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Performance and endurance of a high temperature PEM fuel cell operated on methanol reformat

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ABSTRACT

This paper analyzes the effects of methanol and water vapor on the performance of a high temperature proton exchange membrane fuel cell (HT-PEMFC) at varying temperatures, ranging from 140 °C to 180 °C. For the study, a H₃PO₄ – doped polybenzimidazole (PBI) – based membrane electrode assembly (MEA) of 45 cm² active surface area from BASF was employed. The study showed overall negligible effects of methanol-water vapor mixture slips on performance, even at relatively low simulated steam methanol reforming conversion of 90%, which corresponds to 3% methanol vapor by volume in the anode gas feed. Temperature on the other hand has significant impact on the performance of an HT-PEMFC. To assess the effects of methanol-water vapor mixture alone, CO₂ and CO are not considered in these tests. The analysis is based on polarization curves and impedance spectra registered for all the test points. After the performance tests, endurance test was performed for 100 h at 90% methanol conversion and an overall degradation rate of –55 μV/h was recorded.

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Introduction

Some of the main advantages of fuel cells compared to traditional energy conversion devices are their superior efficiency, fuel flexibility and possibility for renewable power generation. These advantages together with their modular nature are making them increasingly attractive as power sources of the future.

According to the fuel cell industry review by Fuel Cell Today, fuel cells are now commercial and profitable for various applications, with overall fuel cell system shipments (excluding toys and education kits) in 2012 of 45,700, growing

by 86% compared to 2011 [1]. The report forecasts even more success for fuel cells in the near future.

Proton exchange membrane (PEM) fuel cells are the most developed and most commercialized among fuel cell types to date [2]. They have the advantage of working at a relatively low temperature and hence with faster startup and easier manageability they are attractive for several applications, such as automotive, microCHP, uninterrupted power supply (UPS) and auxiliary power units (APUs).

Some of the main drawbacks of fuel cells that are hindering their widespread commercialization are cost, durability and infrastructure. Hydrogen infrastructure can be costly as the initial investment costs are high, even though, production

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costs could be as low as \$2–3/Kg [3]. Moreover, the hydrogen demand for the adoption of the proposed hydrogen economy [4] may not be entirely met by renewable means as natural gas is currently the main source of hydrogen and is not expected to be abandoned in the near future as the demand grows.

Therefore, liquid hydrogen carriers that are easier to handle and can be produced by renewable means are needed. Methanol is such a hydrogen carrier that can be used in fuel cells. It can be obtained from various renewable biomass sources [5] and has the lowest reforming temperature, around 250 °C–300 °C compared to other hydrocarbons, whose reforming temperature can be up to 600 °C–800 °C [6]. These advantage and its presence in liquid form in ambient temperature for easy transportation make it very attractive for use in fuel cells.

Methanol can be used directly in fuel cells, as in the case of direct methanol fuel cells (DMFC). However, the efficiency is significantly lower than both low or high temperature PEMFCs, and they suffer from methanol cross-over [7,8]. For this reason their application is limited to portable applications [7,9].

Another way of using methanol is by means of steam-methanol reforming, where it is used to produce hydrogen rich mixture of gases that can be utilized in high temperature PEM fuel cells. This is done by coupling the fuel cell with a reformer system. The coupling can be done externally, where the reforming takes place in a standalone system or internally, where the reformer is part of the fuel cell [10,11,8].

HT-PEMFCs are typically operated at around 160 °C and they employ a polybenzimidazole (PBI)-based membrane, which is proton conductive under anhydrous conditions, if doped in phosphoric acid. Moreover, PBI is known for its mechanical strength and has high glass transition temperature of 425–436 °C [12]. These characteristics of an HT-PEMFC allow the use of reformat gas mixtures of various alcohols and hydrocarbons without the need of pre-purification. This is mainly due to the lower requirements for the purity grade of the hydrogen needed for HT-PEMFC, owing to the increased tolerance to poisoning from impurities. Up to 2–3% CO can be tolerated without any significant loss in fuel cell performance in HT-PEMFCs, while their low temperature counterparts show significant performance loss at CO concentration of few parts per million [13].

Methanol steam reforming produces impurities like CO₂, CO and unconverted methanol-water vapor mixture. However, the study of the poisoning effects of reformat mixtures is usually limited to CO₂ and CO, perhaps due the fact that they are common to most reforming processes, especially the reforming of alcohols and hydrocarbons. The effects of CO are usually associated to preferential surface adsorption of its molecules on the catalyst, thereby reducing the electro-active area [14]. The effects of CO₂ on the other hand are limited to dilution of the anode feed, with the possibility of chemical or electrochemical reduction into CO [15]. There are also several mitigation techniques suggested for CO and CO₂ poisoning, which include increasing the operating temperature and performing partial oxidation of CO by oxygen bleeding on the anode [12,16]. However, the effects of wet methanol reformat are not well documented and thus the phenomena is not clearly understood. Consequently, there are not many suggestions on how to mitigate the effects.

This study investigates the effects of methanol and water vapor mixture. It is done at different operating temperatures and different concentrations of vapor mixture in anode feed, to understand the degrading phenomena and how they change with other parameters. Methanol is known to cause degradation via cross-over in DMFCs and it is also reported that it undergoes complex reactions on Pt surface [17,18].

In our previous works, preliminary performance and durability studies of an HT-PEMFC at relatively high methanol-water vapor mixture have been presented [19,20]. High methanol concentrations were tested in order to accelerate tests and they revealed that the vapor mixture has degrading effects if present at concentrations of above 3%. The current study focuses on methanol contents between 0 and 3%, which is what can be expected from methanol steam reformers of different efficiencies and different operating temperatures [8,21].

Experimental

The experimental setup used in this study is a Greenlight Innovation test stand, whose schematic is shown in Fig. 1. A single fuel cell assembly is tested, where a Celtec P2100 MEA from BASF is sandwiched between two serpentine flow channels. The MEA's nominal catalyst area is 45 cm². It is H₃PO₄/PBI-based and is produced and doped by means of a sol-gel transition process [22].

The experimental setup incorporates a methanol vaporizer, which is used to supply a controlled amount of methanol to the anode feed. It also has the capabilities for humidifying and preheating the anode feed gases.

Test procedures

The main objective of the study is to characterize the effects of methanol slip in a PBI-based HT-PEMFC.

First, break-in conditioning of the fuel cell was performed according the BASF's recommendations before the start of characterization tests. The conditioning was performed for 100 h at 160 °C, at current density of 0.2 A/cm², and stoichiometric ratios of 1.2 and 4, on the anode and the cathode respectively. Then, Methanol reforming conversions from 90%

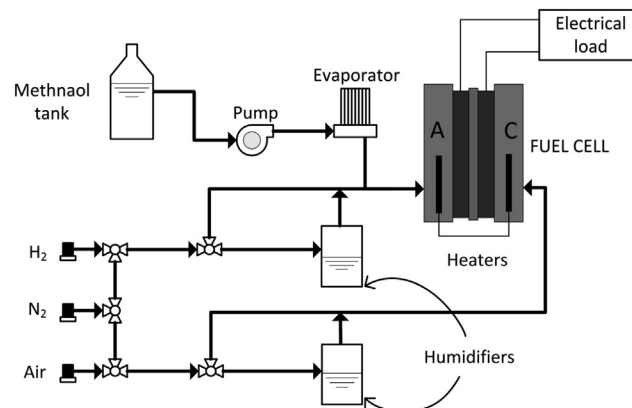


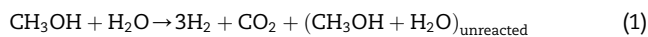
Fig. 1 – Schematic of the experimental setup.

to 100% were tested, starting from pure and dry hydrogen towards higher concentration of unconverted methanol in reformat mixture. Tests with dry hydrogen were carried out as reference for the tests in the presence of vapor mixture in the anode feed. Preheating of anode gases is also tested to see whether this affects the performance of a fuel cell.

Finally, after the performance characterization tests, an endurance test was conducted for 100 h at 160 °C. This was done to see if the effects exacerbate when the fuel cell is exposed to the methanol slip for prolonged period of time. A methanol conversion of 90%, which corresponds to 3% of methanol slip in anode feed gas, was chosen for the endurance test.

Test conditions

The following reaction was considered for the steam methanol reforming process;



where a steam to carbon (S/C) ratio of 1.5 is considered for the steam methanol reforming prior to feeding to the anode. This is an overall reaction excluding methanol decomposition and reverse water gas shift reaction, both of which give rise to CO formation. The methanol and water contents of the different conversion rates were calculated based on this overall reaction. To isolate the effects of methanol-water vapor mixture on the performance of the HT-PEMFC at varying temperatures, CO and CO₂ are not considered in the simulation of the reformat mixture in the current work.

The methanol concentrations and water vapor content of the anode feed are given in tab.1. These test points are repeated for temperatures between 140 °C and 180 °C at a temperature step of 10 °C.

Methanol was provided by means of an integrated methanol vaporizer in the test stand, and water vapor was provided as humidification by controlling the dew point of the anode gases. The dew point temperature of gaseous reactants is calculated using Magnus formula for every relative humidity corresponding to each reformer conversion ratio as follows [23];

$$\text{RH} = \frac{e}{e_s} 100 \quad (2)$$

$$e_s(T_d) = e(T) \quad (3)$$

$$e_s = C_1 \exp \left(\frac{A_1 T}{B_1 + T} \right) \quad (4)$$

where RH is the relative humidity, T is the anode feed temperature, T_d is the dew point temperature, e is the vapor pressure and e_s is the saturation vapor pressure. The coefficients' values are; A₁ = 17.625, B₁ = 243.04 °C, and C₁ = 610.94 Pa. Substituting Eq. (4) in Eq. (3) and combining with Eq. (2) gives the conversion from RH to T_d for a given temperature of gases, T.

$$T_d = \frac{B_1 \left[\ln \frac{\text{RH}}{100} + \left(\frac{A_1 T}{B_1 + T} \right) \right]}{A_1 - \ln \frac{\text{RH}}{100} - \left(\frac{A_1 T}{B_1 + T} \right)} \quad (5)$$

Data analysis

To characterize the fuel cell comprehensively, polarization curves and EIS measurements were analyzed in complementarity to each other for every test point. The polarization curves were taken between 0 and 60 A at a current ramp rate of 1 A/sec in ascending current direction.

EIS was performed between 10 kHz and 0.1 Hz in a galvanostatic mode, in which AC current was applied and voltage response was registered. The interpretation of EIS data usually requires a model, whether physical or empirical, to be fitted to the measurements. In the current work an equivalent circuit (EC) model was used to translate the trends of impedance spectra and extract physical meaning from the data. The model used is shown in Fig. 2.

Results and discussion

Performance characterization

The performance of a H₃PO₄/PBI-based HT-PEMFC is mapped against operating temperature and methanol content of the anode feed. Temperature was varied, not only to test the effects of temperature on the fuel cell performance, but also to investigate whether the effects of methanol slip vary with temperature. Temperature is known to enhance the kinetics of the reactions that take place in a fuel cell [24,13,8]. Fig. 3 shows the effects of varying the operating temperature and preheating the anode gases. It can be seen that the performance of the fuel cell increases with increase in temperature. This is intuitive and in agreement with literature, as the reaction kinetics improve with increase in temperature, giving rise to better performances [25,13].

The effects of preheating the anode feed gas on the fuel cell performance is also tested. As shown in Fig. 3 the effects are negligible. Given the fact that CO is the main impurity whose effects are highly dependent on temperature [13], it is expected that preheating of the anode feed gas would have effects in the presence of CO. However, in the current study no CO is present in the anode feed, and therefore, the performance remains unaltered when anode gases are preheated. It could also be that even in the case where the anode feed gas is not preheated, the gases heat up immediately as they come into contact with the hot end plates.

With increase in temperature the impedance spectra in Fig. 4 shrink as a sign of decreasing impedance and therefore, increasing performance. This shrinking happens throughout the measured frequency range. This means that there is enhancement in all the fuel cell activities, electrode kinetics (the high frequency region), membrane conductivity (the real-

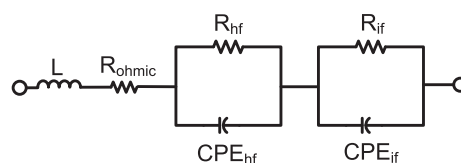


Fig. 2 – The equivalent circuit model used to fit the measured impedance spectra.

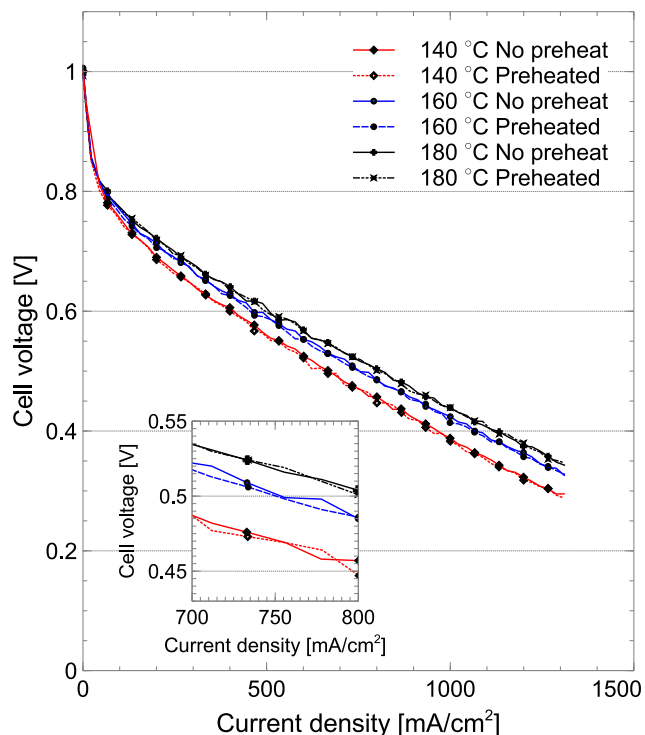


Fig. 3 – I–V curves showing the effect of varying the operating temperature and preheating the anode feed gas on the fuel cell performance.

axis intercept of the spectra) and mass transport (the low frequency region).

The increase in membrane conductivity with temperature is not linear, and there seems to be an optimal conductivity at around 160 °C. Above this temperature proton conductivity decreases for operation in dry hydrogen and remains unaltered or slightly decreases in the presence of vapor mixture of water and methanol. This is seen from the position of the real-axis intercept of the impedance spectra in Fig. 4 and the ohmic resistances in Fig. 5(a).

Fig. 5 shows both the effects of methanol slip and temperature. As already seen from the impedance spectra in Fig. 4, temperature enhances the performance at most ranges of frequency and for all concentrations of methanol. The only exceptions are the ohmic resistances above 160 °C and high frequency resistances above 170 °C for operation at 90% conversion, which increase with temperature. These suggest that temperature improves the electrode reaction kinetics and mass transport in the GDL. Xiao et al. [26] found that the conductivity of a typical phosphoric acid-doped PBI membrane made by the sol–gel process with approximately 32 mol of PA per PBI repeat unit increases with increasing temperature up to 200 °C. This is not entirely confirmed in the current work as the decrease in ohmic resistance, which is indicative of the increase in membrane conductivity, is clear only until 160 °C. Afterwards it either slightly increases or remains unaltered. It is not clear if this slight increase in ohmic resistance above 160 °C is related to phosphoric acid leaching, but it is known that the free nature of the phosphoric acid makes it volatile at higher operating temperatures, especially above 200 °C [26]. This can cause the fuel cell performance to

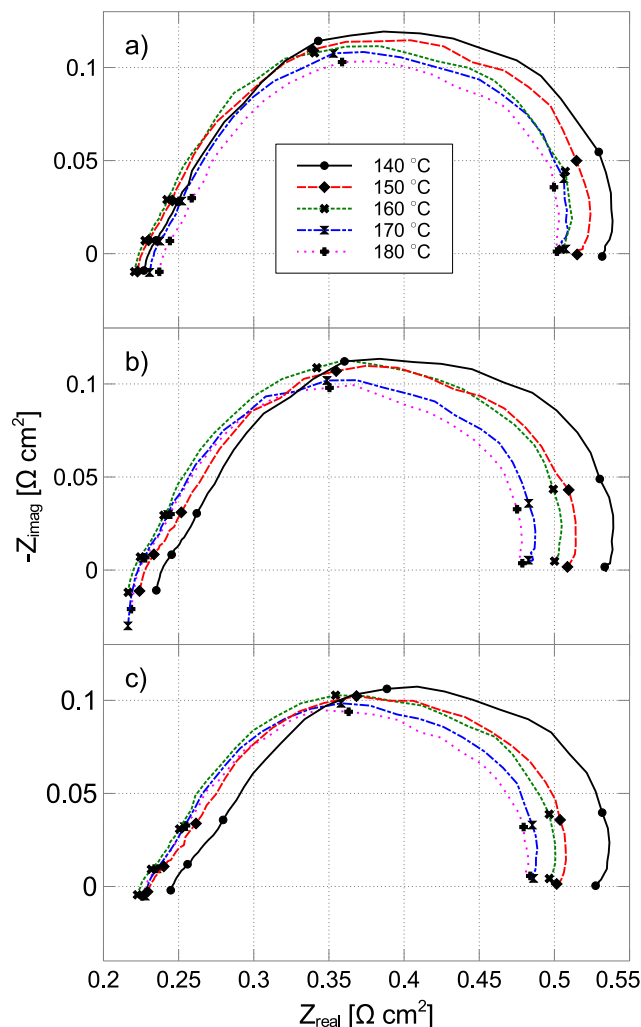


Fig. 4 – Impedance spectra showing the effects of temperature for different anode compositions a) dry and pure hydrogen b) wet hydrogen with water alone c) wet hydrogen with water and methanol with the assumption of 90% conversion of methanol.

decrease, due to the evaporation of phosphoric acid, which can lower the membrane conductivity.

To investigate the effects of methanol slip the performance mapping has been done by varying the concentration between 100% reformer conversion ratio and 90% conversion. These test points were chosen due to the trade-off in a methanol reformer between methanol conversion rate and CO formation, i.e., as reformer temperature increases, methanol conversion rate increases, and at the same time the rate of reverse water gas shift reaction increases producing more CO [27]. Kim [21] achieved a methanol conversion higher than 90% at temperature higher than 250 °C and at feed rate of methanol of 2 ml/h. At higher temperatures the conversion rate can go close to 100% [28]. Therefore, a methanol conversion range between 90% and 100% was chosen in order to investigate the effects of high concentrations of methanol slip, since the trade-off suggests that higher methanol slip corresponds to lower CO concentration, which is a known poison to PEM fuel cells.

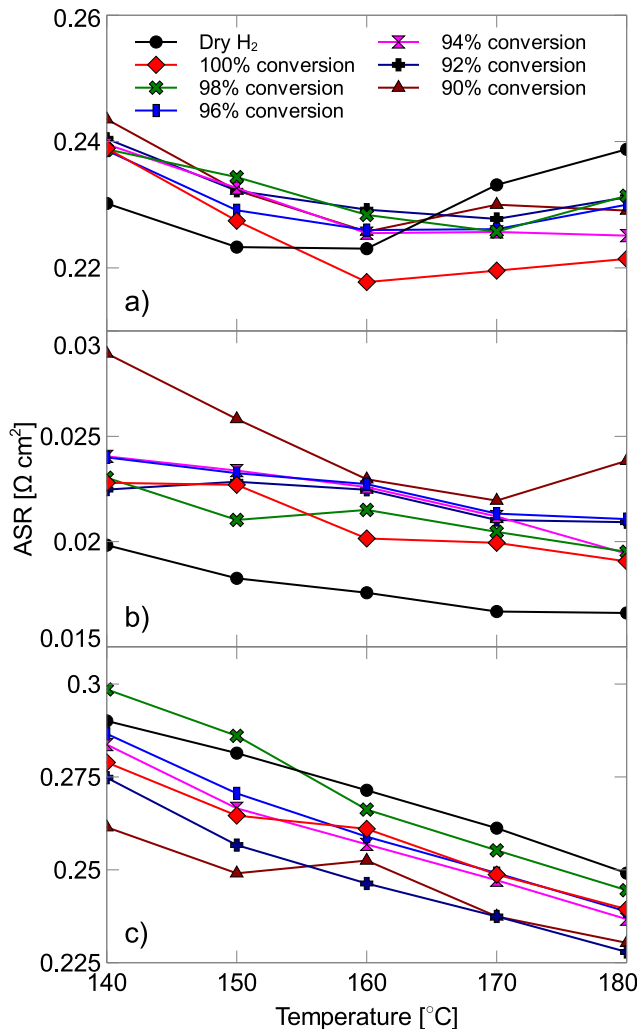


Fig. 5 – Fitted resistances for varying temperatures and anode compositions a) ohmic resistances b) high frequency resistances c) intermediate-low frequency resistances.

The results reveal that the effects of methanol on the overall performance of the fuel cell are negligible at all the tested concentrations. This can be noticed in the polarization curves in Fig. 6, where the different methanol concentrations are shown at 160 °C. The effects remain unaltered for the entire range of methanol conversion rates tested. A slight decrease in performance is seen when water vapor is added with respect to dry hydrogen operation. This decrease in performance corresponds to the decrease in hydrogen flow rate with decrease in conversion rate given in Table 1, especially from test point 1 to 2. Other studies state that the proton conductivity of PBI increases with increase in relative humidity, which suggests that if water vapor was added without decreasing the hydrogen flow rate, the performance would increase due to enhanced proton conductivity [29,12,30]. However, it is also stated that water produced from the electrochemical reaction at the cathode is capable of hydrating the polymeric material and promoting the cell performance, without the need for humidification [30].

The generally little or no effects of methanol-water vapor mixture are also confirmed from the impedance spectra in

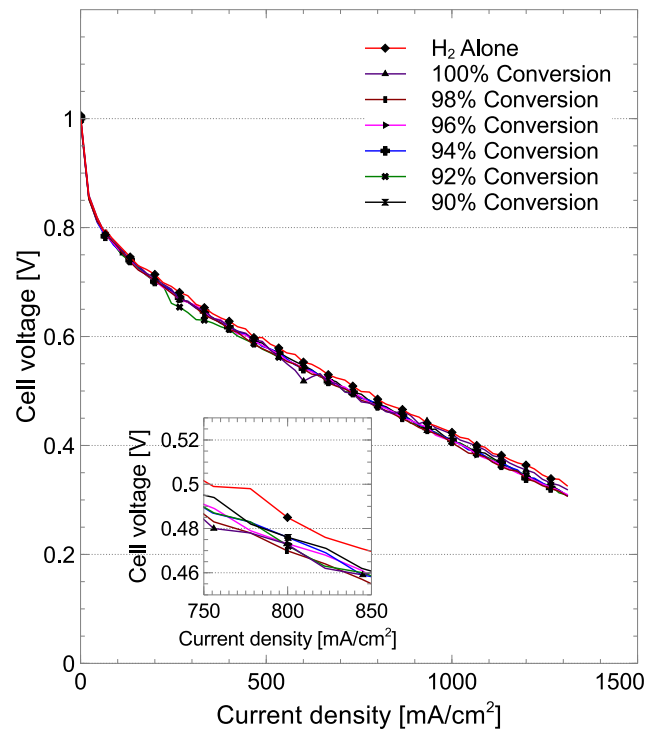


Fig. 6 – I–V curves showing the effects of methanol slip at different simulated reforming conversion rates at 160 °C. The percentage values represent the conversion of methanol considered.

Fig. 7. They show similar spectra for all measurements in the presence of methanol, from 98% to 90% methanol conversion, and similar spectra for the ones without methanol slip. These impedance spectra were recorded at 160 °C. The real-axis intercepts of the spectra, which denote the ohmic resistance of the fuel cell, move to the left in the case of 100% conversion. In this case the anode feed is composed of hydrogen and water vapor, and the shift towards left of the intercept may be attributed to the humidification of the membrane.

A closer look into the spectra by means of equivalent circuit fitting reveals more details and small changes due to methanol slip. The first observable change happens when water alone is added to the anode feed gas, as a simulation of 100% conversion ratio of a reformer running at S/C of 1.5. This corresponds to the addition of 14.29% by volume of water vapor and the decrease of hydrogen concentration by the same percentage by volume in the anode feed. There is an increase in ohmic resistance from dry hydrogen to 100% conversion at 140 °C and 150 °C, which can be attributed to decrease in hydrogen flow rate. Above 160 °C the ohmic resistances increase slightly for reformat operating conditions, but it does so more significantly for dry hydrogen operation. This could be due to the drying of the membrane in the case of dry hydrogen operation. In reformat operation on the other hand the presence of water vapor in the mixture keeps the membrane hydrated. The lowest ohmic resistances are achieved for 100% conversion at 160 °C, i.e., humidified hydrogen feed. Here the negative effect of reduced hydrogen concentration is overwhelmed by the positive effect of membrane humidification. At temperatures above 170 °C, the presence of

Table 1 – Operating parameters for tests between 140 °C and 180 °C at a temperature step of 10 °C.

Exp. id	Conversion	H ₂	H ₂	CH ₃ OH	H ₂ O
	[%]	[NLPM]	[% Volume]	[% Volume]	[% Volume]
1	H ₂ (20 °C)	0.124	100	0	0
2	H ₂ (140 °C)	0.124	100	0	0
3	100	0.106	85.71	0	14.29
4	98	0.105	84.48	0.57	14.94
5	96	0.103	83.24	1.16	15.61
6	94	0.102	81.98	1.74	16.28
7	92	0.100	80.70	2.34	17.65
8	90	0.098	79.41	2.94	19.96

methanol-water vapor mixture seems to prevent the membrane from drying out. However, the slightly higher resistances in the presence of methanol compared to water alone suggest that methanol vapor has slight negative effect on the ohmic resistances, and therefore, the membrane conductivity.

The high frequency resistances increase with increase in methanol slip, Fig. 5(b). This could be due to dehydrogenation process that methanol undergoes on platinum surface that can also lead to CO formation and therefore, can affect the electrode kinetics negatively [18]. In Fig. 5(b) it can be noticed that there is a significant increase in the resistances between dry H₂ and 100% conversion and then the increase slows with the addition of methanol. It can be said that the vapor mixture of methanol and water has generally negative effect on this frequency range. However, further isolation of the effects of methanol is required to have a more conclusive remarks on its effects. This frequency range is representative of the anodic processes, and therefore, the negative effect could be due to the dilution of the anode feed with the addition of the vapor mixture and the decrease of hydrogen flow rate. The complex reactions methanol is said to undergo on Pt surface could also play a role in these losses [18,31].

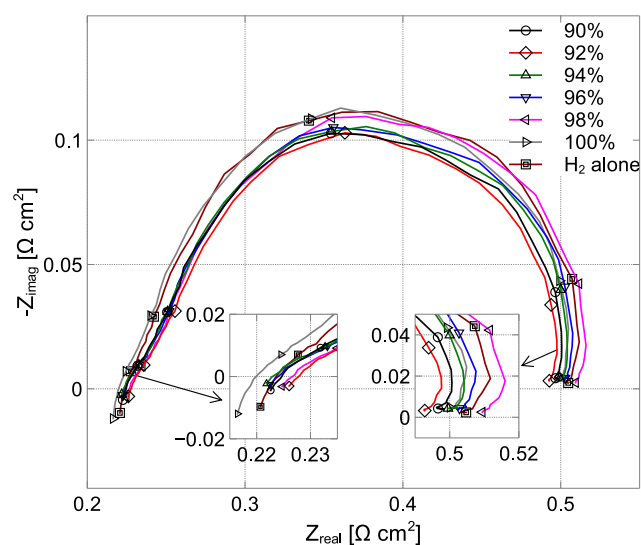


Fig. 7 – Impedance spectra showing the effects of methanol slip at different simulated reforming conversion rates at 160 °C. The percentage values represent the conversion of methanol considered.

Low frequency resistances have decreasing trend both with increase in temperature and methanol slip. The resistances at this frequency range are the highest at 98% conversion ratio. Contrary to the general trend, this conversion ratio also shows higher resistance compared to 100% conversion ratio. This could suggest that methanol has a slightly negative effect on the phenomena represented in this frequency range, the cathodic activities and the diffusion limitations. However, these negative effects are masked for the rest of the conversions by the positive effects of humidification as both methanol and water contents in the anode feed increase.

Overall, the effect of methanol-water vapor mixture on performance is negligible for the measured concentrations. This is mainly because the dilution and degrading effects seen at high frequency range for anodic activities are balanced out by the enhanced mass transport due to the vapor mixture.

Furthermore, the generally parallel resistance lines in Fig. 5 with few exceptions at high temperature show that the effects of methanol do not depend on the operating temperature. An exception is seen in Fig. 5(b) at 90% conversion ratio, in both ends of the temperature range. This shows that at such low reformer conversion rates, it is best to operate the fuel cell at the typical operating temperatures of 160 °C and 170 °C. This also suggests that at low fuel cell operating temperature, low reformer conversion can have negative effects on the anode kinetics.

Endurance test

After the performance characterization tests, an endurance test was conducted in the presence of methanol in the anode feed. The fuel cell was operated at constant current density of 0.33 A/cm² at constant temperature of 160 °C and hydrogen and air stoichiometry of 1.2 and 4, respectively. A simulated reformat of 90% conversion, was used for the anode feed composition.

The voltage profile in Fig. 8 shows how the cell potential changes during the 100 h of endurance test. For the chosen operating conditions the overall degradation rate is $-55 \mu\text{V/h}$. This is ten times the reported degradation rate of a Celtec MEA, at constant current density of 0.2 A/cm² at 160 °C and using dry gases over 18,000 h of operation [22]. On the other hand Hu et al. [32] found a higher degradation rate of $-150 \mu\text{V/h}$ over 400 h of operation following 100 h of conditioning at constant load of 0.64 A/cm² at 150 °C for their home-made unit

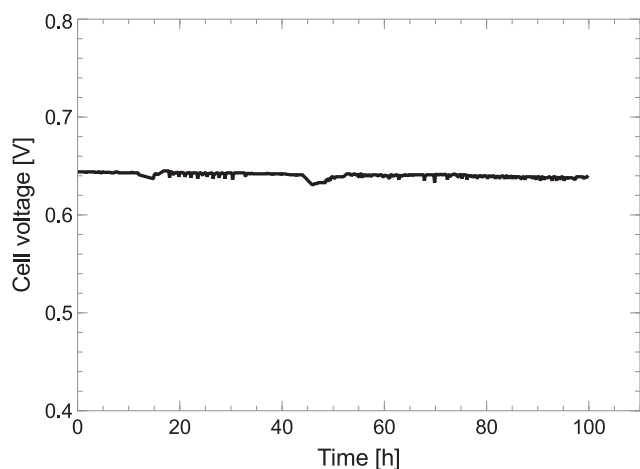


Fig. 8 – Durability tests in the presence of methanol at 160 °C.

cell assembly. Other degradation rates at similar conditions as the current work but pure hydrogen operation include, Modestov et al. [33] and Galbiati et al. [34] at 0.2 A/cm² at 160 °C, with degradation rates of $-25 \mu\text{V/h}$ and $-10 \mu\text{V/h}$, respectively. The difference in degradation rates may be attributed, other than the different operating conditions, also to the different MEA manufacturing and doping processes. Some test bench specific factors, such as the techniques used to assemble the fuel cell and the balance of plant of the fuel cell system may also affect the operation of the fuel cell, and therefore, the degradation rate. In general, it can be said that the degradation rates in this work are above the average of pure hydrogen operations in literature, implying that part of the degradation may be caused by the presence of the reformate vapor.

However, negligible effect on performance and not significant degradation on endurance tests mean simpler fuel cell and reformer design, and overall simpler system integration. There is increasing interest in using renewable methanol as a viable hydrogen carrier as it offers higher energy density, and is more economical compared to pure hydrogen. This has led some to consider internal reforming of methanol in fuel cells or coupling methanol reformers and fuel cells in compact systems [11,8]. The results of the current work suggest that such a reformer can be run at conversion rates as low as 90%, with negligible effects on the performance of the fuel cell and no significant degradation up to 100 h. This means it can be run at temperatures comparable to that of the fuel cell and produce lower CO concentrations.

Conclusions

The effects of methanol-water vapor mixture at different concentrations and varying operating temperatures on the performance of PBI-based HT-PEMFC were studied. Endurance test was also performed for 100 h at 90% conversion.

The overall effects of methanol-water vapor mixture on the performance are negligible at all the measured vapor concentrations. However, from the impedance measurements it is

found that the vapor mixture has negative effects on the high frequency region and positive effects on the low frequency region. Therefore, the membrane conductivity and the electrode activities are slightly degraded, whereas the mass transport losses are slightly reduced. This results in an overall balancing of positive and negative effects on the fuel cell performance.

An overall degradation of $-55 \mu\text{V/h}$ over a 100 h of endurance tests at 90% conversion was registered. This is above the average degradation rate for pure hydrogen operations in literature, implying that part of the degradation may be caused by the presence of the reformate vapor.

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