



Study of the catalytic layer in Polybenzimidazole-based High Temperature PEMFC: Effect of Platinum content on the carbon support

Justo Lobato, Pablo Cañizares, Manuel A Rodrigo, Jose J Linares, Diego Ubeda, Francisco J Pinar

► To cite this version:

Justo Lobato, Pablo Cañizares, Manuel A Rodrigo, Jose J Linares, Diego Ubeda, et al.. Study of the catalytic layer in Polybenzimidazole-based High Temperature PEMFC: Effect of Platinum content on the carbon support. *Fuel Cells*, 2010, 10 (2), pp.312. 10.1002/fuce.200900088 . hal-00552355

HAL Id: hal-00552355

<https://hal.science/hal-00552355>

Submitted on 6 Jan 2011

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Study of the catalytic layer in Polybenzimidazole-based High Temperature PEMFC: Effect of Platinum content on the carbon support



Journal:	<i>Fuel Cells</i>
Manuscript ID:	fuca.200900088.R2
Wiley - Manuscript type:	Original Research Paper
Date Submitted by the Author:	23-Dec-2009
Complete List of Authors:	LOBATO, JUSTO; University of Castilla-La Mancha, Chemical Engineering Department Cañizares, Pablo; University of Castilla-La Mancha, Chemical Engineering Rodrigo, Manuel; University of Castilla-La Mancha, Chemical Engineering Linares, Jose; University of Castilla-La Mancha, Chemical Engineering Ubeda, Diego; University of Castilla-La Mancha, Chemical Engineering Pinar, Francisco; University of Castilla-La Mancha, Chemical Engineering
Keywords:	Catalyst Layer, High Temperature, PBI, Pt/Vulcan Catalyst, Electrochemical Surface Area (ESA)



**Study of the catalytic layer in Polybenzimidazole-based High Temperature
PEMFC: Effect of Platinum content on the carbon support.**

Justo Lobato*, Pablo Cañizares, Manuel A, Rodrigo, José J. Linares, Diego Úbeda and
F. Javier. Pinar.

*Chemical Engineering Department, University of Castilla-La Mancha, Av. Camilo Jose
Cela, n 12. 13071, Ciudad Real (Spain).*

* Corresponding author: Phone: +34 926 29 53 00 Ext. 3418. Fax: +34 926 29 52 56.
Email: Justo.Lobato@uclm.es

ABSTRACT

In this work, the effect of platinum percentage on the carbon support of commercial catalyst for electrodes to be used in a Polybenzimidazole (PBI)-based PEMFC has been studied. Three percentages were studied (20 %, 40 % and 60 %). In all cases, the same quantity of PBI in the catalyst layer was added, which is required as a “binder”. From Hg porosimetry analyses, pore size distribution, porosity, mean pore size, and tortuosity of all electrodes were obtained. An increase in the amount of mesopores the lower is the platinum percentage in the catalytic layer, which reduced the overall porosity, the mean pore size, and increased the tortuosity. The electrochemical characterization was performed by voltamperometric studies, assessing the effective electrochemical surface area of the electrodes, by impedance spectroscopy (IS), determining the polarization resistance, and by the corresponding fuel cell measurements. The best results were obtained for the electrodes with a content of 40 % Pt on carbon, as a result of an adequate combination of catalytic activity and mass transfer characteristics of the electrode. It has been demonstrated that the temperature favours the fuel cell performance, and the humidification does not have remarkable effects on the performance of a PBI-based PEMFC.

1 Introduction

In recent years, there has been an intense research interest in the development of high temperature ($> 120^{\circ}\text{C}$) polymer electrolyte membrane fuel cells (HT-PEMFC's). This is due to the numerous advantages of a PEMFC technology operating above 100°C : kinetics of both electrode reactions are enhanced [1, 2], no need for humidification [3], tolerance of the Pt/C electrodes to carbon monoxide is increased (when a fuel cell is operated at 200°C , even 1 % CO in the reformat gas does not deteriorate the fuel cell performance), and the integration of a PEMFC with a methanol reformer is more simple [4]. Three different types of membranes are being investigated for operating at temperature higher than 100°C : modified perfluorosulphonated membranes, alternative sulphonated polymers and their composite, and finally acid-base polymer membranes [1, 5].

The poly[2,2-(m-phenylene)-5,5-bibenzimidazole] (named commonly polybenzimidazole, PBI) is a serious candidate for being used in HT-PEMFCs because of its low-cost and high operational temperature. The key for the proton conduction in polybenzimidazole-based membranes is their impregnation with an acid [6-10]. PBI membranes doped with phosphoric acid are able to work at temperatures up to 200°C . Our group has been working on the synthesis of membranes for their use in PBI-based HT-PEMFC's during the recent years [5, 8-11].

As it is well known, the membrane-electrode-assembly is the heart of a fuel cell. This consists of several elements susceptible of being studied for the optimization of a fuel cell performance. One of them is the catalyst layer, where the electrochemical reactions

1 take place in it, and whose formulation must be optimized in order to improve the
2 performance of the PEMFC's [6, 12]. To catalyse the reactions that take place on the
3 PEMFC, platinum is the most active noble metal. It is the catalyst surface area that
4 matters, not the weight, so it is important to have small platinum particles with large
5 surface area finely dispersed on the catalyst support surface, typically carbon powders.
6 In the last years, the great price of platinum and limited availability promote platinum
7 alloys with other metals, e.g. Pt-Ru, Pt-Sn, Pt-Cr, to decrease the platinum loading on
8 the catalyst layer, or a better distribution of the platinum added. However, performances
9 of these alloys are lower than those obtained with pure platinum for hydrogen oxidation
10 [13, 14]. Other alternative is the use of different catalyst deposition techniques to
11 decrease the catalyst loading on the electrodes [15]. Another element of the catalyst
12 layer is the polymeric "binder". This acts like a link between the catalyst particles,
13 avoids the agglomeration of catalyst particles, and favours the formation of the three
14 boundary surface if protons can travel along it, enhancing the activity of the catalyst
15 active sites, so that the own polymer electrolyte is normally used as "binder" [16-18].

16
17 In order to optimize the composition of the catalyst layer, the influence of Pt percentage
18 on the carbon support on a PBI-based High Temperature PEMFC has been studied in
19 this work. Thus, electrodes with different platinum percentage on the carbon support,
20 and with the same PBI content, normalized with respect to the C/PBI weight ratio
21 (C/PBI = 20) (optimized in previous work [19]) were prepared. The electrodes were
22 characterized by Hg-porosimetry, and by different electrochemical techniques: cyclic
23 voltammetry, polarization curves and impedance spectroscopy.

Moreover, to study the effect of temperature and feed stream humidification, some tests in a 5 cm² single cell were also carried out at different cell temperatures, and humidifier temperatures (keeping the cell temperature constant), using the optimum amount of platinum under usual operation conditions.

2. Experimental

2.1. Preparation of the membrane-electrode-assemblies

On top of a gas diffusion media (Toray Graphite Paper, TGPH-120, 350 μm thick, 10% wet-proofing, BASF Fuel Cell, Inc.), a microporous layer (MPL) was deposited by N₂-spraying, consisting of 2 mg/cm² Vulcan XC-72R Carbon Black (Cabot Corp.) and 10% PTFE (TeflonTM Emulsion Solution, Electrochem Inc.). Next, the catalytic layer was also deposited by N₂-spraying, composed of Pt/C catalyst (20, 40 and 60 % Pt on Vulcan XC-72R Carbon Black, ETEK-Inc.), PBI ionomer (3.7 wt. % PBI in *N,N*-dimethylacetamide, DMAc), and DMAc as solvent. In order to improve the N₂-spray process to avoid the electrodes flooding, the electrodes were heated at 60 and 90 °C for spray the microporous and catalyst layer respectively. In all cases, the Pt loading on both electrodes was 0.5 mg Pt/cm², a C/PBI weight ratio of 20 was used, electrode area was 5 cm², the DMAc volume added as ink solvent was 25 ml, and the platinum loading was controlled by the electrode weight increase. Once deposited all the layers, the electrodes were dried at 190 °C for 2 hours. Afterwards, the electrodes were wetted with a solution of 10% H₃PO₄, and left to absorb the acid for one day. The electrodes prepared were divided into four pieces. Two of them were used to prepare the membrane-electrode-assembly (MEA), whereas the other two were used for the structural studies [11].

For the preparation of the MEA, a PBI membrane was taken out from a 75 wt. % phosphoric acid bath. Doping level acquired by the membrane was 6.6 molecules of acid per polymer repeating unit. The superficial acid onto the membrane was thoroughly wiped off with filter paper, and subsequently, it was used to prepare the MEA. The doped membrane was sandwiched between two electrodes, hot-pressing the whole system at 150 °C and 100 kg/cm² for 15 min. Once the MEA was ready, it was inserted into the cell.

2.2. Structural Characterization

Hg-porosimetry analyses were performed on a Micromeritics AutoPore IV 9500 and the electrode pore size distribution was obtained.

2.3. Fuel Cell Tests

Cell hardware consisted of two bipolar plates made of graphite (Sofacel, Spain), into which it was machined channels with parallel geometry. Within the graphite plates, heating rods were fitted in order to heat the fuel cell up. During the measurements, the fuel cell was fed with pure hydrogen and oxygen, at a 0.134 l/min for H₂, and 0.076 and 0.4 l/min for O₂ and air, respectively, at atmospheric pressure. Temperature was controlled with the aid of a temperature controller (CAL 3300, Cal Controls Ltd., U.K) [11, 20].

The procedure to perform polarization curves and impedance spectra can be depicted as follows. Firstly, the fuel cell was kept at constant temperature (125°C) for 24 h, monitoring the cell voltage at a constant current density of 0.215 A/cm², with a potentiostat/galvanostat Autolab PGSTAT30 (Ecochemie, The Netherlands).

Measurement of the effective electrode electrochemical surface area (ESA) was carried out by cyclic voltammetry (CV), using humidified N₂ (200 ml/min) through the cathode (working electrode), and humidified H₂ (134 ml/min) through the anode (counter/reference electrode), at room temperature. The effective electrochemical surface area, ESA (m²/g Pt), is given by the following formula:

$$ESA = \frac{A_{Pt}}{\nu C L_e} \quad (1)$$

The parameter A_{Pt} (A·V/cm²) is the area under the hydrogen desorption peak obtained by the CV measurements, ν (V/s) is the sweep rate, 20 mV/s, C represents the charge required to reduce a monolayer of protons on active platinum, 0.21 mC/cm², and L_e (0.5 mg Pt/cm²) is the platinum load in the catalyst layer.

Fuel cell studies were carried out in the cell at 125°C. 20% Pt/C was selected in the electrode that was not optimized, i.e., it was selected as reference electrode for all measurements, in order to compare with the results obtained for the electrode under optimisation (20, 40, and 60 % Pt/C). Impedance Spectra (IS) were performed at a potential of 0.6 V, running O₂ or air through the cathode (working electrode), and H₂ in the anode (counter/reference electrode), under the fuel cell conditions. Frequency ranged from 10 kHz down to 100 mHz, with a potential wave of 10 mV rms [5].

The temperature effect on fuel cell performance was analysed by increasing the cell temperature in the uprising sequence 125, 150, 175 and 200 °C (398, 423, 448, and 473 K, respectively). For the study of the humidification, either the oxidant or the fuel streams were humidified, by bubbling them through hot water chambers. The temperatures of the water chambers in this study were 50 and 90°C.

3. Results and discussion

3.1. Pore size distribution of the electrodes

The results obtained for the pore size distribution by Hg-porosimetry for the three electrodes are shown in Figure 1. Only the pores ranging between 7 to 1000 nm has been scaled, since pores larger than this size are related to the macroporous carbon support [21,22]. In this range, porosity is due to the microporous and catalytic layer [23].

Micropores are defined as pores of less than 2 nm, being from 2 to 100 nm the size of mesopores. It can be seen that the majority of pore ranges from 50 to 120 nm, which indicates the existence of a marked mesoporosity in the catalytic/microporous layer independently of the Pt content on the carbon support. This corresponds with the space between the particles that form the catalyst, i.e., between the carbon particles [23, 24]. Logically, the lower the platinum percentage (higher carbon content), the larger amount of mesopores that are present in the electrode.

Figure 1

Table 1 collects the values of the overall porosity, tortuosity, and mean pore size of the three electrodes. Before analyzing these results, it is important to point out that the higher the platinum percentage in the catalyst layer (the lower the carbon content), the thinner the catalyst, and therefore, the preponderance of the macroporous carbon support becomes larger. This explains the increase in the overall porosity of the sample,

and in the mean pore size as the platinum percentage increases. On the other hand, a thinner catalyst makes the transport of any fluid less tortuous.

Table 1

3.2. Effective Electrochemical surface area

The ESA of electrodes prepared with different Pt content catalyst was evaluated by cyclic voltammetry measurements, from the hydrogen desorption peaks of the voltamograms (not shown). Table 1 collects the different ESA values obtained for the different electrodes prepared. It can be observed that as the platinum percentage increases, the ESA decreases. The higher the platinum percentage in the catalyst, the larger the platinum particle size becomes (see Table 1), resulting in a lower catalyst surface area. This could explain the decrease in the ESA. Values of the catalyst utilisation are also shown in Table 1. The catalyst utilisation slightly increases as the platinum percentages also does. Despite this slight larger utilisation, the absolute values of the ESA lower. On the other hand, the similarities in the values of the catalyst utilisation may be an indication of a similar distribution of all the elements that form the catalytic layer (platinum, carbon, PBI, and phosphoric acid) independently of the platinum percentage of the catalytic layer. Prasanna et al. [25] and Ralph and Hogarth [26] observed the same behaviour of the electrochemical active surface as the platinum percentage in the catalyst increases.

3.3. Influence of the platinum percentage in the cathode catalyst on the cell performance

Figure 2a shows the polarization curves carried out with cathode prepared with different Pt percentages on carbon support when oxygen was used as comburent. In the anode, it was used in the catalyst layer a 20 % of platinum on carbon support, and the same PBI

content than in the cathode (C/PBI=20). Slight fuel cell performance improvement was obtained when the platinum percentage in the catalyst was increased from 20 to 40 %. This could be due to the reduction in the catalytic layer thickness, facilitating the access of reactant gases towards the catalyst active sites. Electrode thickness can be assumed proportional to carbon loading, since most of the catalytic layer thickness comes from the carbon support, which, in this range of platinum percentage in the catalyst, is not far from reality [18]. The carbon loading for each electrode was: 2, 0.75 and 0.33 mg C/cm² for 20, 40 and 60 % Pt/C respectively. An estimation of the catalytic layer thickness is collected in Table 1, calculated from the carbon loading, the density of the Vulcan XC-72R carbon black (6 lbs/ft³), and the BET surface area (250 m²/g) [27], assuming a spherical geometry of the carbon particles. A lower catalyst layer thickness is expected to lead to a reduction in the mass transport limitations. Another reason that may lead to the slight improvement of the fuel cell results for the 40% Pt/C catalyst is the observation mentioned by Kongstein et al. [28]. They observed that a mixed catalytic layer, with a combination of a 50% Pt/C catalyst in the proximities of the interface electrode-membrane, and a 20% Pt/C in the zone close to the gas diffusion layer, performed the best. The use of the 40% Pt/C might be a “similar approach” (despite its lower ESA), as it lies between the two previous values, larger concentration of platinum sites than 20% Pt/C in the membrane-electrode interface, and a lower concentration of the catalyst in the proximities of the gas diffusion layer. According to Seland et al [18], the Pt active sites in contact with the membrane are the zones where the higher weight of the electrochemical reactions takes place.

Figure 2

By contrast, the 60% Pt/C electrode shows the lowest performance. This can be explained in terms of the lower ESA of the electrodes, and, in consequence, the lower electrochemical activity of the electrode. This result resembles with that of Paganin et al. [29], who also observed the performance deteriorated as the Pt/C ratio was increased beyond 40 % for a low temperature PEMFC.

When air was employed as comburent (Figure 2b), it was observed a similar behaviour of the system. Thus, the same reasons exposed above may be used to explain the fuel cell performance when air is the comburent, though in this case, the decrease on fuel cell performance at high current densities between the samples with 20 % and 40 % on platinum percentage in the catalyst layer is higher. The use of air may emphasize the effect of a thicker catalytic layer, enlarging the differences between these two platinum percentages.

Table 1 collects the values of the Tafel slopes of the different polarization curves in order to compare each electrode performance, after fitting the experimental cell voltage (E) data to the semi-empirical equation $E = E_0 - b \cdot \log(j) - R \cdot j$, where E_0 is the open circuit voltage, b is the Tafel slope, related to the electrode performance when the rate-limiting step is the electrocatalytic reaction, R is the slope of the linear region of the polarization curves (related to the ohmic resistance of the system, but also can contain small contributions coming from linear mass transport limitations, and from the polarization resistance of the hydrogen oxidation reaction [30]), and j is the current density. As it can be seen, the lowest Tafel slope is obtained, both in the case of oxygen, and air, for the electrode prepared with a catalyst 40% Pt/C, showing the best efficiency of this electrode for the electrochemical reactions.

A simple way to evaluate the oxygen transport across the electrodes, and therefore the mass transfer is through the oxygen gain parameter [31, 32], quantifiable by the Equation 2.

$$\Delta V(O_2/Air) = V_{O_2}(i) - V_{Air}(i) \quad (2)$$

The parameter $\Delta V(O_2/Air)$ is the oxygen gain, $V_{O_2}(i)$ represents the cell potential for a current density when oxygen was used as comburent, and $V_{Air}(i)$ is the potential when air was used as comburent at the same current density. Thus, better oxygen access to the catalyst active sites is obtained for small values of the oxygen gain at high current densities. Figure 3 shows the values obtained for the oxygen gain.

Figure 3

It can be observed that the cathode with a catalyst layer with a 20 % of platinum on the carbon support has the largest oxygen gain at high current densities, which indicates a limited oxygen transport due to the highest thickness of this electrode. The 60 % Pt/C on catalyst layer sample has a similar oxygen gain than 40 % Pt/C sample, despite lower values may be expected. As Prasanna et al.[25] mentioned, this result implies that the expected decrease in the mass transport limitations can not balance the lower ESA, which enlarges its influence when air is used.

In order to further support the fuel cell results, Nyquist plots of the different electrodes, for both oxygen, and air, are displayed in Figure 4, under the same fuel cell performance conditions. A very good approach to evaluate the suitability of a catalytic layer is by polarization resistance obtained from impedance spectroscopy, since this is composed

by the charge transfer (linked to the kinetic of the electrochemical reaction), and the mass transport processes that take place in the catalyst layer [33, 34] (through the agglomerate of catalyst particle, and within the agglomerate, especially through the thin-film of electrolyte surrounding the catalyst sites [11, 35]). Table 1 also shows the polarization resistances, after fitting the experimental data to the equivalent circuit showed in Figure 4a, described elsewhere [19].

Figure 4

As in the case of the Tafel slope, the lowest polarization resistance is achieved for the 40% Pt/C catalyst, indicating that this percentage of platinum gives the best combination of catalytic activity, and mass transfer characteristic within the catalytic layer, leading to the best fuel cell performance. In the case of the 20% Pt/C, despite the larger ESA, the thicker catalytic layer seems to impair the reactive gases access, and the exit of the water vapour produced, resulting in a slight increase of the polarization resistance. In the case of the 60% Pt/C catalyst, the polarization resistance notably increases, which is attributed to the reduction in the ESA. Similarly to the oxygen gain, the reduced catalytic activity of this electrode seems to depress the performance of this electrode, in spite of the higher concentration of active sites in the interface of the electrode-membrane, and the reduced thickness of the electrode.

3.3. Influence of the platinum percentage in the anode catalyst on the cell performance

A similar study was carried out in the anode side. Figure 5 shows the polarization and power density curves of the different anodes prepared. As in the study of the cathode, the highest performance was reached by the anode electrode prepared with a 40 % platinum percentage on the catalyst, although the difference between anode samples are

lower than between cathode samples. This behaviour is explained taking into account that the oxygen reduction reaction mostly controls the performance in this kind of PEM fuel cells [36]. Notwithstanding, contrary to perfluorosulphonated electrolyte-based PEMFCs, due to the low hydrogen permeability of phosphoric acid-doped PBI and more sluggish hydrogen oxidation kinetic [18], the anode can not be considered negligible as it occurs in Nafion[®]-based PEM fuel cells [37]. Nevertheless, in order to explain fuel cell performance with the different platinum percentages in the anode, it can be used the same reason as in the case of the influence of the platinum percentage on the cathode. The adequate combination of catalytic activity and mass transfer characteristics of the electrode for the 40% Pt/C account for the best performance of the cell when this anode is used.

Figure 5

3.5. Temperature and humidification fuel cell test

A brief study of some operation variables was done to analyze the fuel cell performance. Thus, fuel cell temperature, and cathode-anode humidification were studied. Taking into account the previous results, both electrodes were prepared with catalyst that contained 40 % of platinum on the Vulcan XC-72R carbon black support.

Figure 6 shows the temperature effect on the fuel cell performance. In this figure the temperature was expressed in thermodynamic temperature, in other words, in Kelvin for the analyses of the effect of the temperature. An increase in temperature improves fuel cell performance due to both the enhancement of the kinetics and diffusion processes, and the increase of electrolyte conductivity [1, 8, 18, 28, 38]. On the other hand, it can be observed that the enhancement on fuel cell performance is lower when temperature

was increased. In order to help to interpret the results, the experimental data were fitted to the semi-empirical model proposed previously to estimate the Tafel slopes. The values of each parameter are collected in Table 2. In order to further evaluate the catalytic activity, the exchange current density is also calculated from E_0 , by applying the following expression: $E_0 = E_r + b \cdot \log j_0$, where E_r is the thermodynamic open circuit voltage, and j_0 is the exchange current density, related to the reaction rate of the oxygen reduction reaction [39].

Table 2

In Table 2, it can be seen that the exchange current density increases with the temperature. This is due to the intrinsic enhancement of the electrocatalytic activity with the temperature. In the case of the Tafel slope, the minimum value is achieved at 150°C, increasing at higher temperatures. In order to understand this behaviour, it will be firstly analyzed the behaviour of the slope of the linear region of the polarization curves (R), mostly dependant on the electrolyte conductivity [2]. The higher the temperature, the lower is R , due to the increase of the H₃PO₄ doped PBI membranes conductivity with the temperature [11, 20]. However, this increase slows down with the temperature. In the conductivity measurements performed to H₃PO₄ doped PBI membranes, in some cases [5], it has been reported that this decreases above 423 K when the measurements were carried out under very low humid conditions, due to the self-dehydration of the phosphoric acid, leading to the formation of the less conductive species pyrophosphoric acid. Therefore, the lower increase in R the higher the temperature could be explained in terms of the more intense self-dehydration phenomenon of the phosphoric acid (especially taking into account that the measurements were carried out from 398 to 473 K), which offsets the intrinsic increase of the electrolyte conductivity with the

temperature. The electrolyte is also an active element in the electrode, since it transports the protons within the catalytic layer. Therefore, the slight increase in the Tafel slope with the temperature may be due to the own self-dehydration of the electrolyte contained in the electrode, which does not result beneficial for the electrode performance, despite the increase of the intrinsic catalytic activity with the temperature.

Figure 6

Figure 7 shows fuel cell performance when the cathode (Fig. 7a), and the anode (Fig. 7b) feed streams, were humidified at two different temperatures. The humidifier temperatures chosen for this study were 50 and 90°C.

Figure 7

The results obtained in this study are quite interesting. On the one hand, it can be observed that humidifying the cathode hardly affects the cell performance. Nevertheless, an increase in the humidity enhances the proton electrolyte conductivity [1, 5, 8, 35], and so does the oxygen solubility of PBI, which is strongly beneficial for the diffusion of reactant gases to active sites [40]. This should lead to an enhancement of the cell performance. However, the oxygen partial pressure drop that takes place when feed streams are humidified, in addition to the water vapour generated on cathode, may create a water vapour partial pressure in excess, reducing the oxygen partial pressure, and hence, increasing the mass transport limitations and offsetting the expected performance enhance.

In the case of the cathode, the effect of the humidification is more beneficial. This can be explained taking into account that the anode works under completely dry conditions,

and therefore, the presence of water vapour benefits its performance due to the increase of the electrolyte conductivity, and also to the expected increase in the solubility of hydrogen in the PBI. Nevertheless, when the temperature of the humidifier increases from 50 to 90°C, the cell performance almost keeps constant. Again, if the level of humidification is too high, the partial pressure of the reactant drops too much, offsetting the beneficial effects of a higher degree of humidification in the membrane-electrode-assembly.

These results show that in the case of PBI-based high temperature PEMFC, the pressurization to enable the increase of the operational temperature, and the pre-humidification of the reactant streams, is not be required, making the system simpler and cost-saving.

4. Conclusions

In this work, electrodes with different Pt percentage on the carbon support (20, 40, and 60%) were prepared, physicochemical and electrochemically characterized, and their performance in an actual single fuel cell was tested.

Pore size distribution measurements seemed to preliminarily postulate the 60% Pt/C as the most suitable catalyst in terms of mass transfer characteristics. On the other hand, as the Pt content on carbon support increased, the ESA decreased, so that 20% Pt/C seemed to be the most active catalyst. Actual fuel cell test revealed that the optimum Pt content on the carbon support was 40% Pt/C for both electrodes, as a result of the

1 combination of a suitable catalytic activity, and mass transfer characteristics, leading to
2
3
4
5 the maximum fuel cell performance and minimum polarization resistance.
6
7
8
9

10 As it was expected, the higher the temperature, the better the cell performed, as a
11
12 consequence of the increase in the electrolyte conductivity and enhancement on the
13
14 reactions kinetic. Nonetheless, the higher the temperature, the lower was the
15
16 performance enhancement, due to a possible electrolyte dehydration phenomenon. From
17
18 humidification tests, it can be said that this is not required for the cathode, and only if
19
20 the fuel stream is humidified, a slight increase in the performance was observed.
21
22
23 Therefore, in the PBI-based systems, the humidification does not play an important role
24
25
26 on the cell performance.
27
28
29
30
31

32 Acknowledgements

33
34 Authors would like to thank the “Junta de Comunidades de Castilla-La Mancha
35
36 (JCCM)” and the Company CLM-H2 for the financial support through the Project
37
38 PBI08-151-2045. Also, authors would like to thank the Spanish Government
39
40 (Ministerio de Ciencia e Innovación) for the FPU grant AP2007-02713 awarded to
41
42
43 Diego Úbeda.
44
45
46
47

48 References

- 49
50
51 [1] Q. Li, R. He, J.O. Jensen, N.J. Bjerrum, Fuel Cells 4 (2004) 147.
52
53 [2] Q. Li, R. He, J.-A. Gao, J.O. Jensen, N.J. Bjerrum, J. Electrochem. Soc. 150 (2003)
54
55 A1599.
56
57 [3] M. K. Daletou, J. K. Kallitsis, G. Voyiatzis, S.G. Neophytides, J. Membrane Sci.
58
59 326 (2009) 76.
60

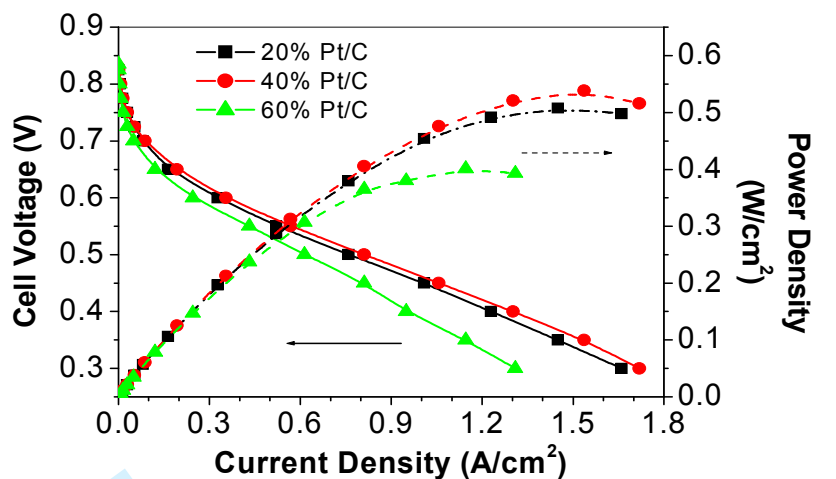
- [4] C. Pan, R. He, Q. Li, J. O. Jensen, N. J. Bjerum, H. A. Hjulmand, A. B. Jensen, J. Power Sources 145 (2005) 392.
- [5] J. Lobato, P. Cañizares, M.A. Rodrigo, J.J. Linares, J.A. Aguilar, J. Membr. Sci. 306 (2007) 47.
- [6] R. Bouchet, E. Siebert, Solid State Ionics 118 (1999) 287.
- [7] R. Bouchet, S. Miller, M. Duclot, J.L. Souquet, Solid State Ionics 145 (2001) 69.
- [8] J. Lobato, P. Cañizares, M.A. Rodrigo, J.J. Linares, G. Manjavacas, J. Membr. Sci. 280 (2006) 351.
- [9] J. S. Wainright, J. -T. Wang, D. Weng, R. F. Savinell, M. Litt, J. Electrochem. Soc. 142 (1995) L121.
- [10] J. -T. Wang, R. F. Savinell, J. Wainright, M. Litt, H. Yu, Electrochim. Acta 41 (1996) 193.
- [11] J. Lobato, P. Cañizares, M.A. Rodrigo, J.J. Linares, Electrochim. Acta 52 (2007) 3910.
- [12] J. Lobato, M.A. Rodrigo, J.J. Linares, K. Scott, J. Power Sources 157 (2006) 284.
- [13] P. Costamagna, S. Srinivasan, J. Power Sources 102 (2001) 242.
- [14] N. M. Markovic, T. J. Schmidt, V. Stamenkovic, P. N. Ross, Fuel Cells 1 (2001) 105.
- [15] S. Litster, G. Malean, J. Power Sources 130 (2004) 61.
- [16] E. Antolini, J. Appl. Electrochem. 34 (2004) 563.
- [17] S. Litster, G. Mclean, J. Power Sources 130 (2004) 61.
- [18] F. Seland, T. Berning, B. Børresen, R. Tunold, J. Power Sources 160 (2006) 27.
- [19] J. Lobato, P. Cañizares, M.A. Rodrigo, J.J. Linares, D. Ubeda, F.J. Pinar, Int. J. of Hydrogen (In press, 2009).

- [20] J. Lobato, P. Cañizares, M. A. Rodrigo, J. J. Linares, C-G. Piuleac, S. Curteanu. J. Power Sources 192 (2009) 190.
- [21] J. Lobato, P. Cañizares, M.A. Rodrigo, C. Ruiz-López, J.J. Linares, J. Appl. Electrochem. 38 (2008) 793.
- [22] J. Lobato, P. Cañizares, M.A. Rodrigo, D. Úbeda, F. J. Pinar, J.J. Linares, Fuel Cells (submitted 2009).
- [23] H. Watanabe, M. Tomikawa, S. Motoo, J. Electroanal. Chem. 195 (1985) 81.
- [24] J. Nordlund, A. Roessler, G. Lindbergh, J. Appl. Electrochem. 32 (2002) 259.
- [25] M. Prasanna, H. Y. Ha, E. A. Cho, S. -A. Hong, I. -H. Oh, J. Power Sources 137 (2004) 1.
- [26] T.R. Ralph, M.P. Hogarth, Platinum Metal Reviews 46 (2002) 3.
- [27] http://www.cabot-corp.com/wcm/download/en-us/sb/VULCAN_XC72R1.pdf (Access on December 15, 2009)
- [28] O.E. Kongstein, T. Berning, B. Brresen, F. Seland, R. Tunold, Energy 32 (2007) 418.
- [29] V.A. Paganin, E.A. Ticianelli, E.R. Gonzales, J. Appl. Electrochem. 26 (1996) 297.
- [30] E. Antolini, R.R. Passos, E.A. Ticianelli, J. Appl. Electrochem. 32 (2002) 383.
- [31] M. Prasanna, H.Y. Ha, E.A. Cho, S.-A. Hong, I.-H. Oh, J. Power Sources 131 (2004) 147.
- [32] Y.-G. Yoon, G.-G. Park, T.-H. Yang, J.N. Han, W.-Y. Lee, C.-S. Kim, Int. J. Hyd. Energy 28 (2003) 657.
- [33] T.E. Springer, T.A. Zawodzinski, M.S. Wilson, S. Gottesfeld, J. Electrochem. Soc. 143 (1996) 587.
- [34] M. Ciureanu, R. Roberge, Phys J., Chem. B. 105 (2001) 3531.

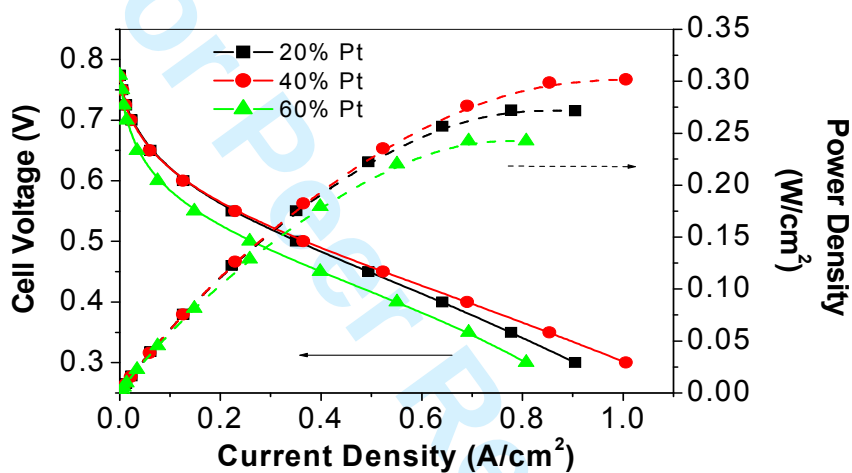
- [35] J. S. Wainright, J.-T. Wang, D. Weng, R. F. Savinell, J. Electrochem. Soc. 142 (1995) L121.
- [36] N. H. Jalani, M. Ramani, K. Ohlsson, S. Buelte, G. Pacifico, R. Pollard, R. Staudt, R. Datta, J. Power Sources 160 (2006) 1096.
- [37] D. Cheddie, N. Munroe, Energy Conversion and Management 47 (2007) 1490.
- [38] Q. Li, R. He, J. O. Jensen, N. J. Bjerrum, Chem. Mater. 15 (2003) 4896.
- [39] T. Mennola, Thesis for the degree of Licentiate of Technology, Helsinki University of Technology, November 2000.
- [40] Z. Liu, J.S. Wainright, M.H. Litt, R.F. Savinell, Electrochem. Acta 51 (2006) 3914.

CAPTION FOR FIGURES

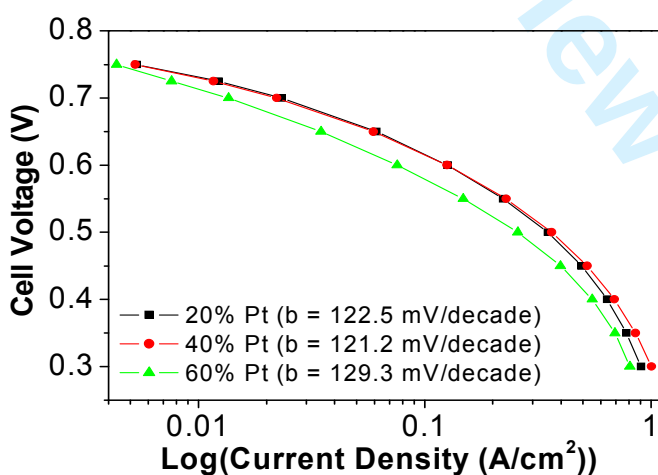
- Figure 1.** Hg-porosimetry of the electrodes with different Pt/C ratio.
- Figure 2.** Polarization curves for the different Pt/C content in cathode catalyst layer. 20% Pt/C in anode. Pt loading = 0.5 mg/cm² on both electrodes. T = 125 °C; (a) O₂ was used as comburent; (b) air was used as comburent.
- Figure 3.** Oxygen gain for different Pt/C ratio in cathode catalyst layer. 20 % Pt/C in anode T = 125 °C.
- Figure 4.** Nyquist plots of the different Pt/C ratio in the cathode catalyst layer. (a) Equivalent circuit; (b) O₂ was used as comburent; (c) air was used as comburent.
- Figure 5.** Polarization curves for the different Pt/C ratio in anode catalyst layer. 20 % Pt/C in cathode. Pt loading = 0.5 mg/cm² on both electrodes. T = 125 °C. Comburent = O₂.
- Figure 6.** Performance fuel cell at different temperatures. 40 % Pt/C in both electrodes. Platinum loading = 0.5 mg/cm². O₂ used as comburent.
- Figure 7.** Effect of humidification on a PBI-based high temperature PEMFC. 40 % Pt/C in both electrodes. Platinum loading = 0.5 mg/cm². O₂ used as comburent. T= 125 °C. (a) Cathode humidified at two temperatures; (b) Anode humidified at two temperatures.
- Table 1.** Different physical and electrochemical parameters of the electrodes prepared with different platinum percentage in the catalytic layer.
- Table 2.** Influence of the temperature on the open circuit voltage, exchange current density, Tafel slope and slope of the lineal region of the polarization curves showed in Fig. 6.



(a)



(b)



(c)

Figure 2

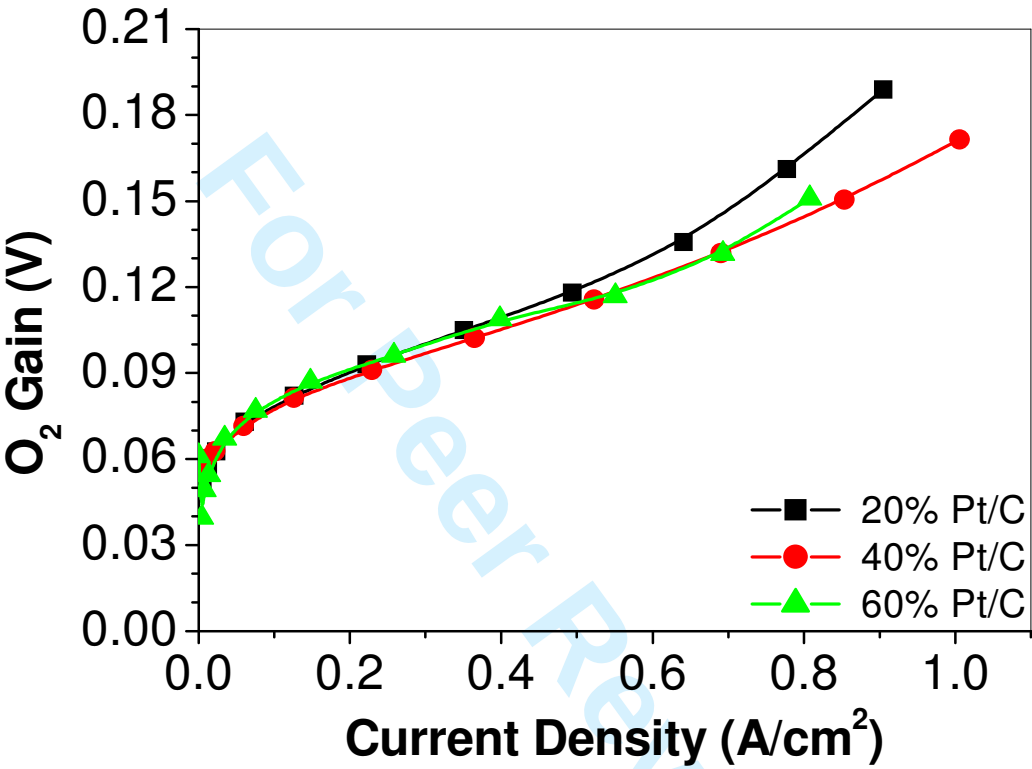
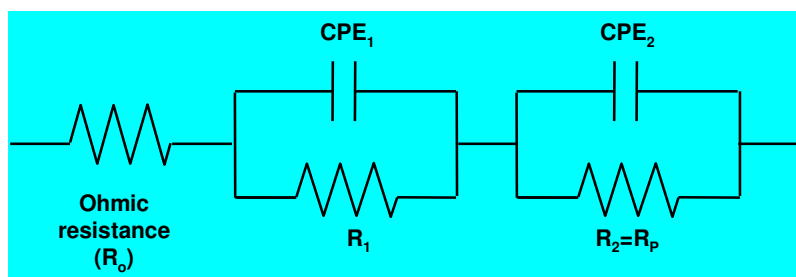
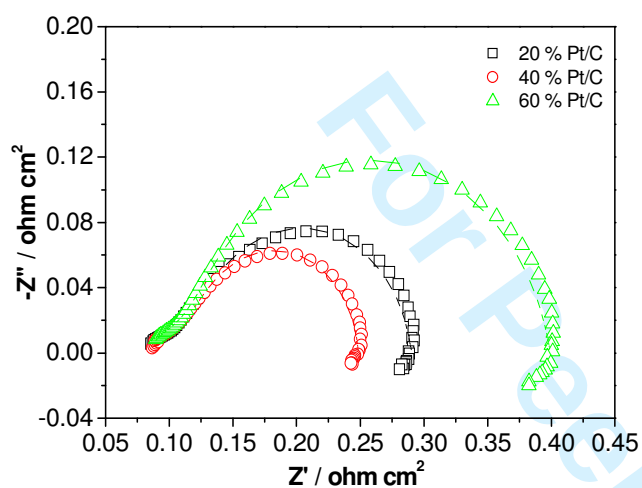


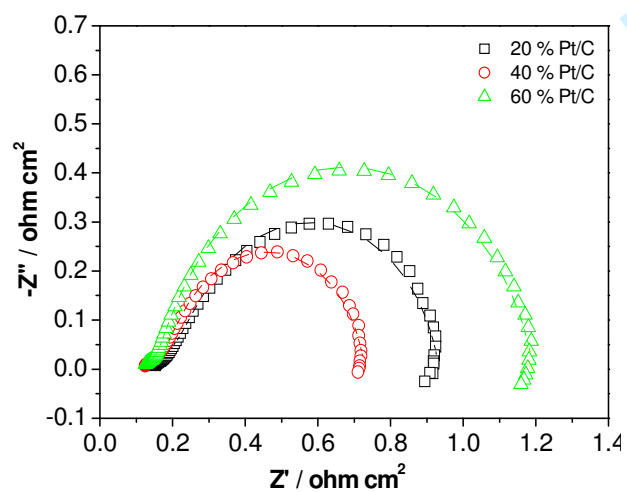
Figure 3



(a)



(b)



(c)

Figure 4

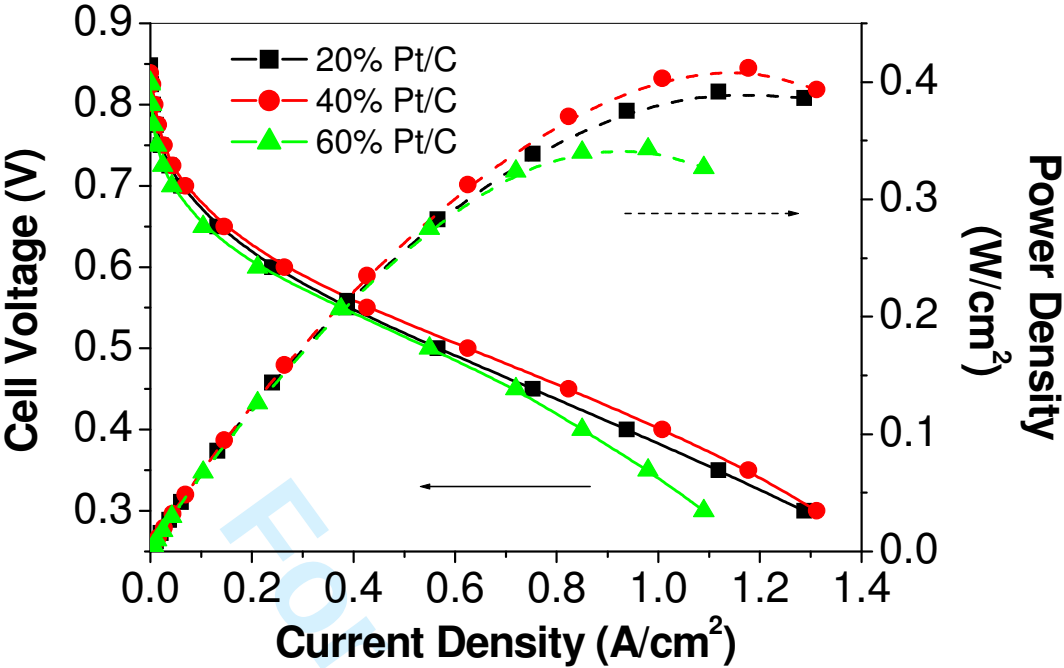


Figure 5

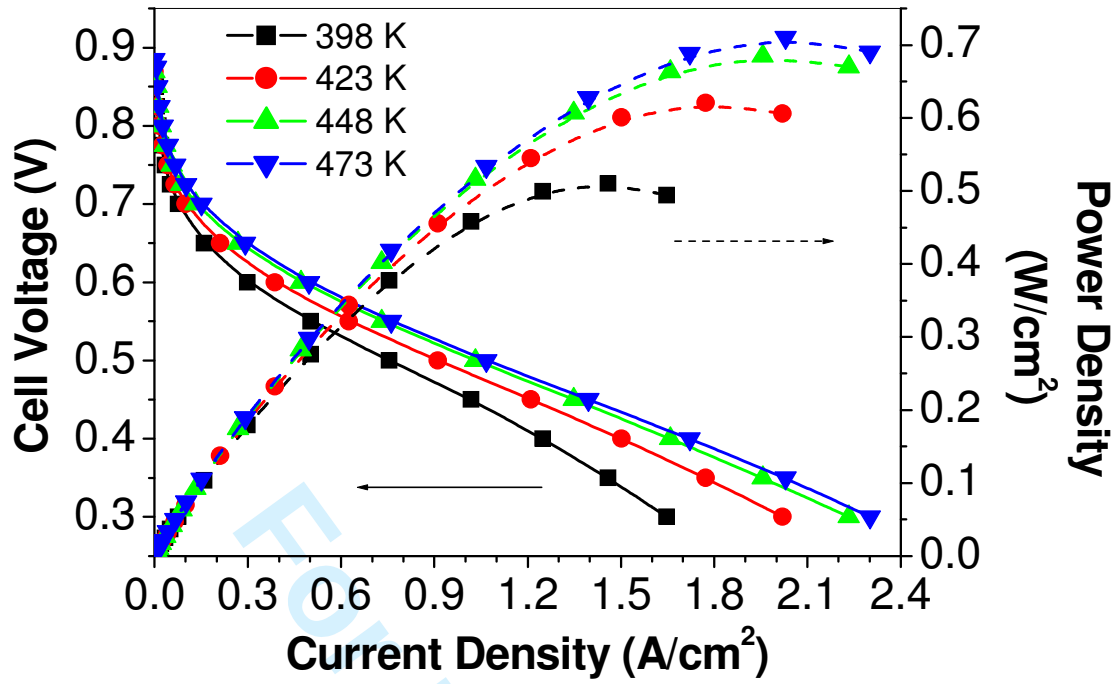
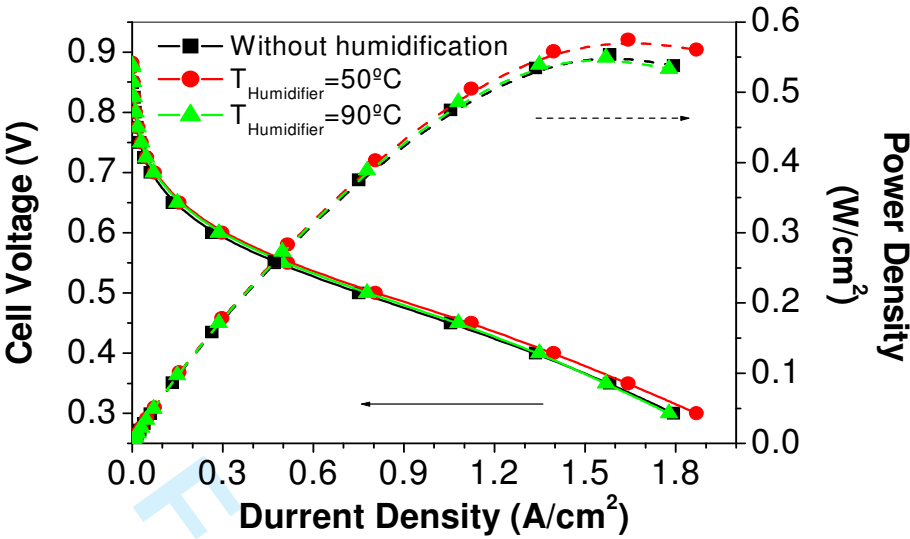
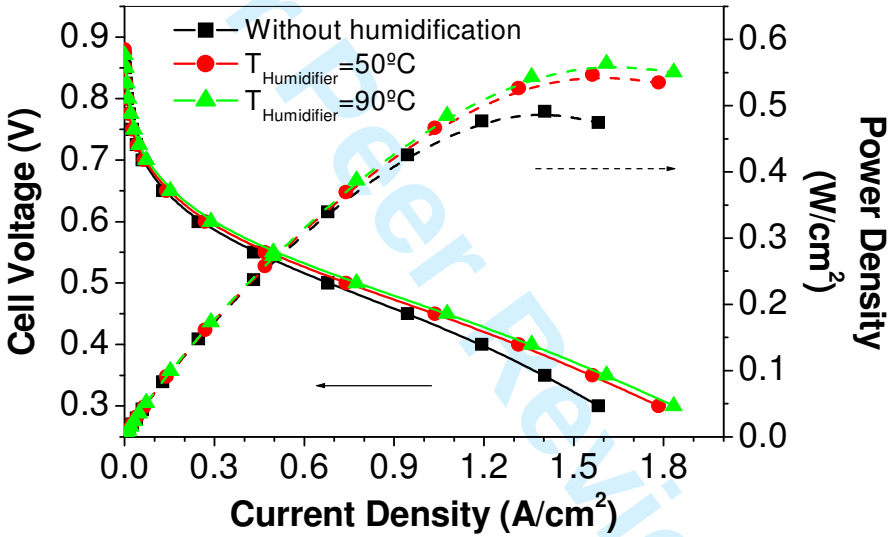


Figure 6



(a)



(b)

Figure 7

Table 1

	% Pt/C		
	20	40	60
Porosity (%)	55.3	57.9	60.1
Tortuosity (%)	4.70	4.46	4.36
Mean pore size (μm)	30.3	31.2	31.8
ESA ($\text{m}^2/\text{g Pt}$)	54.8	50.8	41.2
Diameter of Pt particles (nm)*	2.2	2.9	3.7
Available catalyst surface area ($\text{m}^2/\text{g}_{\text{Pt}}$)	120	100	78
Platinum utilisation (%)	46	50	52
Estimated catalyst thickness (μm)	49	18	8
b (mV/dec) (1)	69.3	68.2	74.0
b (mV/dec) (2)	86.2	84.0	98.7
$R_{p,c}$ ($\Omega\cdot\text{cm}^2$) (1)	0.102	0.097	0.169
$R_{p,c}$ ($\Omega\cdot\text{cm}^2$) (2)	0.373	0.355	0.611

(1) O_2 as comburent

(2) Air as comburent

* Provided by manufacturer

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Table 2

	Temperature			
	398 K	423 K	448 K	473 K
E_0 (mV)	913.4	921.1	938.0	955.3
$10^5 j_0$ (mA/cm ²)	5.96	6.23	11.7	30
b (mV/dec)	70.2	68.7	69.2	72.3
R (Ω cm ²)	0.193	0.165	0.155	0.150