

Performance of a poly(2,5-benzimidazole) membrane based high temperature PEM fuel cell in the presence of carbon monoxide

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Abstract

The performance of a poly(2,5-benzimidazole) (ABPBI) membrane based high temperature PEM fuel cell in presence of carbon monoxide, at various temperatures is reported here. The ABPBI was synthesized by polymerization of 3,4-diaminobenzoic acid in a polymerization medium containing methanesulfonic acid ($\text{CH}_3\text{SO}_3\text{H}$) and phosphorous pentoxide (P_2O_5). The ABPBI membranes were characterized by fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM). A maximum conductivity of 0.026 S cm^{-1} at 180°C was obtained for the membrane doped with 1.2 molecules of phosphoric acid (H_3PO_4) per polymer repeat unit. Fuel cell performance was evaluated using dry hydrogen/oxygen gases and was comparable with that reported in the literature. Performance of a single cell at different temperatures was studied with 0.48 and 1.0 vol.% of CO in the hydrogen fuel. The studies lead to the conclusion that CO poisoning is not a serious problem above 170°C . Performance of the fuel cell operating at 210°C is not at all affected by 1.0 vol.% of CO in the hydrogen feed.

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1. Introduction

Polymer electrolyte membrane (PEM) fuel cells are just being introduced in the market for various applications ranging from mobile phones, laptop computers and residential power generation [1,2]. However, some technological advancements are yet to be made for widespread market penetration. At present, PEM fuel cell stacks are fabricated using Nafion membranes manufactured by DuPont. Fuel cells with Nafion membranes cannot be operated at temperatures above 80°C due to membrane dehydration and the resulting loss in conductivity. A maximum operating temperature of 80°C is a serious impediment to commercialization of PEM fuel cells. Low temperature operation (80°C) leads to difficulty in heat rejection for automobile applications and poisoning of active sites of Pt catalyst by carbon monoxide (CO) present in the hydrogen (H_2) fuel at concentration levels above 10 ppm [3]. Low (10 ppm) level CO tolerance of conventional PEM fuel cells puts stringent requirements on the

quality of the H_2 fuel. As of now, H_2 is mainly produced from reformation of hydrocarbon feed stocks [4,5]. Reformate gas streams obtained from the reformer after partial oxidation will contain about 3.0 vol.% of CO. This is normally reduced to about 0.5–1.0 vol.% by a water gas shift reaction [6,7]. Further reduction of the CO to the required level of 10 ppm is quite challenging, involving a combination of various chemical or physical processes to achieve this [7]. Selective removal of CO by passing reformate gas through hydrogen selective Pd permeation membranes [8], methanation of CO over transition metal catalysts based on Co, Ni, Rh, Ce, etc. [9] and preferential oxidation (PROX) of CO over noble metal catalysts such as Pt, Ru, Pd, Rh and Au [10] are the popular options reported in the literature. The first two options have some disadvantages when compared with the PROX process and hence PROX is the established industrial method to reduce the CO level in reformate hydrogen streams [6]. Normally multi stage PROX reactors are used to achieve the required 10 ppm CO level in H_2 [10]. Since the PROX process uses noble metal catalysts, the capital cost is higher and precise temperature control of PROX reactors needs advanced control circuits [6]. The above complex issues involved in CO clean-up can be avoided if reformate hydrogen containing 0.5–1.0 vol.%

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of CO can be directly fed to fuel cell. This will simplify the design and operation of fuel reformers and they can be easily integrated with the PEM fuel cell without the above mentioned difficulties. The aim of the present study is to explore means to accomplish the above task.

Different solutions have been reported for CO poisoning of Pt catalyst. Gottesfield and Pafford [11] have studied CO removal by oxygen (O_2) injection along with fuel gas. The same performance as in pure hydrogen was observed with fuels containing 100–500 ppm of CO. Difficulties in this approach are that the selectivity of bleed oxygen is poor and it also consumes hydrogen and it requires extensive control systems to monitor the oxygen content due to safety concerns. Many CO tolerant bifunctional alloy catalysts are also reported in the literature [12,13]. The bifunctional alloy catalysts promote CO oxidation and removal from active Pt sites by formation of surface OH groups at lower potentials. However, alloy catalysts can tolerate only up to 100–200 ppm of CO even with very high loading [12]. Hence, the above approaches cannot be considered for high CO content in the fuel gas.

It has been reported that the absolute free energy of adsorption of CO on Pt has a larger positive temperature dependence than that of H_2 [14]. The CO tolerance level of Pt catalysts increases with increase in temperature and phosphoric acid fuel cell power plants operating at 200 °C can tolerate about 1.0% CO [14]. Hence, operation of PEM fuel cells at high temperatures is an attractive option to mitigate CO poisoning and also to circumvent other disadvantages associated with the use of a Nafion membrane. Savinell and co-workers [15,16] have proposed that polybenzimidazole (PBI) can be used as a high temperature polymer electrolyte after doping with strong acids such as phosphoric acid (H_3PO_4) or sulphuric acid (H_2SO_4). The PEM fuel cell application of PBI has been extensively studied and PBI based membrane electrode assemblies (MEAs) are now commercially available. Li et al. [17] have studied CO poisoning of platinum (Pt) catalyst in a PBI membrane based PEM fuel cell in the temperature range of 125–200 °C using various concentrations of CO in hydrogen feed. They have reported significant performance loss at temperatures below 175 °C and a performance decrease of 1.3% at the cell voltage of 0.50 V for the feed gas with 1.0 vol.% of CO at 175 °C. At higher temperatures (200 °C) even 3.0 vol.% of CO in hydrogen fuel results in no significant performance loss. Poly(2,5-benzimidazole) (ABPBI) is another benzimidazole polymer having comparable thermal and conductance properties as that of PBI [18,19]. The ABPBI is synthesized from a commercially available, cheap, single monomer and hence will be cheaper than PBI. Synthesis and fuel cell performance of ABPBI is already reported in the literature [18,19]. We were interested in further exploring a high temperature operation of ABPBI membrane based PEM fuel cell. The aim of the present work was to identify suitable experimental conditions to operate an ABPBI membrane based high temperature PEM fuel cell with 1.0 vol.% of CO in the hydrogen feed without significant loss in performance. Such a study may open up the possibility of eliminating the complex CO clean up steps in fuel processing. Preparation of ABPBI membrane, characterization and high temperature operation of ABPBI membrane based

PEM fuel cell with mixed gases of 0.48 and 1.0 vol.% of CO are reported in the present communication.

2. Experimental

2.1. Materials

3,4-Diaminobenzoic acid (DABA), 97% from Aldrich was purified before use. Phosphorous pentoxide (P_2O_5), 98%, methanesulfonic acid (CH_3SO_3H), 99.5%, lithium chloride (LiCl), 99% from Aldrich, polybenzimidazole (PBI) powder of mean particle size 100 μm from Goodfellow Corporation, Huntingdon, UK, hydrazine hydrate ($NH_2NH_2H_2O$), 99%, acetic acid (CH_3COOH), 99.9%, dimethylacetamide (DMAc), 99.9% from Junsei Chemicals Co. Ltd., Japan, were used without further purification.

2.2. Purification of 3,4-diaminobenzoic acid

The DABA was purified by salt formation with hydrazine as reported in the literature [18]. The DABA (20 g) was dispersed in 150 ml of demineralised (DM) water at 70 °C, $NH_2NH_2H_2O$ was then added to get a homogeneous solution. Then, 2 g of activated charcoal was added and stirred for 30 min. The solution was filtered through a celite bed and cooled to room temperature. Then, CH_3COOH was slowly added in drops until DABA starts precipitating. The precipitate was cooled to 20 °C, filtered and the crystals were dried in a vacuum oven at 110 ° for 24 h. The melting point of purified DABA was determined as 215 ° by DSC.

2.3. Polymerization of 3,4-diaminobenzoic acid

Polymerization of DABA was carried out in a polymerization medium containing CH_3SO_3H and P_2O_5 as reported in the literature [18]. The experiment was carried out in a four neck round bottom flask over an oil bath under mechanical stirring. The P_2O_5 , 3 g was dissolved in 20 ml of CH_3SO_3H and 2 g of purified DABA was added. The reaction mass under mechanical stirring was heated to 150 °C in 30 min and maintained for same duration. The viscosity of the solution increased and the hot polymer solution was poured as a thin stream into 300 ml of DM water. The ABPBI polymer fibers were stirred overnight with 1% ammonia solution for complete removal of H_3PO_4 . The fibers were then dried under vacuum at 110 °C for 24 h.

2.4. Viscosity measurement

Viscosities of dried ABPBI samples were determined at a concentration of 0.5 g dl^{-1} in 96% H_2SO_4 using Ubbelohde capillary viscometer in a water bath at 30 °C.

2.5. Preparation of ABPBI membrane and H_3PO_4 doping

The ABPBI was dissolved in CH_3SO_3H at 130 °C to make 4.0% solution. The hot viscous solution was cast onto flat bottom Petri dishes and solvent was removed by heating over hot plate

in a ventilated oven up to 200 °C. The Petri dishes were cooled down to 100 °C and hot water poured to peel off the membranes. The membranes were then dried in a vacuum oven at 110 °C for 2 days. Dried membranes were carefully stored to avoid any moisture absorption before characterizations. All characterizations were carried out with the dried membrane samples.

Dried membranes were weighed and immersed in 40 wt.% H₃PO₄ for 36 h at room temperature. The H₃PO₄ doping level was calculated by drying the membranes at 110 °C for 24 h. The dried membranes had about 50–52 wt.% H₃PO₄ which corresponds to approximately 1.2 molecules of H₃PO₄ per polymer repeating unit.

2.6. Characterizations

2.6.1. FT-IR

FT-IR spectra of dry membrane samples were recorded in the ATR mode in the frequency range of 4000–650 cm⁻¹ on a JASCO FT-IR 470plus instrument. The spectrum was recorded as the average of 50 scans with the resolution of 4 cm⁻¹. Equal pressure was applied for all samples to avoid differences caused by pressure and penetration depth.

2.6.2. SEM morphology

Morphology of membranes was investigated using a scanning electron microscope (S-4700, HITACHI). Fresh cross-sectional cryogenic fractures of the MEA as well as the surface of the membranes were vacuum sputtered with a thin layer of Pt/Pd prior to the analysis.

2.6.3. Proton conductivity

Proton conductivity of the membranes was measured by ac impedance spectroscopy using a Solartron 1260 gain phase analyzer interfaced to a Solartron 1480 multistat. The measurement was carried out in the potentiostatic mode over the frequency range of 0.1 Hz–10 MHz with an oscillating voltage of 5 mV. A homemade four-probe conductivity cell was used which had the configuration similar to that reported in the literature [20]. The conductivity cell had two platinum foils for carrying current and two platinum wires 1 cm apart to sense the potential drop. The membrane sample (2 cm length, 1 cm wide) was placed over the platinum foils in the lower compartment; the upper compartment along with potential sensing platinum wires was clamped to the lower compartment. The cell was kept in a temperature controlled sealed off vessel. The conductivity of the samples was calculated from impedance data using the relation $\sigma = d/RS$ where d and S are the thickness and cross-sectional area of the samples, respectively, and R is derived from the impedance value at zero phase angle.

2.6.4. Fabrication of membrane electrode assembly

The 40 wt.% Pt/C from E-TEK (1.2 g) and 2 wt.% PBI solution (15.60 g) in DMAc (stabilized by 0.1 wt.% LiCl) were used for the catalyst ink preparation. The ink was stirred thoroughly with a magnetic stirrer for 24 h. The ink was brushed onto carbon cloth, dried at 110 °C in a convection oven to calculate catalyst loading. The PBI content in dry electrodes will be 20%. Platinum

loading for both anode and cathode was 0.50 mg cm⁻². The catalyst coated carbon cloths were immersed in DM for 24 h to remove LiCl. They were then doped with H₃PO₄ by dipping in 5% H₃PO₄ solution for 1 day and dried in oven at 110 °C. The membrane electrode assembly was prepared by sandwiching the membrane between two pieces of catalyst coated carbon cloth and hot pressing with 0.5 t cm⁻² at 150 °C for 10 min. The outer surface of the MEA was brushed with 50 wt.% H₃PO₄ before assembling into test fixture.

Single cell performance was evaluated using a homemade 10 cm² active area test fixture. The test fixture was composed of a pair of graphite plates with serpentine flow fields and two brass end plates to hold the graphite plates in place. Rod like heaters were inserted into the end plates to control cell temperature. Performance was evaluated using dry H₂/O₂ gases at the flow rate of 65.0 ml min⁻¹. Load was varied using a rheostat when voltage (V)–current density (I) curve was recorded.

3. Results and discussion

The inherent viscosity of 0.5 g dl⁻¹ of ABPBI in 96% H₂SO₄ was determined as 2.2 dl g⁻¹ which is close to the value of 2.4 dl g⁻¹ reported in an earlier study [19]. Hence, the molecular weight of the ABPBI synthesized in the present study will be comparable with the value reported earlier [19]. The ABPBI dissolves only in CH₃SO₃H, which poses some difficulty in preparation of membranes. The solution is very viscous and probably membrane formation is not going through a proper sol–gel transition. Presumably the polymer settles at the bottom and solvent evaporates from the top. The opaque nature of the membranes, non-uniform thickness in the periphery, middle portions and occasional pinhole formation are all indicate that the membrane formation process does not involve a complete sol–gel transition. The physical appearance of the top and bottom faces of the membrane is also a little different, the top face is dull, somewhat rough and the bottom face is glossy in appearance. SEM micrographs of the top and bottom faces of the ABPBI membrane are shown in Fig. 1. The top face shows non-uniform aggregates that might have formed due to solvent removal from the top as mentioned earlier and the bottom face appears smooth. Pinhole free membranes with reproducible thickness could be obtained by using a sufficient quantity of polymer solution. However, better solvent or solubilization conditions may simplify the membrane preparation procedure.

The FT-IR spectrum of pristine ABPBI and that of acid doped ABPBI are given in Fig. 2. Noticeable differences could be observed in the spectrum of acid doped ABPBI when compared with that of the pristine polymer. On doping with H₃PO₄, a broad band appears between 2500 and 3000 cm⁻¹ due to N⁺–H stretching vibrations in the acid doped ABPBI, the O–H stretching in H₃PO₄ leads to a broad band at 2500–2250 cm⁻¹. The spectrum of H₃PO₄ doped ABPBI presents one region around 1250–750 cm⁻¹ which is also due to H₃PO₄ [19].

Proton conductivity of H₃PO₄ doped ABPBI membrane was measured under zero humidity conditions by keeping the conductivity cell inside a thermostated sealed off vessel. The ves-

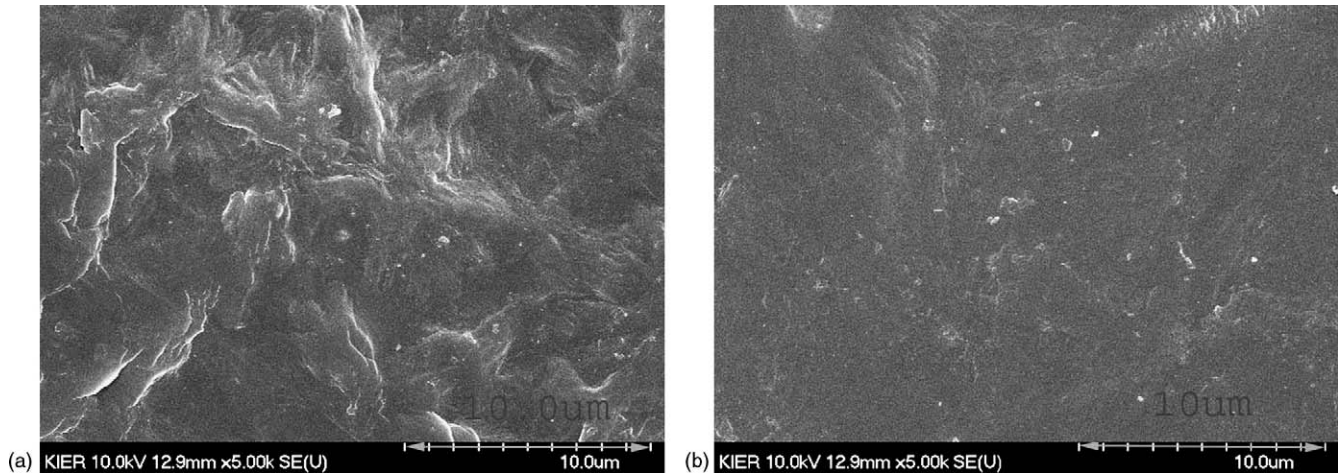


Fig. 1. SEM micrographs of the ABPBI membrane surfaces. (a) Top and (b) bottom.

sel was flushed with nitrogen to remove any moisture inside the vessel before starting the experiment. The H_3PO_4 doped ABPBI membranes show zero phase angle with no imaginary response over a wide frequency range in the impedance spectrum thus behaving as true resistors. Proton conductivity results of ABPBI– $1.2\text{H}_3\text{PO}_4$ membrane as the function of temperature is given in Fig. 3. The conductivity increased with increase in temperature and a maximum conductivity of 0.026 S cm^{-1} was obtained at 180°C . The conductivity value is comparable to that reported in the literature for the ABPBI membranes with similar doping level [18]. The conductivity was reduced beyond 180°C , which is reported to be due to the formation of polyphosphoric acid at high temperatures under low relative humidity conditions [21].

Even though acid doped ABPBI membranes are very flexible, bonding the catalyst coated carbon cloth to the membrane was difficult. It took considerable effort to identify proper conditions for the preparation of MEA. Since ABPBI membranes disintegrate in presence of concentrated H_3PO_4 , one has to be careful in

treating the MEA with H_3PO_4 . The SEM cross-sectional view of the MEA is given in Fig. 4. The catalyst layer along with adsorbed carbon fibers could be observed on the membrane surface. Total thickness of MEA was $1000 \mu\text{m}$, $350 \mu\text{m}$ thick gaskets were used on both sides to provide approximately 30% compression to MEA.

Single cell performance at various temperatures with non-humidified H_2/O_2 is shown in Fig. 5. An open circuit voltage up to 0.98 V was obtained during the experiments. Reproducibility of the I – V performance of the MEAs was very good during repeated testing. The I – V curves show a high activation loss when compared with the data reported for a PBI membrane based PEM fuel cell [17]. However, activation losses observed in the present study are comparable with that reported for ABPBI membrane based fuel cells [19]. A high activation loss shows that the bonding of the catalyst onto the ABPBI membrane is not as good as that obtained with a PBI membrane [17]. Proper bonding of the catalyst onto the ABPBI membrane becomes a tough task due to the inert nature of the ABPBI membrane. There is good scope for improving the

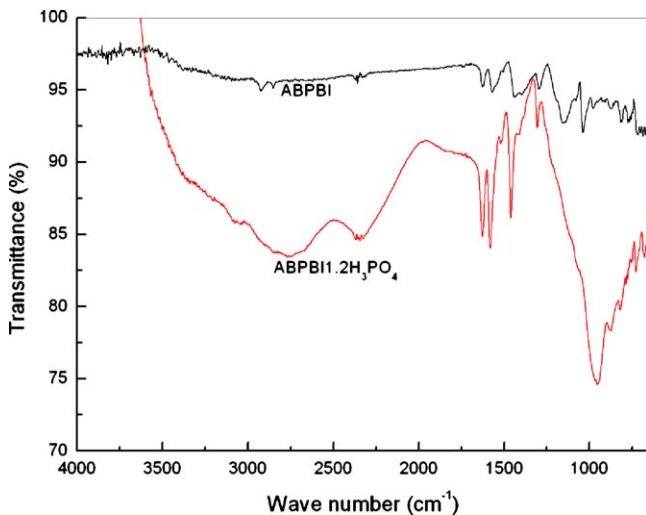


Fig. 2. FT-IR spectra of ABPBI and ABPBI– $1.2\text{H}_3\text{PO}_4$ membranes.

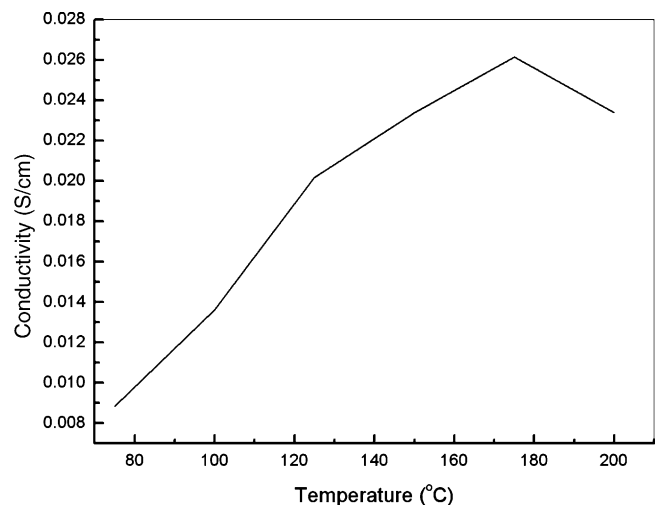


Fig. 3. Conductivity of ABPBI– $1.2\text{H}_3\text{PO}_4$ membrane at different temperatures.



Fig. 4. SEM micrograph of cross-section of membrane electrode assembly.

performance of ABPBI membrane based PEM fuel cells by adopting better MEA preparation methods. The cell performance continuously increased with increase in temperature up to 210 °C. This observation is similar to that reported earlier for the PBI membrane based fuel cell [22]. A maximum power density of 150 mW cm⁻² (current density: 0.450 A cm⁻², cell voltage: 0.333 V) was obtained at 210 °C which is almost similar to that reported earlier at 180 °C [19]. Of course there are noticeable differences between the two studies, the earlier study was carried out with ABPBI–2.8H₃PO₄ membrane and room temperature humidified gases. Whereas experiments in the present study were carried out with ABPBI–1.2H₃PO₄ and dry reactant gases, continuous improvement in performance up to 210 °C is contrary to what can be expected based on conductivity measurements. Probably, excess water generated in the fuel cell at high temperature avoids the possibility of polyphosphoric acid formation and hence the conductivity of the membrane under the actual fuel cell working condition may not be decreasing with increase in temperature.

CO poisoning of the Pt catalyst was studied at different temperatures using mixed fuel gases of two compositions one with 0.48 vol.% of CO, remaining H₂ and the other with 1.0 vol.%

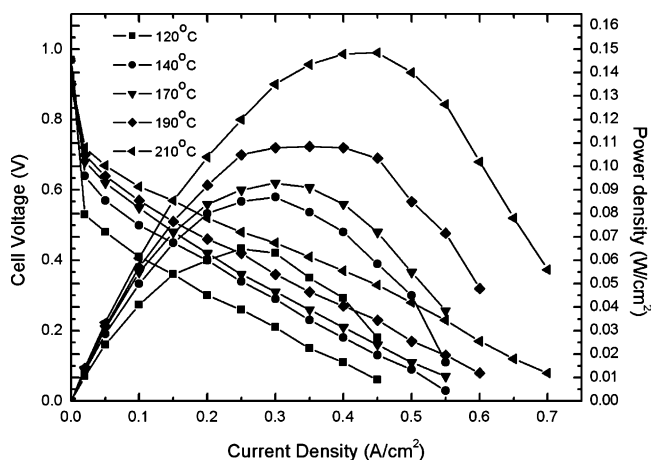


Fig. 5. *I*–*V* performance at different temperatures with unhumidified H₂/O₂.

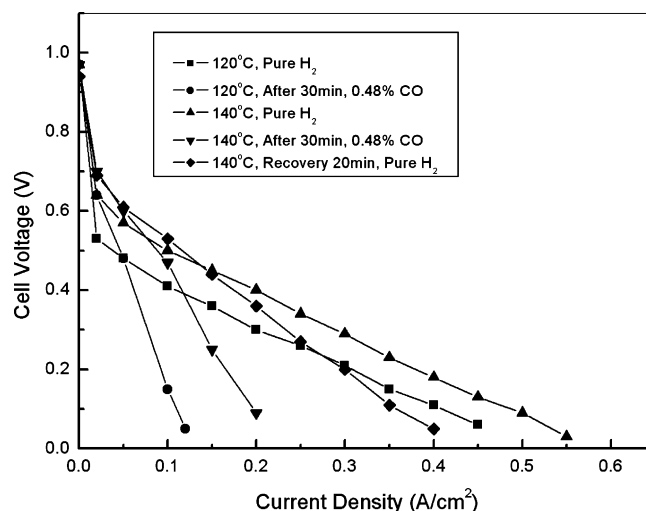


Fig. 6. *I*–*V* performance at 120 and 140 °C with 0.48 vol.% CO.

of CO, remaining H₂. The single cell was run with a particular mixed gas for the duration of 30 min at a given temperature and performance was checked. The fuel gas stream was then switched over to pure H₂ and recovery of cell performance was checked by monitoring the current density at 0.40 V as well as recording the *I*–*V* curve at 10 min intervals. Experimental results at two temperatures, i.e. 120 and 140 °C with 0.48 vol.% CO in the H₂ feed are given in Fig. 6. The performance of the cell was greatly reduced at 120 °C and recovery was impossible and performance (not shown here) was almost the same after running with pure H₂ for 30 min. This result indicates that the reversal of heavy CO poisoning at 120 °C is very unlikely. Almost the same observation has been reported for the operation of PBI membrane based PEM fuel cell at 125 °C [17]. The performance of the cell after running with 0.48 vol.% of CO at 140 °C is better than that observed at 120 °C because more Pt active sites will be available for H₂ oxidation at 140 °C. The performance of the poisoned cell at 0.40 V recovered to 85% of the original level after running for 20 min with pure H₂ at 140 °C. But the performance at higher current densities is lower than that of the unpoisoned cell even after running for 20 min with pure H₂ at 140 °C. However less performance loss has been reported at all current densities even with 1.0% CO at 150 °C for the PBI membrane based fuel cell [17]. The better CO tolerance reported in the latter study might be mainly due to the availability of more Pt active sites for hydrogen oxidation. Since hydrogen oxidation kinetics is so rapid on Pt, little variation in the fraction of active sites available for H₂ oxidation will have great impact on *I*–*V* performance of single cell under the given set of conditions. Higher activation losses reported earlier in the present study obviously mean the presence of fewer active sites which result in higher performance losses in the presence of CO. Probably it may be possible to improve the *I*–*V* performance in the presence of CO by improving the performance of the MEA.

The experimental results at 170 and 190 °C with 0.48 vol.% CO are plotted in Fig. 7. The performance at these temperatures is reasonably good even after running with 0.48 vol.% CO for 30 min. Moreover, the original performance is totally regained

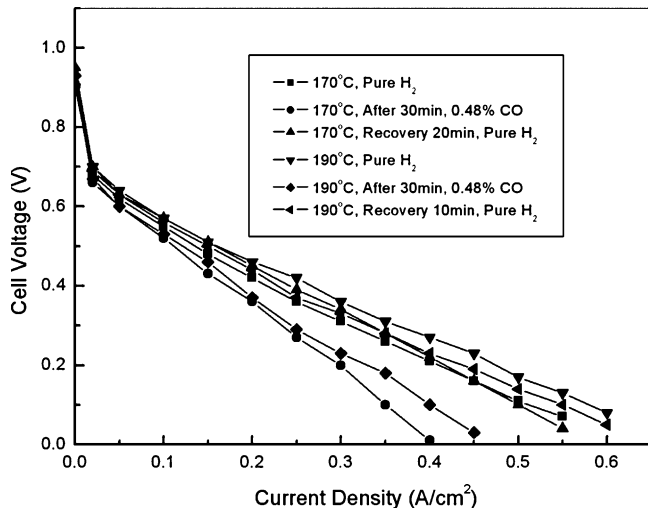


Fig. 7. *I*-*V* performance at 170 and 190 °C with 0.48 vol.% CO.

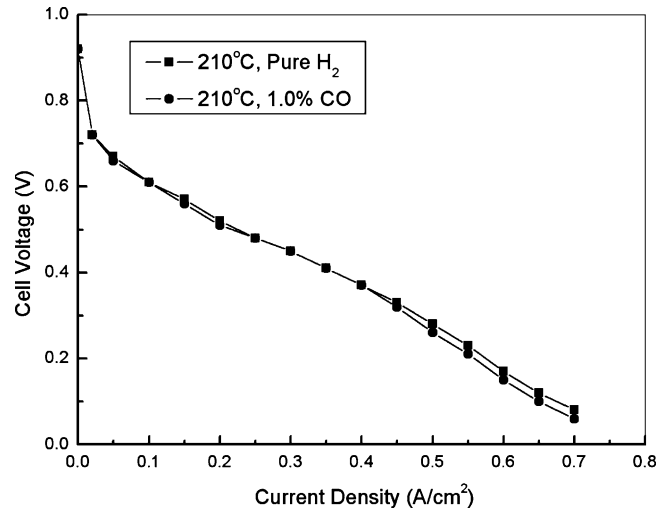


Fig. 9. *I*-*V* performance at 210 °C with pure H₂ and with 1.0 vol.% CO.

on switching to pure H₂ within 20 min at 170 °C and almost 90% performance is regained at 190 °C within 10 min. The performance at low current densities is almost the same with or without CO. Hence, at temperatures around 170–190 °C, the PEM fuel cell can tolerate up to 0.48 vol.% of CO in the hydrogen stream without any problem at low current densities. Even though the performance will be affected at higher current densities, the original performance could be easily restored on switching over to pure H₂ fuel for a while.

Single cell performance with 1.0 vol.% of CO at 140 and 170 °C is presented in Fig. 8. At 140 °C, the performance at 0.4 V has come down by almost 50% within 30 min. The performance has not recovered completely even after passing pure hydrogen for 20 min. There is a significant loss in performance at higher current densities even at 170 °C after passing 1.0 vol.% of CO for 30 min but the original performance has almost been regained on passing pure H₂ for 20 min. Since there was a slight performance loss even at 190 °C with 0.48 vol.% of CO, further experiments with 1.0 vol.% of CO were tried at 210 °C. The results obtained at 210 °C for the feed gas having 1.0 vol.% of CO and that with pure

H₂ are given in Fig. 9. The performance was not at all affected on continuous operation with 1.0 vol.% CO at this temperature. These studies help to establish the fact that CO poisoning of Pt catalyst is not a serious problem if the PEM fuel cell could be operated at temperatures above 170 °C. In the temperature range of 170–200 °C, there may be a slight performance loss at high current densities but the original performance could be brought back by switching to pure H₂ for a while. At 210 °C, there was no performance loss at all current densities even after extended operation.

4. Conclusions

Operation of a ABPBI membrane based PEM fuel cell was studied up to 210 °C and a maximum performance of 150 mW cm⁻² was obtained.

The CO poisoning studies of the Pt catalyst at various temperatures show the possibility of eliminating CO clean up stages and directly integrating the reformer with the PEM fuel cell if the fuel cell could be operated at 210 °C. A PEM fuel cell operating at 210 °C can tolerate about 1.0 vol.% of CO in the H₂ feed without any performance loss.

The temperature limits observed in the present study may very well go down if the performance of the ABPBI membrane based PEM fuel cell could be improved by reducing the activation loss.

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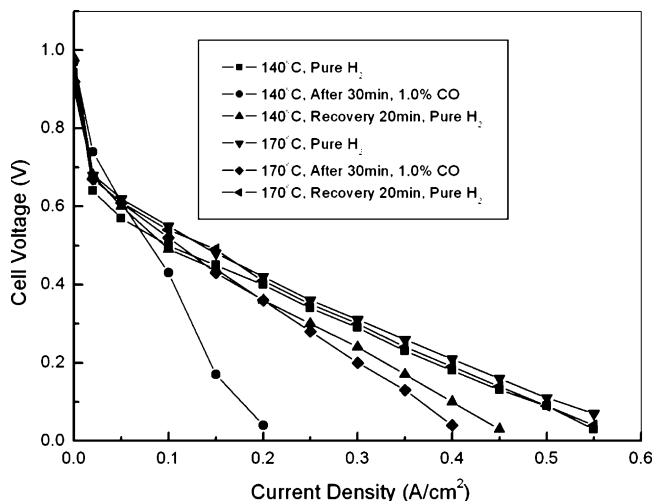


Fig. 8. *I*-*V* performance at 140 and 170 °C with 1.0 vol.% CO.

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