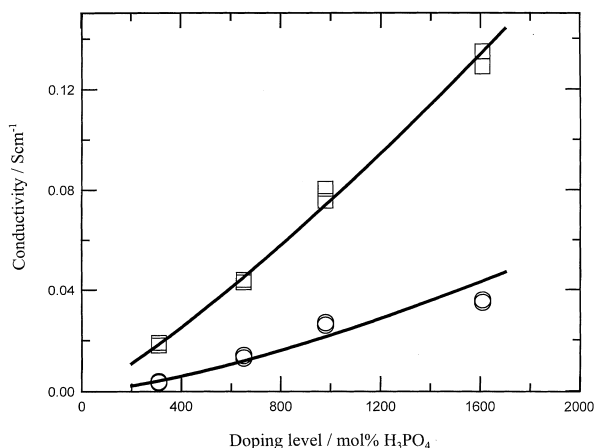


Fig. 3. Conductivity of PBI membranes as a function of the doping level at temperature of 25 °C (○) and 150 °C (□). Relative humidity 80–85%.

anion chain may be necessary, as suggested by Bouchet et al. [25]. At high acid doping levels, however, the average P–P distance could be small, compared to the N–N distance in the imide groups and therefore might allow for proton jump between the anions. The nearly zero water drag coefficient, to be discussed in section 3.5, favours this assumption.

In the present study, the acid doping range is from 300 to 1600 mol % H_3PO_4 , much higher than that studied by Bouchet et al. (20 to 305 mol % H_3PO_4) [25]. The dependence of the conductivity on the acid doping level at both 25 °C and 150 °C is shown in Figure 3. The conductivity is found to increase as a function of the 1.47th power and the 1.21th power of mol % H_3PO_4 , respectively. As a comparison, Bouchet et al. [25] reported a function of the fourth power of the acid doping level in the small range of doping level examined.

3.4. Mechanical strength

For the acid-doped PBI membranes, high doping levels give high electric conductivity. On the other hand, the mechanical properties of the membranes is poor at high doping levels. The tensile strength was measured as the ultimate tensile stress, when the membrane sample broke. Figure 4 shows the results as a function of the doping level at temperatures of 25 °C and 150 °C, respectively. The tensile strength of acid-doped PBI membranes is reduced significantly as the acid doping level increases ($\sim(\text{mol \% H}_3\text{PO}_4)^{-1.67}$ at 25 °C and $\sim(\text{mol \% H}_3\text{PO}_4)^{-1.25}$ at 150 °C, respectively). At the doping level between 600–660 mol % H_3PO_4 , a tensile strength of 1255–1440 N cm^{-2} and 411–600 N cm^{-2} is obtained at 25 °C and 150 °C, respectively.

If only the conductivity and mechanical strength are considered, a useful doping level can be suggested to be between 350 and 750 mol % H_3PO_4 , corresponding to an electrical conductivity of 0.02–0.06 S cm^{-1} and a tensile stress of 200–750 N cm^{-2} at temperatures around 150 °C.

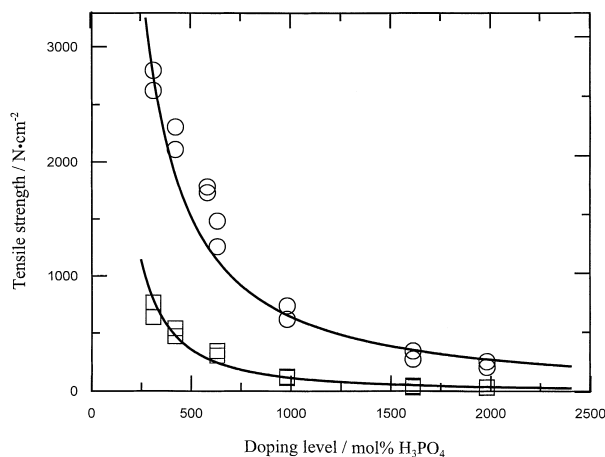


Fig. 4. Tensile strength of PBI membranes as a function of the doping level at temperature of 25 °C (○) and 150 °C (□).

3.5. Electroosmotic drag coefficient of water

The water flux through a polymer electrolyte membrane is a function of the difference in chemical potential of water. The electroosmotic drag is, however, the water drag due to the proton movement and therefore a function of the direct current. The electroosmotic drag coefficient is defined as the molar ratio of water moved with each proton in the absence of a concentration gradient [10].

This coefficient in polymer membrane electrolyte has been determined previously for Nafion[®] [19, 20, 26–29] and PBI [10] membranes. In the present work, a PEM fuel cell was used but operated with humidified hydrogen on both sides. A constant current was applied through the cell and hydrogen was oxidized at the anode side and reduced at the cathode side. The cell voltage of such a cell is stabilized as long as the membrane is saturated with water from the vapour phase and enough water is supplied by the feed gas during the hydrogen oxidation–reduction process. When the feed gases on the both sides were switched to dry hydrogen, the water contained in the membrane was dragged out by the transporting protons. A significant increase in cell voltage was finally observed, corresponding to the drying-out of the membrane. From the time intervals between the dry gas switch and membrane drying-out, the electroosmotic drag coefficient (ξ) of water can be calculated using the following equation:

$$\xi = \frac{N_{\text{H}_2\text{O}}}{N_{\text{H}^+}} = \frac{U_{\text{H}_2\text{O}}F}{it} \quad (2)$$

where $N_{\text{H}_2\text{O}}$ and N_{H^+} are the molar number of water and proton moving through a unit area of the membrane under the current density i (A cm^{-2}) during the period of time t (s), $U_{\text{H}_2\text{O}}$ is the water uptake of the membrane per unit area ($\text{mol H}_2\text{O cm}^{-2}$), which is found to be 4.0×10^{-3} $\text{mol H}_2\text{O cm}^{-2}$ using the water uptake data

Table 1. Electroosmotic drag measurements in Nafion[®] and H₃PO₄-doped PBI membranes

Current density / mA cm ⁻²	Membrane	Temp. / °C	Time interval	Calculated coefficient ξ	Average
400	Nafion [®] 117	80	270 s	3.57	3.2
400	Nafion [®] 117	80	295 s	3.27	
400	Nafion [®] 117	80	348 s	2.77	
200	Nafion [®] 117	80	542 s	3.56	
200	Nafion [®] 117	80	657 s	2.94	
200	Nafion [®] 117	80	603 s	3.20	
400	PBI/H ₃ PO ₄	80	>15 h	~0	~0
400	PBI/H ₃ PO ₄	80	>18 h	~0	
400	PBI/H ₃ PO ₄	150	>10 h	~0	
400	PBI/H ₃ PO ₄	150	>10 h	~0	

from vapour phase. F is the faradaic constant. The results are listed in Table 1. It is seen that the electroosmotic drag coefficient of water for Nafion[®] membranes is around 3.2 at 80 °C.

As a comparison, a coefficient of 2.5–3.0 H₂O/H⁺ has been reported for liquid-equilibrated Nafion[®] membranes at room temperature [19, 20, 29]. For Nafion[®] membranes equilibrated with water vapour, a low value around 1.0–1.4 H₂O/H⁺ at room temperature was reported, depending on the water vapour activity [26, 27]. Considering the water uptake difference on Nafion[®] 117 membranes from liquid and vapour phases, a smaller water drag coefficient in Nafion[®] membranes equilibrated with water vapour than with liquid water is not surprising, since the water mobility will be consequently lower due to stronger water-ion interactions and narrower nanopores in the vapour-equilibrated membranes. Moreover, Ren et al. [28] found that the water drag coefficient increases with temperature, from 2.0 H₂O/H⁺ at 15 °C to 5.1 H₂O/H⁺ at 130 °C. It should be remarked that the result of the present work, 3.2 H₂O/H⁺ for membranes equilibrated with water vapour, is obtained at 80 °C.

Similar measurements were performed on PBI membranes at 80 and 150 °C. Upon switching from a humidified gas to dry hydrogen, however, no potential variation was observed during a measuring period of more than 10 h, indicating that the water drag coefficient is essentially zero for PBI membranes. Weng et al. [10] reported similar results for phosphoric acid doped PBI membranes. This is an indication that humidification may not be necessary for operation of PBI-based PEM fuel cells.

3.6. Fuel cell test

Figure 5 shows fuel cell performance curves as a function of temperature. The noble metal (Pt) catalyst loading in both electrodes is 0.45 mg cm⁻². The PBI membrane is doped by 620 mol % H₃PO₄. It should be noted that this PBI-based fuel cell operates with no humidification for either hydrogen or oxygen. Both gases are under the atmospheric pressure. This result is comparable to the cell performance obtained by Wang

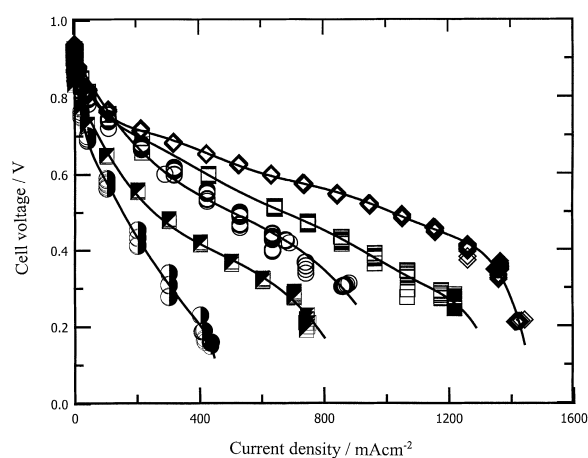


Fig. 5. Performance curves of PBI fuel cell at different temperatures. Cell operates with hydrogen–oxygen at atmospheric pressure and flow rate of 32 ml min⁻¹ cm⁻² without humidification. Platinum catalyst loading 0.45 mg cm⁻² (both electrodes). Key: (◇) 190, (□) 170, (○) 150, (■) 100 and (●) 55 °C.

et al. [13] at 150 °C for PBI fuel cells operating with hydrogen and oxygen. As seen from the figure, an increase in the operational temperature from 55 to 190 °C significantly improves the cell performance. Figure 6 shows the calculated power output as a function of current density at temperature of 150, 170 and 190 °C. At 190 °C and atmospheric pressure, the highest power output around 0.55 W cm⁻² is obtained at current density of 1.2 A cm⁻².

The poisoning effect of carbon monoxide for platinum catalysts has been shown to be a simple competition with hydrogen for active sites, since the strong chemisorptive bond of the carbon monoxide molecule may lead to a surface blockage for hydrogen oxidation [2]. As expected, this effect can be sufficiently suppressed by elevating the operational temperature. At 190 °C, at least 3 vol % carbon monoxide in the hydrogen fuel can be tolerated without significant performance loss, as seen from Figure 7.

4. Conclusions

A polymer electrolyte membrane fuel cell operational at temperatures around 150–200 °C is desirable for

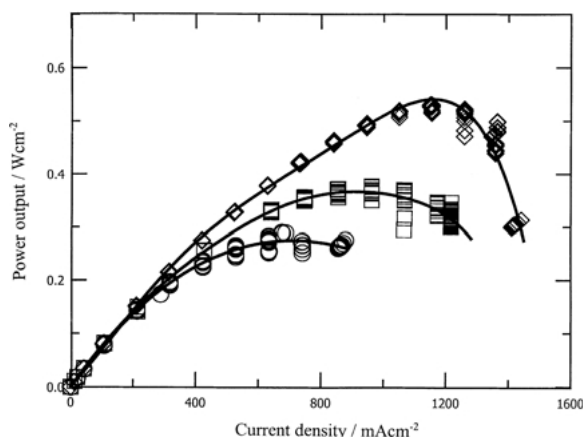


Fig. 6. Power output of the PBI fuel cell at different temperatures. Cell operates with hydrogen–oxygen at atmospheric pressure and flow rate of $32 \text{ ml min}^{-1} \text{ cm}^{-2}$ without humidification. Platinum catalyst loading 0.45 mg cm^{-2} (both electrodes). Key: (\diamond) 190, (\square) 170 and (\circ) 150 °C.

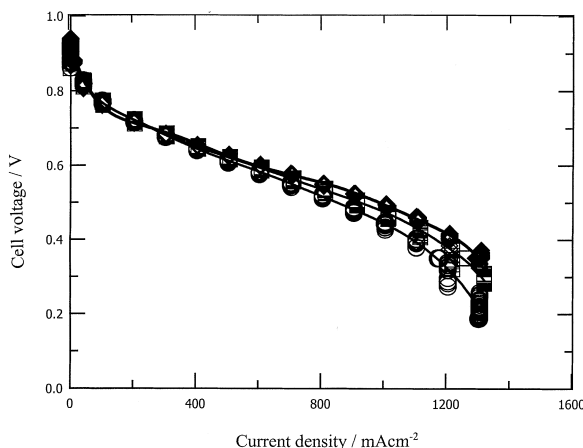


Fig. 7. Performance curves of PBI fuel cell at 190 °C. Platinum catalyst loading 0.45 mg cm^{-2} (both electrodes). Oxygen at 1 atm and $40 \text{ ml min}^{-1} \text{ cm}^{-2}$. Hydrogen contained 0 and 3 vol % CO at 1 atm and $32 \text{ ml min}^{-1} \text{ cm}^{-2}$. CO: (\diamond) 0%, (\square) 1% and (\circ) 3%.

fast electrode kinetics and high tolerance to fuel impurities. For this purpose temperature-resistant polymer electrolyte membranes based on polybenzimidazole (PBI) doped with phosphoric acid have been prepared and characterized. Water uptake of the polymer is around 3.5 water molecules per repeat unit. Electric conductivity is found to be insensitive to moisture but much dependent on the acid doping level. At a temperature of 160 °C and with an acid doping level around 1300–1600 mol % H_3PO_4 a conductivity as high as 0.13 S cm^{-1} is obtained. Mechanical strength measurements show, however, that a high acid doping level results in poor mechanical properties. The electroosmotic drag coefficient of water in the PBI polymer electrolyte is found to be virtually zero, allowing a fuel cell operation with no external humidification. At operational temperatures up to 190 °C, fuel cells based on this polymer membrane

have been tested with both hydrogen and hydrogen containing carbon monoxide.

Acknowledgement

This work received financial support from the European Commission in the framework of the Non Nuclear Energy Programme JOULE III (contract JOE3-CT970045).

References

1. S. Gottesfeld and T.A. Zawodzinski, in R.C. Alkire, H. Gerischer, D.M. Kolb and C.W. Tobias (Eds), 'Advances in Electrochemical Science and Engineering', Vol. 5, (Wiley-VCH, Weinheim, 1997), p. 195.
2. X. Gang, Li Qingfeng, H.A. Hjuler and N.J. Bjerrum, *J. Electrochem. Soc.* **142** (1995) 2890.
3. S. Gottesfeld and J. Pafford, *J. Electrochem. Soc.* **135** (1998) 2651.
4. J.C. Amphlett, R.F. Mann and B.A. Peppley, *Int. J. Hydrogen Energy* **21** (1996) 673.
5. M.P. Hogarth and G.A. Hards, *Platinum Metal Rev.* **40** (1996) 150.
6. J.S. Wainright, J.-T. Wang, D. Weng, R.F. Savinell and M. Litt, *J. Electrochem. Soc.* **142** (1995) L121.
7. X. Glipa, M.E. Haddad, D.J. Jones and J. Rozière, *Solid State Ionics* **97** (1997) 323.
8. J.-T. Wang, S. Wasmus and R.F. Savinell, *J. Electrochem. Soc.* **143** (1996) 1233.
9. S.R. Samms, S. Wasmus and R.F. Savinell, *J. Electrochem. Soc.* **143** (1996) 1225.
10. D. Weng, J.S. Wainright, U. Landau and R.F. Savinell, *J. Electrochem. Soc.* **143** (1996) 1260.
11. S.K. Zecevic, J.S. Wainright, M.H. Litt, S. Lj. Gojkovic and R.F. Savinell, *J. Electrochem. Soc.* **144** (1997) 2973.
12. Li Qingfeng H.A. Hjuler and N.J. Bjerrum, *Electrochim. Acta* **45** (2000) 4219.
13. J.-T. Wang, R.F. Savinell, J. Wainright, M. Litt and H. Yu, *Electrochim. Acta* **41** (1996) 193.
14. J.-T. Wang, J.S. Wainright, R.F. Savinell and M. Litt, *J. Appl. Electrochem.* **26** (1996) 751.
15. J.-T. Wang, W.F. Lin, M. Weber, S. Wasmus and R.F. Savinell, *Electrochim. Acta* **43** (1998) 3821.
16. M. Weber, J.-T. Wang, S. Wasmus and R.F. Savinell, *J. Electrochem. Soc.* **143** (1996) L158.
17. R. Bouchet, E. Siebert and G. Vitter, *J. Electrochem. Soc.* **144** (1997) L95.
18. E. Fekete, Z. Peredy, E. Földes, F.E. Karasz and B. Puánszky, *Polymer Bull.* **39** (1997) 93.
19. T.A. Zawodzinski, Jr., T.E. Springer, J. Davey, R. Jestel, C. Lopez, J. Valerio and S. Gottesfeld, *J. Electrochem. Soc.* **140** (1993) 1981.
20. T.A. Zawodzinski, Jr. C. Derouin, S. Radzinski, R.J. Sherman, V. T. Smith, T. E. Springer and S. Gottesfeld, *J. Electrochem. Soc.* **140** (1993) 1041.
21. J.T. Hinatsu, M. Mizuhata and H. Takenaka, *J. Electrochem. Soc.* **141** (1994) 1493.
22. K. Broka and P. Ekdunge, *J. Appl. Electrochem.* **27** (1997) 117.
23. T.-S. Chung, *Rev. Macromol. Chem. Phys.* **C37** (1997) 277.
24. J.J. Fontanella, M.C. Wintersgill, J.S. Wainright, R.F. Savinell and M. Litt, *Electrochim. Acta* **43** (1998) 1289.
25. R. Bouchet and E. Siebert, *Solid State Ionics* **118** (1999) 287.
26. T.F. Fuller and J. Newman, *J. Electrochem. Soc.* **139** (1992) 1332.
27. T.A. Zawodzinski, J. Davey, J. Valerio and S. Gottesfeld, *Electrochim. Acta* **40** (1995) 297.
28. X. Ren, W. Henderson and S. Gottesfeld, *J. Electrochem. Soc.* **144** (1997) L267.
29. G. Xie and T. Okada, *J. Electrochem. Soc.* **142** (1995) 3057.