

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/ijhydene

Influence of the relative volumes between catalyst and Nafion ionomer in the catalyst layer efficiency

Rafael Nogueira Bonifácio*, Almir Oliveira Neto, Marcelo Linardi

IPEN – Instituto de Pesquisas Energéticas e Nucleares, Av. Lineu Prestes 2242, Cidade Universitária, CEP, 05508-000, São Paulo, SP, Brazil

ARTICLE INFO

Article history:

Received 6 March 2014

Received in revised form

19 June 2014

Accepted 1 July 2014

Available online 2 August 2014

Keywords:

Membrane electrode assembly

Catalytic layer

Amount of Nafion ionomer in the catalyst layer

Catalyst

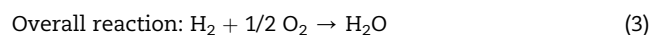
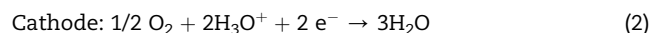
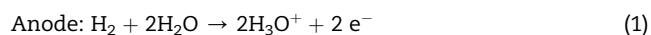
Volume of the support material

ABSTRACT

Over the years, studies have analyzed the composition of the catalyst layer using commercial platinum catalyst, supported on Vulcan XC72 with 20% of metal loading (Pt/C 20%_{MW}), and found that values between 20 and 40% of Nafion ionomer related to the mass of the catalyst layer (% NI_w) have resulted in more efficient electrodes for PEMFC. Recent studies with catalysts synthesized on Vulcan XC72 resulted in 59% NI_w as the best formulation. In this work, the commercial and the synthesized Pt/C 20%_{MW} catalyst were evaluated by Gas Pycnometry, Gas Adsorption (through BET and BJH), and Mercury Intrusion Porosimetry. The results showed volumetric differences between the Vulcan XC72 used in commercial catalyst and the Vulcan XC72 commercially available for synthesis (as purchased). These differences impair the synthesized catalyst in comparison with the commercial one. Therefore, the relationship between the quantities of catalysts and Nafion ionomer on the catalyst layers must be calculated as a function of the catalysts volumes. Copyright © 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Membrane electrode assemblies (MEAs) are the elements on which occur reactions that generate electricity in a proton exchange membrane fuel cell (PEMFC) [1–4]. This generation, when performed with the use of hydrogen as a fuel, releases heat and is characterized by a high theoretical efficiency and by the formation of water as a product of the reaction [2,3]. The partial and overall reactions to hydrogen and oxygen are shown in the Equations (1), (2), and (3), respectively [2,3]:



Several aspects have been studied to make the actual performance of PEMFC systems closer to the theoretical values, in order to make them viable for wide commercialization [4–80]. In relation to MEAs, it is known that the composition of their electrodes has a strong influence on the performance that can be obtained in the hydrogen oxidation reaction (HOR) at anodes and in the oxygen reduction reaction (ORR) at cathodes [3–56,81]. The structure of MEAs is composed of a polymeric membrane faced with two gas diffusion electrodes (GDE), the anode, and the cathode. Each

* Corresponding author.

E-mail addresses: rafaelnbonifacio@usp.br, rafaelnbonifacio@hotmail.com (R.N. Bonifácio).
<http://dx.doi.org/10.1016/j.ijhydene.2014.07.004>

0360-3199/Copyright © 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

GDE is composed of a catalyst layer and a gas diffusion layer (GDL) [1,2]. The GDL promotes a uniform distribution of reactant gases over the catalyst layer and conducts the electrons generated between the electrodes and the external circuit [2–4,82].

The catalyst layers of the electrodes are formed of a mixture of catalyst and ionomers of the electrolyte material, such as Nafion (a polymer sold by the DuPont Company), with structural porosity for the diffusion of both reactants and products. The catalyst plays the role of speeding up the anodic and cathode reactions. The Nafion ionomer provides a pathway for the protons that were formed in the catalytic sites across the electrode in order to ensure optimal conditions for generating electrical current [2,3]. The Nafion ionomer is used to interconnect the active sites of the catalyst to the faces of the polymeric membrane, allowing protons to flow through in a continuous way, in addition to keeping the catalyst particles bonded together and to the respective GDLs, enabling electron transfer [1,2,56]. Accordingly, it was found that a low quantity of Nafion ionomer results in poor proton conductivity and a high quantity results in limitations on mass transport [56]. Therefore, the appropriate amount of Nafion ionomer allows greater use of the metal nano particles and results in MEA reactions with greater efficiency [54–56,83].

Platinum supported on carbon catalysts (Pt/C) is widely [2–17,22–26,49–56,84–89] used in PEMFC research. Carbon supports provide good chemical stability for the cell environment and good electrical conductivity to the electrodes. Among these supports, Vulcan XC72 has been widely used [10–20,46–59,89–91]. The Pt/C catalyst with 20 percent of metal mass, sold by BASF, is also supported on Vulcan XC72. This catalyst is widely used in PEMFC research for systems development and as a reference material [4,6–14,21,22,38,42–44,49–58,75,80,81,83,84,89].

Although the use of platinum is a standard in PEMFC research, the cost and shortage of the natural reserves of this metal have motivated the study of other metals for HOR and ORR [6,9–17,19–23,43–46,74,81]. In this context, it has recently been found [83] that a palladium catalyst supported on Vulcan XC72 with 20% of metal weight (Pd/C 20%_{MW}) shows its greatest performances in electrodes prepared with 59% of Nafion ionomer on the mass of the catalyst layer (59% NI_w). This percentage of Nafion ionomer is significantly higher than the values between 20 and 40% NI_w obtained in studies [48–56] which investigated the formulation of electrodes with a Pt/C commercial catalyst with a similar composition (20%_{MW} and Vulcan XC72 as support). In these studies, ratios among the masses of platinum and carbon [48], ratios among the masses of carbon and Nafion ionomer [49], ratios among the masses of catalyst and Nafion ionomer [50–54], and ratios among the masses of platinum and Nafion ionomer [55,56] were presented as criteria for formulation of the catalyst layer. Thus, the absence of information about the influence of the change of the metal in the composition of the catalyst layer, and the difference found between the range of formulation presented in the literature (20 and 40% NI_w) [48,56] and the value obtained experimentally (59% NI_w) [83], have motivated the present study.

In this work, Pt/C and Pd/C, both with 20%_{MW}, were synthesized on Vulcan XC72. These catalysts were used to study

the percentage of Nafion ionomer adequate to prepare the catalyst layer with the synthesized Pt/C. Then, comparative analyses between the commercial Pt/C and the synthesized Pt/C and Pd/C catalyst were performed. An analysis of Vulcan XC72 was also performed for better understanding.

Experimental

Synthesis and characterization of the catalysts

Catalysts Pd/C and Pt/C were synthesized with 20% of metal weight by reduction with sodium borohydride method [92,93] using Pd(NO₃)₂ · 2H₂O and H₂PtCl₆ · 6H₂O (Sigma–Aldrich) and carbon Vulcan XC72 (Cabot). These catalysts, along with the commercial Pt/C 20%_{MW} purchased from BASF, were characterized by X-ray diffraction (XRD), Energy Dispersive X-ray (EDX), Gas Pycnometry (GP), Gas Adsorption (GA) according to the BET and BJH equations [94], and Mercury Intrusion Porosimetry (MIP), according to the BJH equation [94]. Images of catalysts were obtained by Transmission Electron Microscopy (TEM). From these images, average particle diameters were estimated, and then the specific surface areas (SSA) of metals were calculated, according to Equation (4) [95,96].

$$SSA = \frac{\sum_A (N_p \times 4\pi R^2)}{\rho \sum_V \left(N_p \times \frac{4}{3} \pi R^3 \right)} \quad (4)$$

where: \sum_A is the sum of the surface areas of all particles in the considered diameters distribution; R is the radius of each particle $\left(\frac{d}{2}\right)$; N_p is the number of particles of each radius R ; \sum_V is the sum of the volumes of all particles in the considered diameter distribution; and ρ is the specific mass of the metallic phase of each catalyst, for platinum $\rho_{Pt} = 21,090 \text{ g cm}^{-3}$ and for palladium $\rho_{Pd} = 12,023 \text{ g cm}^{-3}$.

XRD analyses were performed on a Rigaku miniflex II diffractometer using Cu K α radiation source ($\lambda = 0,154056 \text{ nm}$). XRD patterns were from 20° to 90° with a step size of 0.05° and a scan time of 2 s per step. Lattice parameter calculations were performed according to Bragg's law adjusted to the plan 220. The EDX analyses of the catalysts were carried out in a Hitachi SEM TM3000 Tabletop SEM. The TEM analyses were performed on a JEOL 1010 Transmission Electron Microscope, whose operation was limited to 80 keV beam. GP analyses were carried out on a Quantachrome Ultrapycnometer 1000. GA and MIP analyses were performed on a Micromeritics ASAP 2020 Accelerated Surface Area and Porosimetry System.

Membrane electrode assembly preparation

The synthesized Pt/C 20%_{MW} was used in the preparation of cathodes with Nafion ionomer percentages ranging from 35 to 65% of the total mass of the catalyst layer (% NI_w). The anodes used in MEAs were prepared with Pd/C 20%_{MW} and 59% NI_w, which was the best composition observed in a previous study [83]. MEAs with standard anode and cathode using Pt/C 20%_{MW} commercial catalyst and 35% NI_w [43,69,75] were also

Table 1 – Composition of the electrodes.

Nafion ionomer (% Nl _w)	Catalyst (%w)	Metal mass (mg cm ⁻²)	Catalyst mass (mg cm ⁻²)	Nafion ionomer mass (mg cm ⁻²)
65	35	0.40	2.00	3.71
60	40	0.40	2.00	3.00
59	41	0.40	2.00	2.88
58	42	0.40	2.00	2.76
57	43	0.40	2.00	2.65
56	44	0.40	2.00	2.55
55	45	0.40	2.00	2.44
50	50	0.40	2.00	2.00
45	55	0.40	2.00	1.64
40	60	0.40	2.00	1.33
35	65	0.40	2.00	1.08

evaluated for comparison. Table 1 shows the electrode compositions.

The mixtures of Nafion ionomer and catalyst were adjusted to contain 0.4 mg of metal per cm² of electrode (mg_{metal} cm⁻²), and then placed in ultrasound for 30 min. Electrodes of 5 cm² were then prepared by the hand-painted application of the catalyst layer on GDL MF15 (IPEN Patent: PI 1106530-3). The electrodes were dried at 80 °C for 2 h and then were pressed to the sides of Nafion 115 membranes. The hot pressing process used was to heat the MEA between 105 and 125 °C and then apply pressure of 1.000 kgf cm⁻² for 2 min.

Membrane electrode assembly evaluation

The evaluations of MEAs in a single fuel cell were carried out after 15 h of operation by obtaining polarization curves. Each MEA was evaluated with the hydrogen temperature ranging

from 25 to 100 °C in steps of 5 °C. The oxygen and unit cell temperatures were studied with values between 5 and 15 °C below each hydrogen temperature, according to Table 2. These evaluations were carried out between the open circuit potential and the potential of 300 mV. The best reproductive outcomes of each H₂ temperature are presented in the results. The unit cell was supplied with hydrogen 5.0 (99.999% pure) and flow rate of 160 mL min⁻¹ at 1 atm and with oxygen 4.0 (99.99% pure) and flow rate of 80 mL min⁻¹ at 1 atm. Cathode and anode were saturated with pure water.

Due to the great number of results, the open circuit potentials (OCPs) and the current densities obtained at the potential of 500 mV (Cd_{500mV}) are presented as a function of the temperatures studied. The potential of 500 mV was chosen to be compatible with the region of the electric double layer of the catalysts [19,93,95,97,98] and compatible with the operating potential of power modules [99].

Table 2 – Temperatures used in the MEAs evaluations in single fuel cell.

Conditions	Temperatures (°C)			Conditions	Temperatures (°C)		
	H ₂ ^a	O ₂ ^a	Single fuel cell		H ₂ ^a	O ₂ ^a	Single fuel cell
1	25	25	25	24	70	65	55
2	30	25	25	25	70	65	60
3	35	25	25	26	75	65	60
4	35	30	25	27	75	70	60
5	40	30	25	28	75	70	65
6	40	35	25	29	80	70	65
7	40	35	30	30	80	75	65
8	45	35	30	31	80	75	70
9	45	40	30	32	85	75	70
10	45	40	35	33	85	80	70
11	50	40	35	34	85	80	75
12	50	45	35	35	90	80	75
13	50	45	40	36	90	85	75
14	55	45	40	37	90	85	80
15	55	50	40	38	95	85	80
16	55	50	45	39	95	90	80
17	60	50	45	40	95	90	85
18	60	55	45	41	98	90	85
19	60	55	50	42	98	95	85
20	65	55	50	43	98	95	90
21	65	60	50	44	100	95	90
22	65	60	55	45	100	98	90
23	70	60	55	46	100	98	95

^a Temperature of the humidifiers.

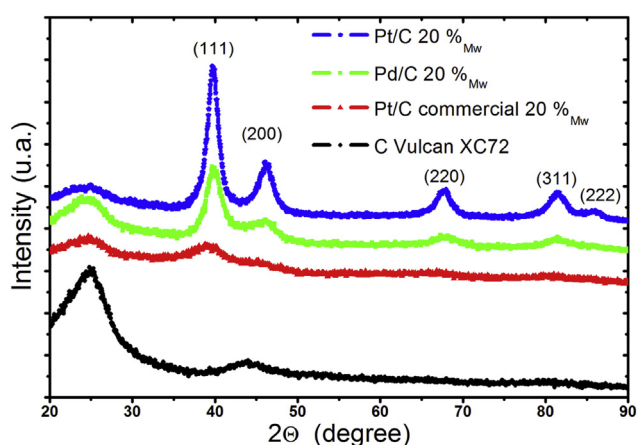


Fig. 1 – X-ray diffractograms of the catalysts and carbon support (Vulcan XC72).

Results

Catalyst characterization

The analysis of X-ray diffraction (Fig. 1) confirmed the formation of platinum and palladium particles in the synthesized catalysts.

A comparison of peak intensities indicated that the commercial Pt/C has smaller particle diameters or less crystallinity than synthesized catalyst. The presence of particles with smaller diameters was confirmed by using images obtained by Transmission Electron Microscopy (Figs. 2–4).

Analyzing Figs. 2–4, it was observed that the platinum particles of the commercial catalyst had smaller diameters and were more dispersed on their support than the synthesized catalyst. Through Fig. 4 it may be seen that Pd/C has particles with diameter from 3 nm, but there was also the formation of large agglomerates, a fact which is typical in syntheses with palladium [47,88,100]. Table 3 presents the mean particle diameters, the specific surface areas calculated by the distribution of particle diameters, the metal mass fractions determined by EDX, and the lattice parameters of each metal.

Although the average diameter calculated for the commercial Pt/C was 4.5 nm, the calculated SSA [95,96] was

$48.1 \text{ m}^2 \text{ g}^{-1}$. This value was lower than that obtained for synthesized Pd/C due to the difference between the specific masses of the two metals ($\text{Pt} = 21,090 \text{ g cm}^{-3}$ and $\text{Pd} = 12,023 \text{ g cm}^{-3}$), which makes the mass of platinum particles greater than those of palladium with the same volume. The synthesized Pt/C has the formation of particles with an average diameter larger than that of other catalysts and SSA consistent with that result.

Single fuel cell evaluation

In Figs. 5 and 6, the open circuit potential (OCPs) and current densities at 500 mV ($\text{Cd}_{500\text{mV}}$) of MEAs evaluated are shown, respectively.

In Figs. 5 and 6 it was found that, similar to the study with Pd/C in both electrodes [83], MEA with synthesized Pt/C on cathode using values between 55 and 60% NI_w resulted in higher performance. The current densities obtained between 25 and 90 °C were similar to those obtained with commercial Pt/C with 35% NI_w , our usual formulation to this catalyst [43,69,75]. Above 90 °C, performance losses occurred due to accumulation of water in the single fuel cell used [43,69,75]. From Fig. 6 it can be seen that MEAs with the synthesized catalyst had a lower drop in performance in this condition; this indicates that the structure of their catalytic layers favors the flow of gases in extreme conditions. If the current densities obtained (Fig. 6) were normalized by SSA of metals (Table 3), the structure of MEAs with the synthesized catalyst would be considered more efficient. These analyses have indicated that there are differences between the catalysts.

In the sequence of experiments, the percentage of Nafion ionomer was evaluated in steps of 1% NI_w in the range between 55 and 60% NI_w . In Fig. 7 and 8, respectively, the OCPs and the $\text{Cd}_{500\text{mV}}$ obtained are presented.

In Fig. 7, it was found that OCP values of MEAs with 55, 59, and 60% NI_w were similar and slightly higher than others. At operation potential (Fig. 8), it was found that MEAs with 59% NI_w showed current densities similar to 55 and 60% NI_w [83]. In the previous study, the variations observed at 57 and 58% NI_w were investigated by scanning electron microscopy of the cross section of MEAs and attributed to transitions in the pore structure of the catalyst layer, which results in changes in the flow mechanism of reactants and products [83].

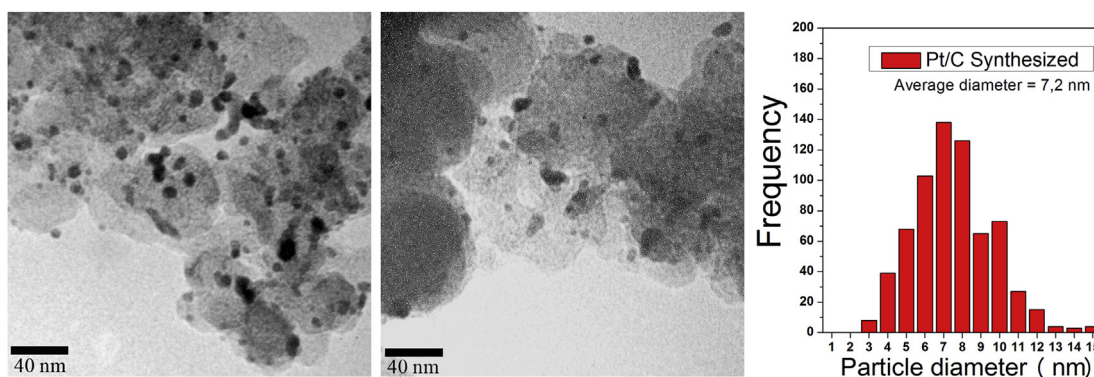


Fig. 2 – Micrographs and particle diameter distribution of Pt/C synthesized catalyst.

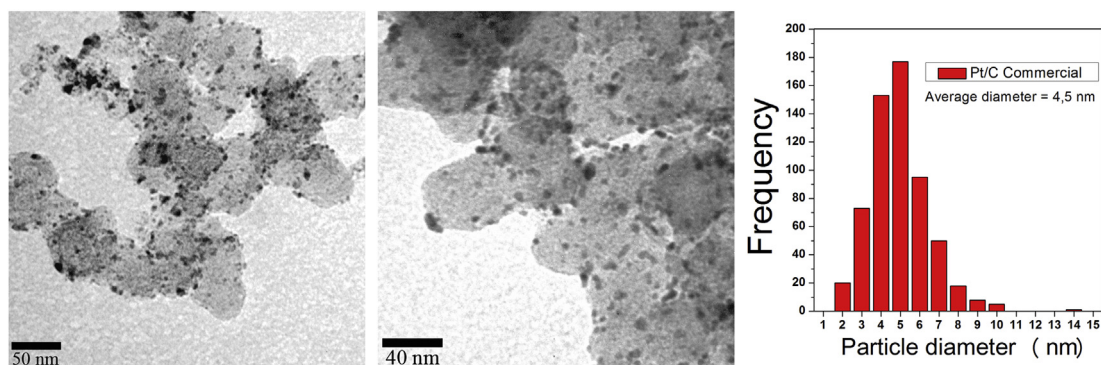


Fig. 3 – Micrographs and particle diameter distribution of Pt/C commercial catalyst.

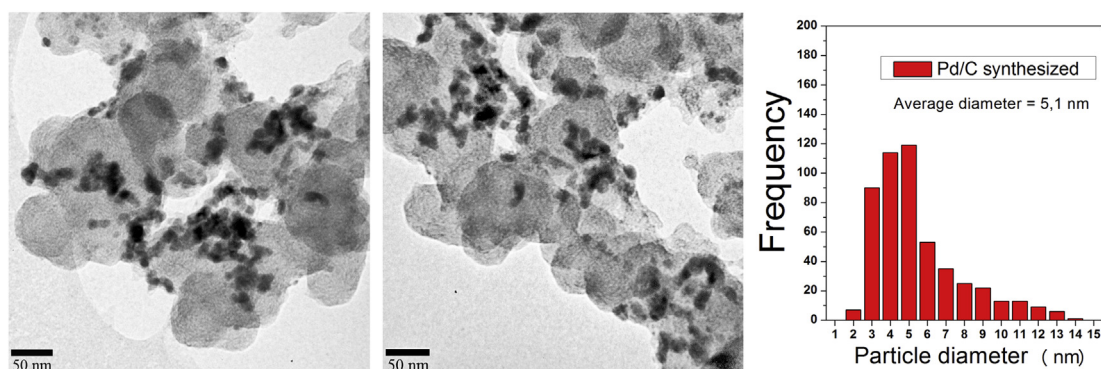


Fig. 4 – Micrographs and particle diameter distribution of the Pd/C synthesized catalyst.

Thus, considering the similarity of the results, it was concluded that the use of 59% NI_w was adequate to prepare MEAs with synthesized Pt/C. Consequently, it was also concluded that, when the catalyst contains 80% of Vulcan XC72 in mass, to change the metal applied on catalyst does not affect the adjustment of the amount of Nafion ionomer to be used in the preparation of MEAs. This conclusion is consistent with a comparison between the volumes of the support and the metals used in the MEAs with synthesized catalysts (Table 4).

From the data in Table 4, it was concluded that the volume of the support is the majority in catalysts with 20% M_w on the Vulcan XC72 commercially available. Given these results, a question was then posed:

Why do studies with commercial Pt/C 20% M_w supported on Vulcan XC72 [48–56] report values between 20 and 40% of Nafion ionomer as the most suitable composition to catalyst layer if two series of experiments (the current and the

previously performed [83]) with synthesized catalysts using 20% M_w on the same support (Vulcan XC72) resulted in 59% NI_w ?

To answer this question, in order to verify if the Vulcan XC72 support used in the synthesis is the same material indicated as support of Pt/C commercial catalyst, comparative analyses became necessary. A direct [101–104] comparison of the volume of the supports could not be performed because there was no sample of the support of the commercial catalyst. Therefore, samples of commercial Pt/C, samples of synthesized Pd/C and Pt/C, and samples of carbon Vulcan XC72 used in syntheses were analyzed by Gas Pycnometry, by Gas Adsorption, according to the BET and BJH equations, and by Mercury Intrusion Porosimetry, according to the BJH equation. The results are shown in Table 5.

Despite the same ratio between the mass of metal and Vulcan XC72 in all catalysts, the analyses indicated that the volumetric characteristics were quite distinct. According to

Table 3 – Catalyst characterization from XRD, EDX and TEM images.

Catalyst	Average particle diameter (nm)	Specific Surface Area ($m^2 g^{-1}$)	Metallic fraction by EDX (% w)		Lattice parameter (nm)	
			Experimental	Nominal	Experimental	Reference
Pt/C synthesized	7.2	32.2	20.04 ± 0.51	20.00	0.3887	0.39206 [90]
Pt/C commercial	4.5	48.1	19.70 ± 0.78	20.00	0.3955	0.39206 [90]
Pd/C synthesized	5.1	58.1	19.90 ± 1.40	20.00	0.3898	0.3890 [47]

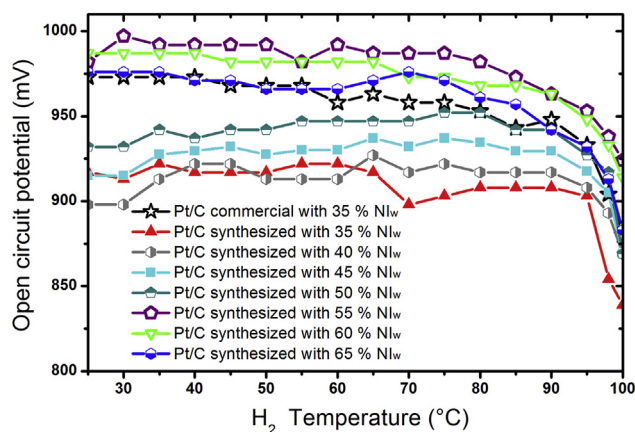


Fig. 5 – Open circuit potentials of MEAs using cathodes with Pt/C (synthesized on Vulcan XC72) and values between 35 and 65% Ni_w, MEAs using cathode with commercial Pt/C and 35% Ni_w [43,69,75]. All anodes using Pd/C and 59% Ni_w [83].

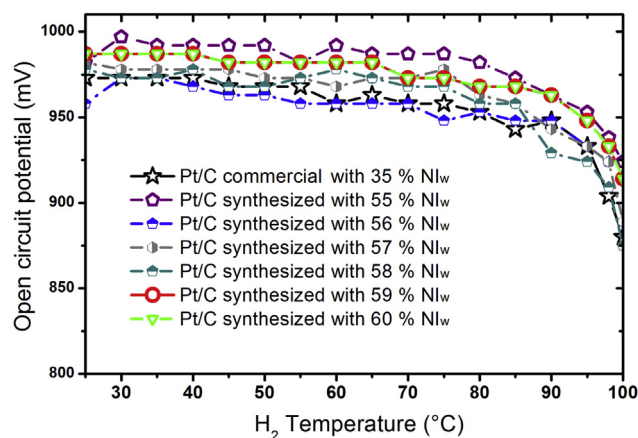


Fig. 7 – Open circuit potentials of MEAs using cathodes with Pt/C (synthesized on Vulcan XC72) and values between 55 and 60% Ni_w, MEAs using cathode with commercial Pt/C and 35% Ni_w [43,69,75]. All anodes using Pd/C and 59% Ni_w [83].

the data obtained by Gas Pycnometry, the specific volume of the commercial Pt/C was about 30% lower than the synthesized catalysts.

It is known that the volume of the metal particles is formed due to the lattice parameter of each metal and that these volumes do not change between the commercial and the synthesized Pt/C catalyst. From Table 3, it was verified that the metallic volumes are negligible in relation to the total volume of a catalyst (Table 4). It was thus concluded that the Vulcan XC72 used in commercial catalyst is different from the commercially available Vulcan XC72 (used in the synthesis). This difference probably results from heat treatment [10,11,46,59], done to make the support, and consequently the catalyst more dense and durable. The hypothesis that the commercial catalyst or its support has passed through a densification process is consistent with the smaller values

obtained for specific surface area, specific volume, and diameters, areas, and volumes of pores verified by Gas Adsorption and Mercury Intrusion Porosimetry.

The volume of commercial Pt/C being smaller than the synthesized catalysts explains why studies of proportions between catalyst and Nafion ionomer with the commercial catalyst have resulted in lower percentages (between 20 and 40% Ni_w [48–56] in the catalyst layers, 1.07 mg Ni cm⁻² to 35% Ni_w) than the experimental values obtained for the synthesized catalyst (59% Ni_w or 2.88 mg Ni cm⁻²). This leads to the conclusion that the relationship between the quantities of catalysts and Nafion ionomer on the catalyst layers must be calculated by a parameter that considers the volumes of the catalysts instead of the use of fixed ratios between the masses.

Since the difference between the synthesized and commercial catalysts are known, based on the data of Fig. 6, it can

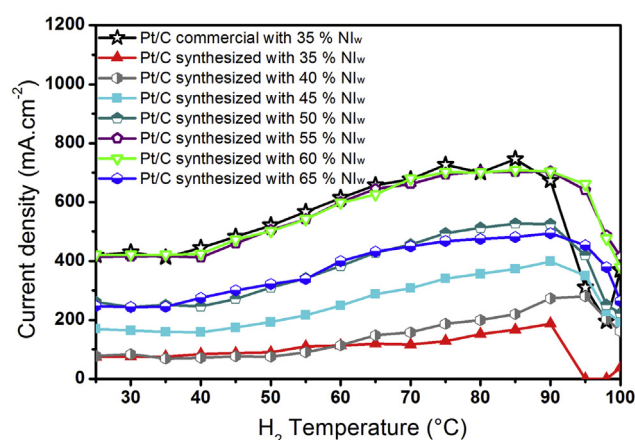


Fig. 6 – Current Densities at 500 mV of MEAs using cathodes with Pt/C (synthesized on Vulcan XC72) and values between 35 and 65% Ni_w, MEAs using cathode with commercial Pt/C and 35% Ni_w [43,69,75]. All anodes using Pd/C and 59% Ni_w [83].

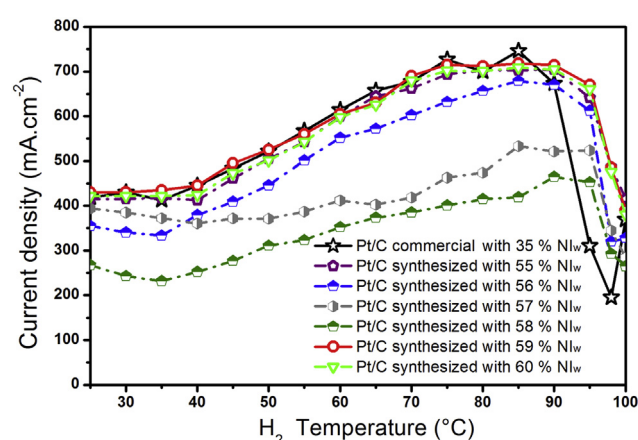


Fig. 8 – Current Densities at 500 mV of MEAs using cathodes with Pt/C (synthesized on Vulcan XC72) and values between 55 and 60% Ni_w, MEAs using cathode with commercial Pt/C and 35% Ni_w [43,69,75]. All anodes using Pd/C and 59% Ni_w [83].

Table 4 – Calculation of catalyst volumes.

Components of synthesized catalysts		Pd	Pt	C
Mass in the catalyst	(%)	20.00	20.00	80.00
Mass in the electrode	(mg cm ⁻²)	0.400	0.400	1.600
Specific mass of component	(g cm ⁻³)	12.023	21.090	0.264 ^a
Volume of components in the electrode	(mm ³ cm ⁻²)	0.033	0.019	6061
Catalysts		Pd/C	Pt/C	
Metal on the catalyst volume	(%)	0.54	0.31	
Vulcan XC72 on the catalyst volume	(%)	99.46	99.69	

^a Vulcan XC72 technical sheet available at: <http://www.cabot-corp.com/Downloads/DL200809231133AM1648>.

be affirmed that when catalysts with different volumes are evaluated on MEAs using values between 20 and 40% NI_w , the synthesized catalyst (under development) is undervalued in comparison with the commercial catalyst, which is evaluated in its best performance condition.

Hence, the formulation of catalyst layers by ratios between the masses of catalyst and ionomer, which is widely used in PEMFC research, tends to inhibit the identification of efficient catalysts. In other words, a systematic error in the evaluation of catalyst in the single PEMFC was verified in this work, and this error can make the performances of good catalysts to be understated and, consequently, slows the advancement of PEMFC catalysis.

Thus, it is quite probable that many results which have been attributed only to the modification of supports also occur due to the volume of each catalyst on the structures of the catalyst layers evaluated, and not only because of the characteristics of the materials evaluated as supports.

The differences between the specific volume, specific surface area, and area, volume, and pore diameter of synthesized Pt/C and Pd/C can be attributed to the higher specific volume of palladium relative to the platinum and to lower average particle diameter experimentally verified (5.1 nm for Pd/C in opposition to 7.2 nm Pt/C). These factors cause the formation of a greater number of particles of palladium with a consequent increase in the exposed surface.

Regarding the analysis of carbon Vulcan XC72, the difference between the specific mass of 2.511 g cm⁻³ determined by Gas Pycnometry and the value of 0.264 g cm⁻³ (informed by the manufacturer) was due to the characteristics of the analysis. In Gas Pycnometry, the regions permeated by gas were

excluded from the sample volume. In analyses of macroscopic characteristics, such as bulk density and tap density, the volume of pore spaces and voids, resulting from higher or lower packaging of the particles, are included on material volume, according to each standard test [101–104]. Thus, in future work, it is necessary to evaluate the best way to determine the volume of the catalysts in order to create volumetric ratios for determining the appropriate amount of Nafion ionomer to use in preparing electrodes with each catalyst in PEMFC studies.

Conclusions

Catalysts synthesized with 20%_{MW} on Vulcan XC72 in nature (as sold) showed the best performance with 59% NI_w , regardless of the metal used. Thus, catalysts prepared with this support and the same metallic percentages are equally affected by the amount of Nafion ionomer used.

The volume of Vulcan XC72 used in commercial Pt/C 20%_{MW} is lower than the volume of Vulcan XC72 available commercially for syntheses. This difference makes MEAs prepared with the commercial catalyst reach their maximum performance condition with values between 20 and 40% NI_w , while MEAs prepared with synthesized catalyst reach their maximum performance with 59% NI_w . Thus, when catalysts with different volumes are evaluated on MEAs using values between 20 and 40% NI_w , the synthesized catalyst (under development) is undervalued in comparison with the commercial catalyst, which is evaluated in its best performance condition. Therefore, there is a systematic error in PEMFC catalyst evaluation, and this error leads good catalysts to have their performance underestimated.

The relationship between the quantities of catalysts and Nafion ionomer on the catalyst layers must be calculated by a parameter that considers the volumes of the catalysts instead of the use of fixed ratios between the masses.

Future work

In future Work, it is necessary to evaluate the best way to determine the volume of the catalysts in order to create volumetric criteria for determining the appropriate amount of Nafion ionomer needed to prepare electrodes with each catalyst studied in PEMFC.

Table 5 – Analyses of the catalysts and support material (Vulcan XC72) by Gas Pycnometry, by Gas Adsorption, according to the BET equation, and by Gas Adsorption and Mercury Intrusion Porosimetry, according to the BJH equation.

Property	Carbon Vulcan XC72	Pd/C 20% _{MW} synthesized	Pt/C 20% _{MW} synthesized	Pt/C 20% _{MW} commercial
Specific mass by Gas Pycnometry (g cm ⁻³)	2.511	2.884	3.101	4.015
Specific volume by Gas Pycnometry (cm ³ g ⁻¹)	0.398	0.347	0.323	0.249
Specific surface area by BET (m ² g ⁻¹)	163.47	167.78	152.27	146.67
Average pore diameter by BET (nm)	9.940	9.444	8.226	7.712
Surface area of pores between 1.7 e 300 nm by BJH (m ² g ⁻¹)	110.76	124.57	96.46	89.95
Pore volume between 1.7 e 300 nm by BJH (cm ³ g ⁻¹)	0.397	0.379	0.288	0.260
Average pore diameter by BJH (nm)	14.347	12.186	11.952	11.572

Acknowledgments

To the Foundation for Research Support of the State of São Paulo (FAPESP 2010/10028-1) for the financial support, to the Energy and Nuclear Research Institute – IPEN/CNEN-SP for the infrastructure, especially the laboratories of the Center for Fuel Cell and Hydrogen (CCCH) and the laboratories of the Center for Science and Materials Technology (CCTM).

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.ijhydene.2014.07.004>.

REFERENCES

- [1] Wendt H, Linardi M, Aricó E. Células a combustível de baixa potência para aplicações estacionárias. *Quím Nova* 2002;25(3):470–6.
- [2] Wendt H, Götz M, Linardi M. Tecnologia de células a combustível. *Quím Nova* 2000;23(4):1–4.
- [3] Liu CY, Sung CC. A review of the performance and analysis of proton exchange membrane fuel cell membrane electrode assemblies. *J Power Sources* 2012;220:348–53.
- [4] Kim CS, Chun YG, Peck DH, Shin DR. A novel process to fabricate membrane electrode assemblies for proton exchange membrane fuel cells. *Int J Hydrogen Energy* 1998;23(11):1045–8.
- [5] Kim SH, Lee TK, Jung JH, Park JN, Kim JB, Hur SH. Catalytic performance of acid-treated multi-walled carbon nanotube-supported platinum catalyst for PEM fuel cells. *Mater Res Bull* 2012;47:2760–4.
- [6] Rego R, Oliveira MC, Alcaide F, Alvarez G. Development of a carbon paper-supported Pd catalyst for PEMFC application. *Int J Hydrogen Energy* 2012;37:7192–9.
- [7] Therdthianwong A, Manomayidthikarn P, Therdthianwong S. Investigation of membrane electrode assembly (MEA) hot-pressing parameters for proton exchange membrane fuel cell. *Energy* 2007;32:2401–11.
- [8] Zhong CJ, Luo J, Fang B, Wanjala BN, Njoki PN, Loukrakpam R, et al. Nanostructured catalysts in fuel cells. *Nanotechnology*, 2010;21(06).
- [9] Rajalakshmi N, Lakshmi N, Dhathathreyan KS. Nano titanium oxide catalyst support for proton exchange membrane fuel cells. *Int J Hydrogen Energy* 2008;33:7521–6.
- [10] Huang C, Liu S, Hwang W. Chelating agent assisted heat treatment of carbon supported cobalt oxide nanoparticle for use as cathode catalyst of polymer electrolyte membrane fuel cell (PEMFC). *Energy* 2011;36:4410–4.
- [11] Hassan A, Carreras A, Trincavelli J, Ticianelli EA. Effect of heat treatment on the activity and stability of carbon supported PtMo alloy electrocatalysts for hydrogen oxidation in PEMFCs. *J Power Sources* 2014;247:712–20.
- [12] Mustain WE, Kepler K, Prakash J. Investigations of carbon-supported CoPd₃ catalysts as oxygen cathodes in PEM fuel cells. *Electrochem Commun* 2006;8:406–10.
- [13] Salomé S, Rego R, Querejeta A, Alcaide F, Oliveira MC. An electrochemical route to prepare Pd nanostructures on a gas diffusion substrate for a PEMFC. *Electrochim Acta* 2013;106:516–24.
- [14] Fang B, Luo J, Njoki PN, Loukrakpam R, Mott D, Wanjala B, et al. Nanostructured PtVFe catalysts: electrocatalytic performance in proton exchange membrane fuel cells. *Electrochem Commun* 2009;11:1139–41.
- [15] Alcaide F, Alvarez G, Cabot PL, Miguel O, Querejeta A. Performance of carbon-supported PtPd as catalyst for hydrogen oxidation in the anodes of proton exchange membrane fuel cells. *Int J Hydrogen Energy* 2010;35:11634–41.
- [16] Escudero MJ, Hontanon E, Schwartz S, Boutonnet M, Daza L. Development and performance characterization of new electrocatalysts for PEMFC. *J Power Sources* 2002;106:206–14.
- [17] Zhao J, Sarkar A, Manthiram A. Synthesis and characterization of Pd-Ni nanoalloy electrocatalysts for oxygen reduction reaction in fuel cells. *Electrochim Acta* 2010;55:1756–65.
- [18] Liu Z, Gan LM, Hong L, Chen W, Lee JY. Carbon-supported Pt nanoparticles as catalysts for proton exchange membrane fuel cells. *J Power Sources* 2005;139:73–8.
- [19] Garcia AC, Paganin VA, Ticianelli EA. CO tolerance of PdPt/C and PdPtRu/C anodes for PEMFC. *Electrochim Acta* 2008;53:4309–15.
- [20] Cho YH, Cho YH, Lim JW, Park HY, Jung N, Ahn M, et al. Performance of membrane electrode assemblies using PdPt alloy as anode catalysts in polymer electrolyte membrane fuel cell. *Int J Hydrogen Energy* 2012;37:5884–90.
- [21] Pascual JJS, Martínez VC, Ortíz AL, Fera OS. Low Pt content on the Pd₄₅Pt₅Sn₅₀ cathode catalyst for PEM fuel cells. *J Power Sources* 2010;195:3374–9.
- [22] Seo MH, Lim EJ, Choi SM, Nam SH, Kim HJ, Kim WB. Synthesis, characterization, and electrocatalytic properties of a polypyrrole-composited Pd/C catalyst. *Int J Hydrogen Energy* 2011;36:11545–53.
- [23] Fıcıcılar B, Bayrakceken A, Eroglu I. Effect of Pd loading in Pd-Pt bimetallic catalysts doped into hollow core mesoporous shell carbon on performance of proton exchange membrane fuel cells. *J Power Sources* 2009;193:17–23.
- [24] Xiong L, Manthiram A. High performance membrane-electrode assemblies with ultra-low Pt loading for proton exchange membrane fuel cells. *Electrochim Acta* 2005;50:3200–4.
- [25] Li X, Park S, Popov BN. Highly stable Pt and PtPd hybrid catalysts supported on a nitrogen-modified carbon composite for fuel cell application. *J Power Sources* 2010;195:445–52.
- [26] Kim KH, Lee KY, Kim HJ, Cho E, Lee SY, Lim TH, et al. The effects of Nafion ionomer content in PEMFC MEAs prepared by a catalyst-coated membrane (CCM) spraying method. *Int J Hydrogen Energy* 2010;35:2119–26.
- [27] Liang ZX, Zhao TS, Xu C, Xu JB. Microscopic characterizations of membrane electrode assemblies prepared under different hot-pressing conditions. *Electrochim Acta* 2007;53:894–902.
- [28] Lai CM, Lin JC, Ting FP, Chyou SD, Hsueh KL. Contribution of Nafion loading to the activity of catalysts and the performance of PEMFC. *Int J Hydrogen Energy* 2008;33:4132–7.
- [29] Jeon S, Lee J, Rios GM, Kim HJ, Lee SY, Cho EA, et al. Effect of ionomer content and relative humidity on polymer electrolyte membrane fuel cell (PEMFC) performance of membrane-electrode assemblies (MEAs) prepared by decal transfer method. *Int J Hydrogen Energy* 2010;35:9678–86.
- [30] Ahn CY, Cheon JY, Joo SH, Kim J. Effects of ionomer content on Pt catalyst/ordered mesoporous carbon support in polymer electrolyte membrane fuel cells. *J Power Sources* 2013;222:477–82.
- [31] Suzuki T, Tsushima S, Hirai S. Effects of Nafion ionomer and carbon particles on structure formation in a proton-

- exchange membrane fuel cell catalyst layer fabricated by the decal-transfer method. *Int J Hydrogen Energy* 2011;36:12361–9.
- [32] Ahn SH, Jeon S, Park HY, Kim SK, Kim HJ, Cho E, et al. Effects of platinum loading on the performance of proton exchange membrane fuel cells with high ionomer content in catalyst layers. *J Int Hydrogen Energy* 2013;38:9826–34.
- [33] Zhao SX, Zhang LJ, Wang YX. Enhanced performance of a Nafion membrane through ionomer self-organization in the casting solution. *J Power Sources* 2013;233:309–12.
- [34] Xie J, Xu F, Wood DL, More KL, Zawodzinski TA, Smith WH. Influence of ionomer content on the structure and performance of PEFC membrane electrode assemblies. *Electrochim Acta* 2010;55:7404–12.
- [35] Ngo TT, Yu TL, Lin HL. Influence of the composition of isopropyl alcohol/water mixture solvents in catalyst ink solutions on proton exchange membrane fuel cell performance. *J Power Sources* 2013;225:293–303.
- [36] Passalacqua E, Lufrano F, Squadrito G, Patti A, Giorgi L. Influence of the structure in low-Pt loading electrodes for polymer electrolyte fuel cells. *Electrochim Acta* 1998;43(24):3665–73.
- [37] Jung CY, Yi SC. Influence of the water uptake in the catalyst layer for the proton exchange membrane fuel cells. *Electrochem Commun* 2013;35:34–7.
- [38] Sung MT, Chang MH, Ho MH. Investigation of cathode electrocatalysts composed of electrospun Pt nanowires and Pt/C for proton exchange membrane fuel cells. *J Power Sources* 2014;249:320–6.
- [39] Fofana D, Natarajan SK, Hamelin J, Benard P. Low platinum, high limiting current density of the PEMFC (proton exchange membrane fuel cell) based on multilayer cathode catalyst approach. *Energy* 2014;64:398–403.
- [40] He Q, Suraweera NS, Joy DC, Keffer DJ. Structure of the ionomer film in catalyst layers of proton exchange membrane fuel cells. *J Phys Chem C* 2013;117:25305–16.
- [41] Murata S, Imanishi M, Hasegawa S, Namba R. Vertically aligned carbon nanotube electrodes for high current density operating proton exchange membrane fuel cells. *J Power Sources* 2014;253:104–13.
- [42] Cho HJ, Jang H, Lim S, Cho E, Lim TH, Oh IH, et al. Development of a novel decal transfer process for fabrication of high-performance and reliable membrane electrode assemblies for PEMFCs. *Int J Hydrogen energy* 2011;36:12465–73.
- [43] Bonifácio RN, Neto AO, Linardi M. High performance carbon supported palladium catalyst in anodes of proton exchange membrane fuel cell. *Int J Electrochem Sci* 2013;8:159–67.
- [44] Li W, Haldar P. Supportless PdFe nanorods as highly active electrocatalyst for proton exchange membrane fuel cell. *Electrochem Commun* 2009;11:1195–8.
- [45] You DJ, Jin SA, Lee KH, Pak C, Choi KH, Chang H. Improvement of activity for oxygen reduction reaction by decoration of Ir on PdCu/C catalyst. *Catal Today* 2012;185:138–42.
- [46] Li B, Qiao J, Yang D, Lin R, Lv H, Wang H, et al. Effect of metal particle size and Nafion content on performance of MEA using Ir-V/C as anode catalyst. *Int J Hydrogen Energy* 2010;35:5528–38.
- [47] Antolini E, Zignani SC, Santos FS, Gonzalez ER. Palladium based electrodes: a way to reduce platinum content in polymer electrolyte membrane fuel cells. *Electrochim Acta* 2011;56:2299–305.
- [48] Antolini E, Giorgi L, Pozio A, Passalacqua E. Influence of Nafion loading in the catalyst layer of gas-diffusion electrodes for PEFC. *J Power Sources* 1999;77:136.
- [49] Gasteiger HA, Kocha SS, Sompalli B, Wagner FT. Activity benchmarks and requirements for Pt, Pt-alloy, and non-Pt oxygen reduction catalysts for PEMFCs. *Appl Catal B* 2005;56:9–35.
- [50] Chaparro AM, Gallardo B, Folgado MA, Martin AJ, Daza L. PEMFC electrode preparation by electrospray: optimization of catalyst load and ionomer content. *Catal Today* 2009;143:237–41.
- [51] Sun CN, More KL, Veith GM, Zawodzinski TA. Composition dependence of the pore structure and water transport of composite catalyst layers for polymer electrolyte fuel cells. *J Electrochem Soc* 2013;160(9):F1000–5.
- [52] Passalacqua E, Lufrano F, Squadrito G, Patti A, Giorgi L. Nafion content in the catalyst layer of polymer electrolyte fuel cells: effects on structure and performance. *Electrochim Acta* 2001;46:799–805.
- [53] Gamburgzev S, Appleby A. Recent progress in performance improvement of the proton exchange membrane fuel cell (PEMFC). *J Power Sources* 2002;107:5–12.
- [54] Qi Z, Kaufman A. Low Pt loading high performance cathodes for PEM fuel cells. *J Power Sources* 2003;113:37–43.
- [55] Sasikumar G, Ihm JW, Ryu H. Optimum Nafion content in PEM fuel cell electrodes. *Electrochim Acta* 2004;50:601–5.
- [56] Sasikumar G, Ihm JW, Ryu H. Dependence of optimum Nafion content in catalyst layer on platinum loading. *J Power Sources* 2004;132:11–7.
- [57] Andersen SM, Borghei M, Lund P, Elina YR, Pasanen A, Kauppinen E, et al. Durability of carbon nanofiber (CNF) & carbon nanotube (CNT) as catalyst support for proton exchange membrane fuel cells. *Solid State Ionics* 2013;231:94–101.
- [58] Wang J, Yin G, Shao Y, Zhang S, Wang Z, GAO Y. Effect of carbon black support corrosion on the durability of Pt/C catalyst. *J Power Sources* 2007;171:331–9.
- [59] Wang MX, Xu F, Xie J. Enhanced carbon corrosion resistance for PEFC Pt/C catalysts using steam-etched carbon blacks as a catalyst support. *Electrochim Acta* 2012;63:295–301.
- [60] Ngo TT, Yu TL, Lin HL. Nafion-based membrane electrode assemblies prepared from catalyst inks containing alcohol/water solvent mixtures. *J Power Sources* 2013;238:1–10.
- [61] Eastcott JI, Easton EB. Sulfonated silica-based fuel cell electrode structures for low humidity applications. *J Power Sources* 2014;245:487–94.
- [62] Kim KH, Lee KY, Lee SY, Cho E, Lim TH, Kim HJ, et al. The effects of relative humidity on the performances of PEMFC MEAs with various Nafion ionomer contents. *Int J Hydrogen Energy* 2010;35:13104–10.
- [63] Eisenberg A, Yeager H. Perfluorinated ionomer membranes. *ACS Symp Ser* 1982;180:487.
- [64] Zawodzinski TA, Springer ET, Urlbe F, Gottesfeld S. Characterization of polymer electrolytes for fuel cell applications. *Solid State Ionics* 1993;60:199–211.
- [65] Yan Q, Toghiani H, Wu J. Investigation of water transport through membrane in a PEM fuel cell by water balance experiments. *J Power Sources* 2006;158:316–25.
- [66] Sharma S, Pollet BG. Support materials for PEMFC and DMFC electrocatalysts – a review. *J Power Sources* 2012;208:96–119.
- [67] Kung HH, Ko EI. Preparation of oxide catalyst and catalyst supports – a review of recent advances. *Chem Eng J* 1996;64.
- [68] Spinacé EV, Neto AO, Franco EG, Linardi M. Métodos de preparação de nanopartículas metálicas suportadas em carbono de alta área superficial, como eletrocatalisadores em células a combustível com membrana Trocadora de prótons. *Quim Nova* 2004;27(4):648–54.
- [69] Bonifácio RN, Paschoal JOA, Cuenca R, Linardi M. Catalyst layer optimization by surface tension control during ink formulation of membrane electrode assemblies in proton exchange membrane fuel cell. *J Power Sources* 2011;196:4680–5.

- [70] Shrestha BR, Nishikata A, Tsuru T. Channel flow double electrode study on palladium dissolution during potential cycling in sulfuric acid solution. *Electrochim Acta* 2012;70:42–9.
- [71] Yazdanpour M, Esmaeilifar A, Rowshanzamir S. Effects of hot pressing conditions on the performance of Nafion membranes coated by ink-jet printing of Pt/MWCNTs electrocatalyst for PEMFCs. *Int J Hydrogen Energy* 2012;37:11290–8.
- [72] Frey T, Linardi M. Effects of membrane electrode assembly preparation on the polymer electrolyte membrane fuel cell performance. *Electrochim Acta* 2004;50:99–105.
- [73] Salgado JRC, Gonzalez ER. Correlação entre a atividade catalítica e o tamanho de partículas de Pt/C preparados por diferentes métodos. *Ecl Quím* 2003;28(2):77–86.
- [74] Hsieh CT, Liu YY, Roy AK. Pulse electrodeposited Pd nanoclusters on graphene-based electrodes for proton exchange membrane fuel cells. *Electrochim Acta* 2012;64:205–10.
- [75] Bonifácio RN, Cuenca R, Linardi M. desenvolvimento de processo de produção de conjuntos eletrodo-membrana-eletrodo para células a combustível baseadas no uso de membrana polimérica condutora de prótons (PEMFC) por impressão a tela. *Quim Nova* 2011;34(1):96–100.
- [76] Xu YSH, Wei Y, Kunz HR, Bonville LJ, Fenton JM. Dependence of high-temperature PEM fuel cell performance on Nafion content. *J. Power Sources* 2006;154:138–44.
- [77] Uma T, Nogami M. Fabrication and performance of Pt/C electrodes for low temperature H₂/O₂ fuel cells. *J Membr Sci* 2007;302:102–8.
- [78] Yang TH, Yoon YG, Park GG, Lee WY, Kim CS. Fabrication of a thin catalyst layer using organic solvents. *J Power Sources* 2004;127:230–3.
- [79] Young AP, Stumper J, Knights S, Gyenge E. Ionomer degradation in polymer electrolyte membrane fuel cells. *J Electrochem. Soc.* 2010;157(3):B425–36.
- [80] Palenzuela AV, Centellas F, Brillas E, Arias C, Rodriguez RM, Garrido JA, et al. Kinetic effect of the ionomer on the oxygen reduction in carbon-supported Pt electrocatalysts. *Int J Hydrogen Energy* 2012;37:17828–36.
- [81] Lopes PP, Ticianelli EA, Varela H. Potential oscillations in a proton exchange membrane fuel cell with a Pd–Pt/C anode. *J Power Sources* 2011;196:84–9.
- [82] Cindrella L, Kannan AM, Lin JF, Saminathan K, Ho Y, Lin CW, et al. Gas diffusion layer for proton exchange membrane fuel cells – a review. *J Power Sources* 2009;194:146–60.
- [83] Bonifácio RN, Neto AO, Linardi M. Current density maximization in palladium-based gas diffusion electrode in proton exchange membrane fuel cell. *Int J Electrochem Sci.* 2013;8:5621–34.
- [84] Satterfield MB, Majsztrik PW, Ota H, Benziger JB, Bocarsly AB. Mechanical properties of nafion and titania/nafion composite membranes for polymer electrolyte membrane fuel cells. *J Polym Sci B Polym Phys* 2006;44(16):2327–45.
- [85] Cho Y, Choi B, Cho Y, Park H, Sung Y. Pd based PdPt (19:1)/C electrocatalyst as an electrode in PEM fuel cell. *Electrochem Commun* 2007;9:378–81.
- [86] Bayrakçeken A, Cangul B, Zhang LC, Aindow M, Erkey C. PtPd/BP2000 electrocatalysts prepared by sequential supercritical carbon dioxide deposition. *Int J Hydrogen Energy* 2010;35:11669–80.
- [87] Kadirgan F, Kannan AM, Atilan T, Beyhan S, Ozenler SS, Suzer S, et al. Carbon supported nano-sized Pt–Pd and Pt–Co electrocatalysts for proton exchange membrane fuel cells. *Int J Hydrogen Energy* 2009;34:9450–60.
- [88] Bianchini C, Shen PK. Palladium-based electrocatalysts for alcohol oxidation in half cells and in direct alcohol fuel cells. *Chem Rev* 2009;109:4183–206.
- [89] Zhao Z, Castanheira L, Dubau L, Berthomé G, Crisci A, Maillard F. Carbon corrosion and platinum nanoparticles ripening under open circuit potential conditions. *J Power Sources* 2013;230:236–43.
- [90] Antolini E, Colmati F, Gonzalez ER. Ethanol oxidation on carbon supported (PtSn)alloy/SnO₂ and (PtSnPd)alloy/SnO₂ catalysts with a fixed Pt/SnO₂ atomic ratio: effect of the alloy phase characteristics. *J Power Sources* 2009;193:555–61.
- [91] Spinace EV, Linardi M, Neto AO. Co-catalytic effect of nickel in the electro-oxidation of ethanol on binary Pt–Sn electrocatalysts. *Electrochem Commun* 2005;7:365–9.
- [92] Brandalise M, Tusi MM, Piasentin RM, Santos MC, Spinacé EV, Neto AO. Synthesis of PdAu/C and PdAuBi/C electrocatalysts by borohydride reduction method for ethylene glycol electro-oxidation in alkaline medium. *Int. J Electrochem Sci.* 2012;7:9609–21.
- [93] Alvarez GF, Mamlouk M, Kumar SMS, Scott K. Preparation and characterization of carbon-supported palladium nanoparticles for oxygen reduction in low temperature PEM fuel cells. *J Appl Electrochem* 2011;41:925–37.
- [94] Teixeira VG, Coutinho FMB, Gomes AS. Principais métodos de caracterização da porosidade de resinas à base de divinilbenzeno. *Quím Nova* 2001;24(6):808–18.
- [95] Zhou Z, Shao Z, Qin X, Chen X, Wei Z, Yi B. Durability study of Pt–Pd/C as PEMFC cathode catalyst. *Int J Hydrogen Energy* 2010;35:1719–26.
- [96] Kim DS, Zeid EFA, Kim YT. Additive treatment effect of TiO₂ as supports for Pt-based electrocatalysts on oxygen reduction reaction activity. *Electrochim Acta* 2010;55:3628–33.
- [97] Savadogo O, Lee K, Oishi K, Mitsushima S, Kamiya N, Ota KI. New palladium alloys catalyst for the oxygen reduction reaction in an acid medium. *Electrochem Commun* 2004;6:105–9.
- [98] Gullon JS, Montiel V, Aldaz A, Clavilier J. Electrochemical and electrocatalytic behaviour of platinum–palladium nanoparticle alloys. *Electrochem Commun* 2002;4:716–21.
- [99] Hwang JJ, Chang WR, Weng FB, Su A, Chen CK. Development of a small vehicular PEM fuel cell system. *Int J Hydrogen Energy* 2008;33:3801–7.
- [100] Li H, Sun G, Jiang Q, Zhu M, Sun S, Xin Q. Synthesis of highly dispersed Pd/C electro-catalyst with high activity for formic acid oxidation. *Electrochem Commun* 2007;9:1410–5.
- [101] Avnimelech Y, Ritvo G, Meijer LE, Kochba M. Water content, organic carbon and dry bulk density in flooded sediments. *Aquacult Eng* 2001;25:25–33.
- [102] Buczek B. Measurement of the apparent density of porous particles by a powder characteristics tester. *Adv Powder Technol* 1991;2(4):315–9.
- [103] Wissler M. Review Graphite and carbon powders for electrochemical applications. *J Power Sources* 2006;156:142–50.
- [104] Buczer B, Geldart D. Determination of the density of porous particles using very fine dense powders. *Powder Technol* 1986;45:173–6.