

Integration of high temperature PEM fuel cells with a methanol reformer

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Abstract

On-board generation of hydrogen by methanol reforming is an efficient and practical option to fuel PEMFC especially for vehicle propulsion purpose. The methanol reforming can take place at temperatures around 200 °C with a nearly 100% conversion at a hydrogen yield of about 400 L (h kg catalyst)⁻¹. The CO content in the reformat gas at this temperature is less than 0.2 vol.%. The recently developed high temperature PEMFC based on acid-doped PBI membranes can operate in the same temperature range and tolerate a few percent of CO in the feeding gas. The high CO tolerance makes it possible to use the reformat gas directly from the reformer without further CO removal. Integration of high temperature PEMFC with a reformer is expected to improve the system efficiency and simplify the system construction and operation. The present work has demonstrated this possibility.

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1. Introduction

Recent advances in the polymer electrolyte membrane fuel cell (PEMFC) have stimulated increased interest in fuel cell driven vehicles [1]. The currently well-developed PEMFC technology is based on perfluorosulfonic acid (PFSA) polymer membranes (e.g., Nafion) as electrolyte with pure hydrogen as fuel. The direct use of pure hydrogen as fuel, however, faces unsolved technological problems with economic uncertainties such as compact and lightweight hydrogen storage and hydrogen supply, distribution, and refueling systems.

Use of methanol is an efficient and economical way of bringing hydrogen to a fuel cell system since its storage and refueling need little infrastructure change. However, the direct methanol fuel cell (DMFC) technology suffers from insufficient activity of anodic catalysts and high methanol crossover through the membranes [2]. Alternatively methanol

is used in an indirect way, i.e., via reforming. The reformat gas contains hydrogen, carbon dioxide, carbon monoxide, residual water and methanol as well [3–5]. The presence of CO in the fuel stream causes catalyst poisoning. This poisoning effect is attributed to the strong adsorption of CO on the catalyst surface. The adsorbed CO is inert in the potential regions where the hydrogen anode operates and therefore reduces the active sites of catalyst for the hydrogen electro-oxidation. This CO poisoning effect is temperature dependent [6]. The operational temperature of the PFSA membrane based PEMFC is limited to be typically 80 °C at atmospheric pressure. At that temperature, a maximum concentration of 25 ppm CO is permitted in the fuel gas on the anode side [7]. As a consequence, considerable efforts have been made to develop CO-tolerant electrocatalysts with Pt/Ru alloys as the most promising candidates [8]. Even with Pt/Ru catalysts, however, a significant performance loss is still observed at a CO concentration above 100 ppm at operational temperatures around 80 °C. Therefore careful purification of the reformed hydrogen is necessary to remove CO. This is carried out by the water-gas shift reaction, preferential oxidation, membrane separation or methanation. The CO removal considerably

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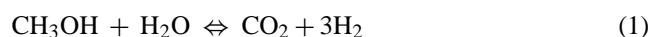
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increases the size and cost of the fuel processing system. For a small dynamic load as in a vehicle, the main challenge for an on-board processing system is the complexity, which not only requires increased cost, size and volume but also reduces the start-up and transient response capacity of the system.

An active subject in the field of PEMFC is the temperature-resistant solid polymer membrane electrolytes [9] such as acid-doped polybenzimidazole (PBI) [10–12]. After doped with phosphoric acid, the PBI membranes possess higher ionic conductivity in a temperature range up to 200 °C [13–17]. At such a temperature, the PEMFC has demonstrated a tolerance of 20,000–30,000 ppm CO [18]. The high CO tolerance makes it possible to use the reformed hydrogen directly from a simple methanol reformer without further CO removal, as also demonstrated by the authors group [19].

Methanol reforming has been extensively investigated through recent years [3–5,20–22]. The typical catalysts have been the Cu/ZnO/Al₂O₃, though new catalysts such as Pd [23], Pd–Zn [24] or other alloy catalysts have also been studied. More development is focused on practical aspects of the technology for mobile applications [25–27], as recently reviewed by Hansen [28] and Reinjng and Petch [29].

Steam reforming of methanol takes place according to the reaction:



which is in fact the sum of the methanol decomposition and the water-gas shift:



Thermodynamically the steam reforming of methanol can take place at temperatures above 160 °C. High conversion of methanol can be achieved at high temperatures and with higher molar ratios of water to methanol (see Table 1). In practice the methanol conversion as well as the reformat gas composition depend on the operating temperature, pressure, catalyst activity and the reformer design (space velocity). In general low operational temperature is preferred when the heat demands, start-up time, CO content and catalyst durability are under consideration. Aiming at integration of a reformer with high temperature PEMFC, the present work examines the methanol reforming in a low temperature range.

Table 1
Calculated thermodynamic conversion of methanol for steam reforming at different temperatures under ambient pressure

Temperature (°C)	Methanol conversion (%)		
	H ₂ O/ CH ₃ OH = 1.0	H ₂ O/ CH ₃ OH = 1.2	H ₂ O/ CH ₃ OH = 1.5
160	92.0	96.7	98.4
185	94.5	98.3	99.3
210	96.1	99.2	99.6
235	97.2	99.6	99.8
260	97.9	99.8	99.9

Reforming reaction (1) is endothermic with a process enthalpy of +57 kJ mol⁻¹. Moreover, preheating and evaporating methanol and water from 25 to 200 °C requires +96 kJ mol⁻¹. On the other hand, the enthalpy of combustion for methanol is -674 kJ mol⁻¹ (lower heating value). If the overall reforming heat is supplied by burning fresh methanol, it will consume about 23% of the fuel supply. In case of high temperature PEMFC, a sufficient amount of heat is available from the stack in the temperature range up to 200 °C, overlapping the temperature range for methanol reforming [30]. In addition, the methanol reforming consumes 1 mol of water for generating 3 mol of hydrogen, while a fuel cell produces 3 mol of water from the 3 mol of hydrogen. An integration of a high temperature PEMFC with a methanol reformer would be possible and expected to significantly improve the system efficiency and simplify the system construction and operation. The present paper is devoted to a demonstration of the thermal integration.

2. Experimental

2.1. Steam reforming of methanol

Catalysts for methanol reforming were prepared from copper, zinc, and aluminum nitrates with a molar ratio of 1:1:0.28. The mixed carbonates were co-precipitated by sodium carbonate at 50 °C, dried after filtering and washing, and finally calcined at 400 °C. The granulated oxide powder was then pelleted and filled in a reformer made of an aluminum tube for some of the reforming tests. The dimension of the reformer tube was 2.4 cm of inner diameter and 19.0 cm long, into which 48 g of the CuO/ZnO/Al₂O₃ catalyst pellets were filled. The catalyst was activated by reducing copper oxide to copper at 150 °C under a hydrogen atmosphere.

In case of the integration test, the catalyst pellets were packed in the enlarged fluid channels of cooling plates made of aluminum. The mixture of methanol and water with a molar ratio from 1.0 to 2.0 was pumped into the catalytic reformer at different pumping rates. The produced hydrogen-rich gas, in a volumetric hydrogen flow rate of L (h kg catalysts)⁻¹, was measured. The residual methanol in the reformat gas was collected in a water condenser kept in an ice bath. From the measured amount of the feed methanol and the amount of the collected methanol in the water condenser, the conversion percentage of methanol during the measuring period was obtained. The CO content in the reformat gas was analyzed by gas chromatography (GC) (HP 6890 Series GC System).

2.2. Preparation of membrane-electrode assemblies (MEAs)

Polybenzimidazole (PBI) was synthesized in this laboratory, as described elsewhere [17]. Membranes were cast from a PBI solution in dimethylacetamide (DMAc), as reported previously [31]. Platinum catalysts (38.6% Pt) supported

on carbon black (Vulcan XC-72R, Cabot) were prepared by chemical reduction of chloroplatinic acid (H_2PtCl_6). The catalysts, in a loading range from 0.5 to 0.65 mg Pt per cm^2 , were applied onto the wet-proofed carbon paper (Toray TGP-H-120) by a tape-casting technique. After drying at 190°C for ca. 1 h, the electrodes were impregnated with 10 wt.% phosphoric acid by brushing. Membrane-electrode assemblies (MEAs) from the impregnated electrodes and the doped polymer membranes were made by hot-pressing at 150°C for 10 min.

2.3. Fuel cell tests

A single test cell (10 cm^2) was made of graphite plates with parallel gas channels. Two aluminum end plates with attached heaters were used to clamp the graphite plates and collect current. Pure hydrogen was first used as a reference fuel. Hydrogen containing 0.1–1.0% CO at 125°C and 1.0–10.0% CO at 200°C was used as fuel for evaluating the CO poisoning effect. Finally the cell was tested with hydrogen-rich reformat gases from the tube reformer operating in a temperature range from 185 to 260°C . In all circumstances oxygen was used as the oxidant. Polarization curves of the fuel cell operating on the reformat gas was recorded with pure hydrogen as a comparison.

A two-cell stack with the active electrode area of 100 cm^2 was constructed with graphite bipolar plates. The flow pattern of the gas channels was parallel so that the gas could be fed under low pressure and low speed. The stack was first tested with hydrogen and hydrogen containing 25% CO_2 as fuel under various flow rates.

The two-cell stack was integrated with a methanol reformer, as shown in Fig. 1. The methanol reformer was made of an aluminum block with large channels filled with the reforming catalysts (149 g). A mixture of 75% H_2 –25% CO_2

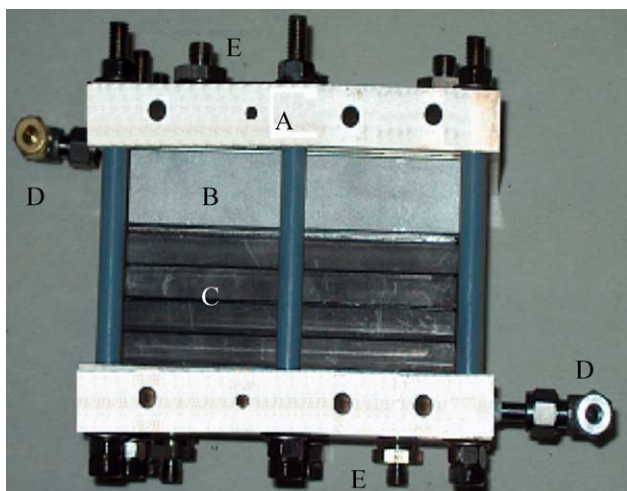


Fig. 1. A two-cell stack with an integrated methanol reformer. The active electrode area is $10\text{ cm} \times 10\text{ cm}$. (A) End plates with heating elements; (B) integrated methanol reformer; (C) PBI cells; (D) fuel inlet and outlet; (E) oxidant inlet and outlet.

was first tested as a reference (flow rate 98 L h^{-1} at 200°C). The stack-reformer system was tested at temperatures of 180, 190 and 200°C , respectively. A mixture of water and methanol (molar ratio 1.5) was fed as vapor through an evaporator (not shown in Fig. 1). The reformat gas entered into the fuel cell stack directly without any further treatment.

3. Results and discussion

3.1. CO poisoning effect

A detailed study of the CO poisoning effect on the PBI based high temperature PEMFC was carried out and published elsewhere [18]. Fuel cell performance curves with pure hydrogen and hydrogen containing carbon monoxide are shown in Fig. 2. At 125°C , CO contents of 0.1, 0.5, and 1.0 vol.% were tested. The CO contents of 0.5–1.0% result in significant performance losses already in the low current density range, while 0.1% CO shows only deviation from the pure hydrogen polarization curve at cell voltages below 0.5 V. At 200°C , 3% CO in hydrogen results in no significant performance loss at current densities up to 1.0 A cm^{-2} or cell voltage above 0.5 V. Significant performance losses were observed at CO contents of 10% at cell voltages below 0.7 V. This should be compared with the tolerance limit of 0.0025% CO (25 ppm) at 80°C at current densities up to 0.2 A cm^{-2} [7].

3.2. Low temperature reforming

Fig. 3a shows the methanol conversion as a function of the feeding rate of the water–methanol mixture at 200°C . The fed mixture was in a water-to-methanol molar ratio of 1.2, 1.5 and 2.0, respectively. At 200°C , close to 100% methanol conversion was achieved only at the feeding rate of below about 50 mL h^{-1} (see Fig. 3a). At the same feeding rate, higher water-to-methanol ratios of the feeding mixtures seemed to give higher methanol conversion. This is primarily due to the fact that, at the same feeding rate, a lower concentration

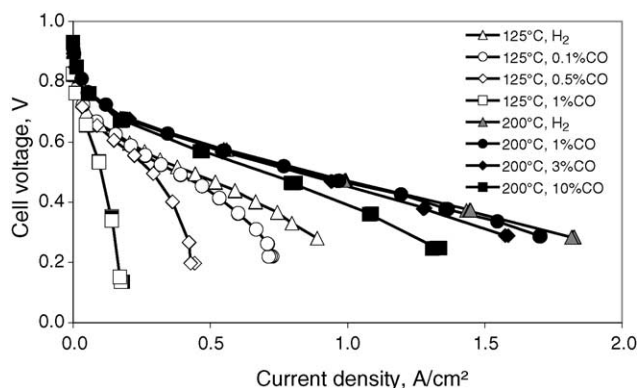
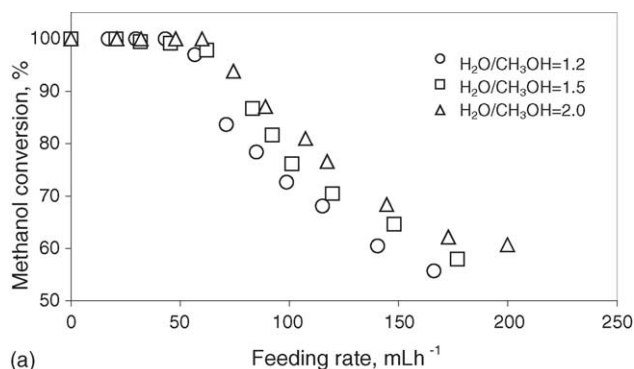
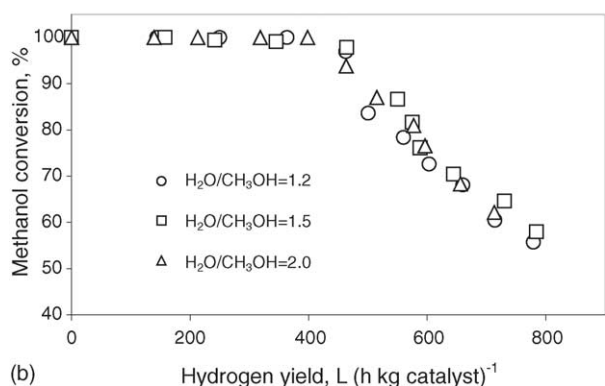


Fig. 2. Polarization curves of a PBI-based PEMFC operating with pure hydrogen and hydrogen containing CO at 125 and 200°C . The CO concentrations are indicated in the figure.



(a)



(b)

Fig. 3. (a) Methanol conversion as a function of the feeding rate of the water methanol mixture (molar ratios are indicated in the figure) at 200 °C. (b) Methanol conversion as a function of the hydrogen yield at 200 °C. The methanol reformer was made of aluminum cooling plates with enlarged channels (of total volume 320 cm³), into which 149 g of CuO/ZnO/Al₂O₃ catalyst pellets were filled.

of methanol in the water mixture would give less yield of the produced hydrogen. When the methanol conversion was plotted as a function of the hydrogen yield (see Fig. 3b), no significant difference was observed.

The hydrogen yield is more dependent on temperature. Fig. 4 shows the methanol conversion rate as a function of hydrogen yield at different temperatures. At 180 °C, a nearly complete conversion of methanol to hydrogen can

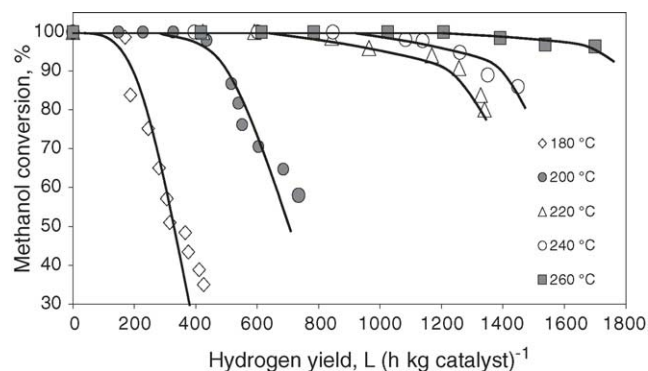


Fig. 4. Methanol conversion at different temperatures. The molar ratio of the fed water and methanol mixture was 1.5. The reformer was the same as described in Fig. 3.

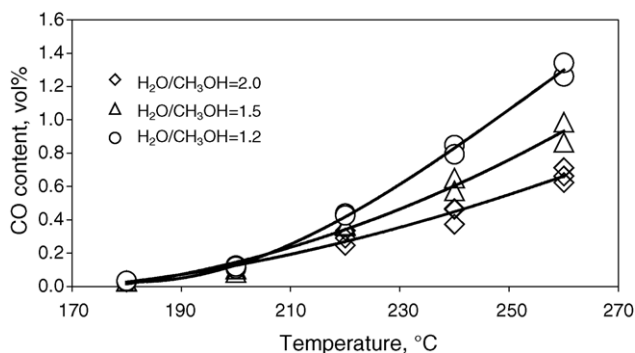


Fig. 5. The CO content in the methanol reformat gas obtained at different reforming temperatures. The ratios of the fed water and methanol mixture were indicated in the figure.

only be achieved at a very low hydrogen yield, i.e. below 200 L (h kg catalyst)⁻¹. At 200 °C, this hydrogen yield is found to be around 500 L (h kg catalyst)⁻¹. Higher temperatures e.g. 260 °C significantly enhance the reforming kinetics and hydrogen yield at close to 100% methanol conversion can be as high as 1700 L (h kg catalyst)⁻¹. These hydrogen yields were achieved under ambient pressure by using the catalyst prepared in this laboratory. As a comparison, Hansen [28] reported a hydrogen yield of 2900 L (h kg catalyst)⁻¹ with another catalyst under 260 °C and 3.8 bar of pressure.

The CO content in the reformat gas is another concern for methanol reforming. For the low temperature methanol reforming in a range from 180 to 260 °C, the measured CO content is shown in Fig. 5. For three compositions of the water methanol mixture (molar ratios 2.0, 1.5, and 1.2), the CO content at 200 °C, for example, is found to be lower than 0.2 vol.%. This is in good agreement with the results by other groups [25]. It is well known that in a temperature range of 250–350 °C, this content is in the range of 1–4% CO [28].

3.3. Single cell test

A direct methanol fuel cell (10 cm²) test system was modified by filling the methanol vaporizer with methanol reforming catalysts, as described previously [19]. By feeding a mixture of water and methanol, the methanol reformer is operated in a temperature range from 185 to 260 °C. The reformat hydrogen from the methanol reformer was used directly as fuel for the fuel cell test. No separate CO shift or cleanup was made, however, before entering into the fuel cell the reformat gas was bubbled through a cold water condenser in order to remove any residual methanol. Fig. 6 shows the fuel cell performance at 200 °C with pure hydrogen and the methanol reformat as fuel. Carbon supported platinum catalysts were used for both anode and cathode, at a loading of about 0.51 mg cm⁻². As discussed above, in this temperature range of methanol reforming, the CO content is within the tolerance capacity of the high temperature PEMFC. As seen from Fig. 6, switching from pure hydrogen to the reformat hydrogen at the reformer temperatures of 185, 210, 235 and

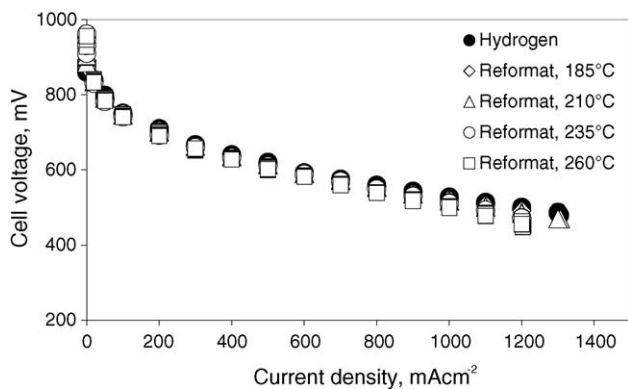


Fig. 6. Cell voltage vs. current density curves of a 10 cm^2 PBI cell using methanol reformat as fuel without further CO removal. The fuel cell was operated under atmospheric pressure at 205°C . Both anode and cathode were prepared with a platinum loading of 0.51 mg/cm^2 . The reforming temperature varied in a range from 185 to 260°C . The molar ratio of the water and methanol mixture was 1.2. The methanol reformer was made of an aluminum tube with an inner diameter of 2.4 cm and a length of 19 cm, into which 48 g of $\text{CuO/ZnO/Al}_2\text{O}_3$ catalyst pellets were filled.

260°C , respectively, results in a slight decrease in the fuel cell performance. As pointed out in our previously work [19], this performance decrease is only partly due to the CO poisoning and more importantly due to the dilution effect by carbon dioxide.

Another series of measurements were performed by keeping the methanol reformer at 210°C while the fuel cell was operated at 100, 135, 170, and 205°C , respectively. As shown in Fig. 7, a significant performance loss was observed at a fuel cell temperature of 100°C when the fuel was switched from pure hydrogen to the methanol reformat. From Fig. 5 it is seen that the methanol reformat at 205°C most likely contained about 0.1–0.2 vol.% CO, which would result in a significant performance loss of the fuel cell at 100°C (see Fig. 2). At the cell temperatures of 135– 170°C , only a slight performance loss was observed, throughout the whole current density range, up to 1.3 A cm^{-2} , when the hydrogen was switched to the methanol reformat gas, at 205°C , however, the two performance curves were identical for pure hydrogen and the methanol reformat gas. It should be remarked that for this test, the flow rate of both hydrogen and the methanol reformat gas was rather high, i.e. about 30 and $45\text{ mL min}^{-1}\text{ cm}^{-2}$, respectively, corresponding to a maximum theoretical current of about 43 A, compared to the maximum measured current of 13 A.

A peak power density as high as 650 mW cm^{-2} at 205°C was obtained for the methanol reformat fuel at a cell voltage of 0.5 V and current density of 1.3 A cm^{-2} . This was achieved with a Pt loading of 0.51 mg cm^{-2} and under atmospheric pressure. Considering the system construction and operation, this performance should probably be compared with a DMFC, which generally has a power density around 0.2 W cm^{-2} at above 0.5 V under operational pressures of 3–5 bars and with noble metal loadings as high as $2\text{--}8\text{ mg cm}^{-2}$ [2].

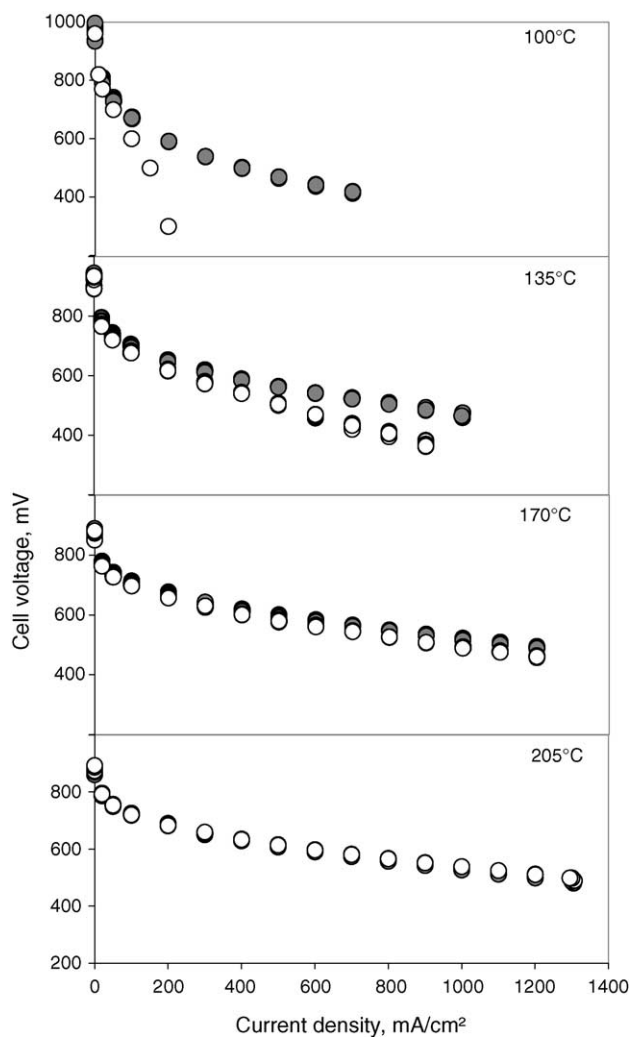


Fig. 7. Performance of a 10 cm^2 PBI-based cell by using methanol reformat directly from a reformer without further CO cleanup (open cycles). The fuel cell performance with pure hydrogen as fuel is used as a reference (solid cycles). The methanol reformat was operated at 210°C with a feeding mixture of water and methanol (the molar ratio was 1.2). The residual methanol was removed by a cold water condenser. Temperatures indicated in the figure are the operating temperature of the fuel cell.

3.4. Stack test

Fig. 8 shows the polarization curves of the two-cell (100 cm^2) stack at 200°C under atmospheric pressure for H_2 and O_2 . The electrodes were made of Pt/C catalysts at a Pt loading of 0.65 mg cm^{-2} . The performance is relatively poor compared with the small single cell, as shown in Figs. 6 and 7. With pure hydrogen as fuel, a current of 28 A was obtained at a stack voltage of 1.2 V, corresponding to a power output of 33.6 W. This was achieved at a hydrogen flow rate of 61 L h^{-1} , above this value no improvement in the stack performance was observed as shown in Fig. 8. As the hydrogen flow rate decreased, limiting currents were observed as shown in the figure. For example, at a hydrogen flow rate of 28 L h^{-1} , a limiting current of 30 A was obtained (open circles), corresponding to a hydrogen utilization of 91%. At

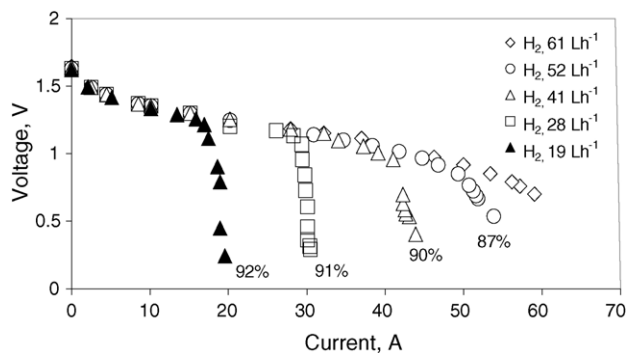


Fig. 8. The two-cell stack performance operating with pure H₂ at different flow rates as indicated in the figure. The active area of the electrodes was 10 cm × 10 cm. The stack temperature was 200 °C and the oxygen flow rate was 100 L h⁻¹.

other flow rates of hydrogen, similar percentages of hydrogen utilization were obtained. It should be noted that the gas channel pattern of the bipolar plates were made in a simple parallel design (depth 2 mm, width 2 mm and rib 1 mm) without optimization. This may primarily account for these low values of the hydrogen utilization, which has been reported to be as high as 97–98% [32].

Using a mixture of 75% H₂ and 25% CO₂ instead of pure hydrogen, similar performance to that of pure hydrogen was observed at high flow rates of the fuel. Fig. 9 shows the results, where the percentage indicated the hydrogen utilization at the limiting current. Efforts were made to integrate the stack with a methanol reformer, as already seen in Fig. 1. Both the stack and reformer were operated at the same temperatures, i.e. 180, 190 or 200 °C. A mixture of water and methanol (molar ratio of 1.5) was fed into the reformer and the reformed hydrogen-rich gas from the reformer entered directly into the stack. The stack performance was shown in Fig. 10, with the performance of 75% H₂ and 25% CO₂ (flow rate of 98 L h⁻¹, corresponding to a net hydrogen flow rate of 73 L h⁻¹) at 200 °C as a reference. From Fig. 4 it was estimated that,

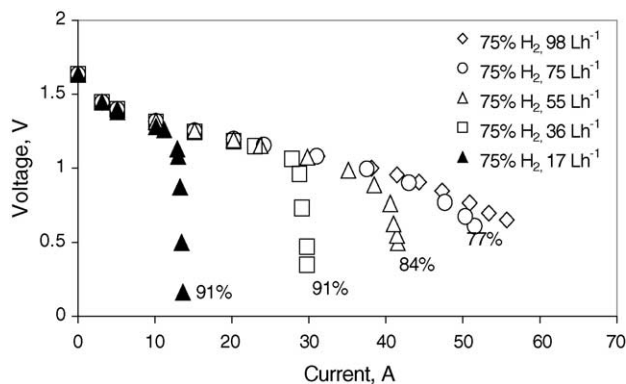


Fig. 9. The two-cell stack performance operating with a mixture of 75% H₂ and 25% CO₂ at different flow rates as indicated in the figure. The active area of the electrodes was 10 cm × 10 cm. The stack temperature was 200 °C and oxygen flow rate was 100 L h⁻¹.

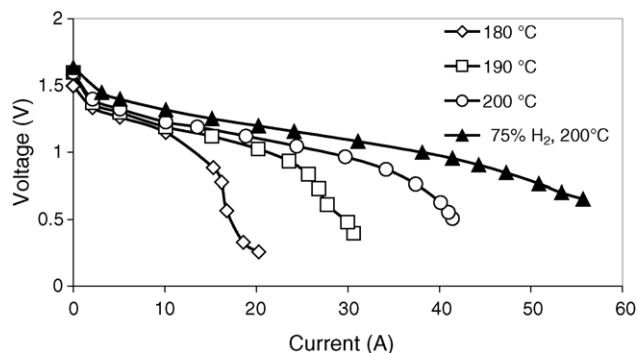


Fig. 10. Performance of the integrated stack-reformer system as shown in Fig. 1. Operating temperatures of the system were 180, 190 and 200 °C. The stack performance operating with a mixture of 75% H₂–25% CO₂ at a flow rate of 98 L h⁻¹ at 200 °C was included for comparison. The active area of the electrodes was 10 cm × 10 cm.

reforming temperatures of 180 and 200 °C and a methanol conversion close to 100%, the hydrogen yield from the integrated reformer should be approximately 30 and 60 L h⁻¹, respectively. The observed limiting currents in Fig. 10 indicate the insufficient fuel supply from the reformer. In the low current density range at 200 °C, however, the stack performance was also lower for the integrated system than that of the stack operating on the 75% H₂ and 25% CO₂ feed. A voltage loss about 160–200 mV was observed. The CO content would not be the major reason for this lowering. An apparent reason could be the effect of residual methanol from the reformer. This effect is under investigation.

4. Conclusion

Methanol reforming took place at temperatures around 200 °C with a nearly 100% conversion though at a low hydrogen yield, about 400 L (h kg catalyst)⁻¹. The CO content in the reformat gas at e.g. 200 °C is lower than 0.2 vol.% when the feed ratios of water to methanol is between 1.2 and 2.0. The recently developed high temperature PEMFC based on acid-doped PBI membranes can operate in the same temperature range and tolerate a few percent of CO in the feeding gas. The high CO tolerance makes it possible to use the reformat gas directly from the reformer without further CO removal. Considering the fact that a reformer is a consumer of heat and water and a fuel cell stack is a producer of heat and water, integration of the stack and the reformer is expected to improve the system performance. This possibility has been demonstrated in the present work.

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