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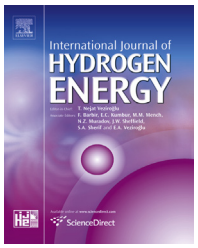

Comparative analysis between mass and volume of catalysts as a criterion to determine the optimal quantity of Nafion ionomer in catalyst layers

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ABSTRACT

Studies in the proton exchange membrane fuel cell (PEMFC) have evaluated different catalyst systems, using fixed mass percentages as the criterion to prepare catalyst layers. Some studies presented masses between 20 and 40% of ionomer in the catalyst layer as best composition; however, they also showed that any modification in the catalyst structure, such as support material or metal percentage, changes remarkably the membrane electrode assembly (MEA) performances. Thus, the volume of a catalyst used changes the amount of Nafion ionomer required to prepare catalyst layers with high efficiency. Consequently, to compare different catalysts in their highest performance conditions, it has become necessary to develop a volumetric criterion to calculate the quantity of Nafion ionomer necessary for each catalyst. In this work, the masses and the volumes of catalysts were compared to three other catalysts as the criterion to transpose the adjustment of the catalyst layer composition made to Pd/C 20%. The use of catalyst volume as the criterion to calculate the quantity of Nafion ionomer in the catalyst layer resulted in MEAs significantly more efficient than those prepared according to the fixed mass percentage.
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Introduction

Membrane electrode assemblies (MEAs) are structures in which electro-chemical reactions occur between a fuel and an oxidant to generate electrical and thermal energy in a proton exchange membrane fuel cell (PEMFC) [1,2]. Over the years, studies have been performed to make the PEMFC systems surpass their demands of efficiency, durability, and cost [1–82]. Many of these studies [2–35] were conducted using the platinum commercial catalyst with 20 percent of metal mass and supported on Vulcan XC72 (Pt/C 20%) sold by BASF (previously by E-tek [28]). Some of these studies have evaluated the relationship between the amount of Nafion ionomer applied to the catalyst layer of MEAs and the respective performance obtained [3–10] and found some criteria to formulate efficient electrodes, such as ratios between the masses of catalyst and Nafion ionomer [3–7], ratios between the masses of support material and Nafion ionomer [8] and ratios between the masses of platinum and Nafion ionomer [9,10].

The formulations obtained in these studies resulted in values between 20 and 40 percent of Nafion ionomer (%NI) in

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relation to the total masses of the catalyst layers as the best setting for electrodes containing values between 0.05 and 0.50 mg of platinum per square centimeter ($mgPt \cdot cm^{-2}$) [3–10]. However, the same studies found that changes in the mass of catalyst applied to the electrodes [9] and changes in the ratio between metal and support [8] modified the required masses of Nafion ionomer which resulted in higher performances. On the other hand, a recent study [83] verified that catalyst with the same support material (carbon) and the same metal loading (20%) can present different volumes due to modifications induced by heat treatment in the support material. It was also shown that these different volumes significantly modify the amount of ionomer needed to prepare catalyst layers with high performance, i.e., the formation of triple phase boundaries with high efficiency [83]. From this conclusion, it is expected that a volumetric criterion should be developed to determine the amount of ionomer to be used in the preparation of catalyst layers for different catalysts in order to make comparisons between them at each one's conditions of greatest efficiency [83].

In this present work, a volumetric criterion to transpose the better adjustment of ionomer quantity in the catalyst layer obtained from Pd/C 20% [12] to three catalysts with other compositions was proposed and evaluated. To verify the efficiency of this criterion without the interference of other factors, MEAs were prepared with catalysts using the same metal and the same support material. Thus, the differences between the catalysts were only the use of metal masses of 10, 20, 40, and 60%. For comparison, electrodes prepared with ionomer quantity determined according to the fixed mass percentage criterion were also evaluated in this study.

In the related previous works [12,34] were performed the comparison between platinum and palladium electrodes, and it was verified that palladium catalyst using carbon Vulcan XC72 as support materials (Pd/C 20%) presented it best performance in catalyst layers with 59%NI [12]. Recently [83], it was verified that this ionomer quantity (59%NI) is higher than usual because the carbon used as support material in these studies is less dense than the carbon used in the commercial catalyst.

Experiments

Catalysts Pd/C with 10, 20, 40, and 60% of metal masses were synthesized by the method of reduction with sodium borohydride [84,85], using $Pd(NO_3)_2 \cdot 2H_2O$ (Sigma–Aldrich) and carbon Vulcan XC72 (Cabot), according to the reactants quantity presented in Table 1.

Table 1 – Reactants used in the synthesis of the catalysts.

Catalyst Pd/C	$Pd(NO_3)_2 \cdot 2H_2O$ solution	$NaBH_4$	Carbon Vulcan XC72
Metal mass (%)	(mL)	(mg)	(mg)
10	1.00	35.50	180.00
20	2.00	71.00	160.00
40	4.00	142.10	120.00
60	6.00	213.20	80.00

These catalysts were characterized by X-Ray Diffraction (XRD), Energy Dispersive X-ray (EDX), and Transmission Electron Microscopy (TEM). The XRD analyses were performed on a Rigaku miniflex II diffractometer using Cu Kα radiation source (λ = 0.154056 nm). The XRD patterns ranged from 20° to 90° with a step size of 0.05° and a scan time of 2 s per step. The calculation of lattice parameters was performed according to Bragg's Law adjusted to plan 220. The EDX analyses of the catalysts were made in a Hitachi SEM TM 3000 Tabletop. The TEM analyses were performed on a JEOL 1010 Transmission Electron Microscope, whose operation was limited to 80 keV beam. The images obtained were used to count and estimate the average particle diameters ($\overline{x}$) and to calculate the specific surface areas (SSA) of palladium from the distributions of diameters, according to Equation (1) [70,71,83]. For these procedures, it was counted more than 600 particles of each catalyst.

$$SSA = \frac{\sum_{A}\left(N_p \times 4\pi R^2\right)}{\rho \sum_{V}\left(N_p \times \frac{4}{3}\pi R^3\right)} \quad (1)$$

Where: $\sum_A$ is the sum of the surface areas of all particles in the considered diameter distribution; R is the radius of each particle ($D/2$); 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 palladium ($\rho_{Pd} = 12.023\ g \cdot cm^{-3}$).

In all catalyst layers of anode and cathode the use of catalyst mass corresponding to 0.4 mg of palladium per square centimeter ($mgPd \cdot cm^{-2}$) in electrodes of 5 cm^2 was considered. The quantities of ionomer were determined by the volume of the catalysts calculated from the sum of the volumes of metal and support used in each. The volumetric calculations considered the specific masses of palladium and carbon (Vulcan XC72), respectively 12.023 $g \cdot cm^{-3}$ and 0.264 $g \cdot cm^{-3}$, and the value of 1.134 $g \cdot cm^{-3}$ determined by pycnometry to the ionomer, obtained from the solution D520, purchased from DuPont. The catalyst layer thicknesses (*CLT*) were estimated according to Equation (2).

$$CLT = \frac{Cv + Iv}{Ea} \quad (2)$$

Where: *Cv* is the catalyst volume. *Iv* is the Ionomer volume and *Ea* is the electrode area (5 cm^2).

Since the catalyst layer thicknesses were calculated from the sum of the volumes of Nafion ionomer and catalyst divided per electrode area, these calculations do not consider electrode porosity and were only used as approximated values, to demonstrate the influence of catalyst layers composition in their thickness. Tables 2 and 3 present the calculations for electrodes prepared according to the correlation of ionomer quantity by catalyst volume.

The use of 2.878 mg of Nafion ionomer per cm^2 (2.538 $mm^3\ cm^{-2}$ or 59%NI) to Pd/C 20% was the reference for calculations because it was the best setting obtained in a previous study that evaluated values from 30 to 70% of ionomer in the catalyst layer composition [12]. In order to compare the efficiency of catalyst layers formulated by catalyst masses and by catalyst volume, the use of a fixed mass

Table 2 – Volume of the catalysts on the electrodes determined by the sum of the volumes of their components.

Catalyst composition				Catalyst volume on the electrodes (Pd + C)
Palladium		Carbon support		
%	mg cm^{-2} g cm^{-3} mm^3 cm^{-2}	%	mg cm^{-2} g cm^{-3} mm^3 cm^{-2}	mm^3 cm^{-2}
10	0.4 ÷ 12.023 = 0.03327	90	3.60 ÷ 0.264 = 13.636	13.670
20[a]	0.4 ÷ 12.023 = 0.03327	80	1.60 ÷ 0.264 = 6.061	6.094
40	0.4 ÷ 12.023 = 0.03327	60	0.60 ÷ 0.264 = 2.273	2.306
60	0.4 ÷ 12.023 = 0.03327	40	0.27 ÷ 0.264 = 1.010	1.043

[a] Pd/C 20% was the reference for calculations [14].

percentage, widely used in PEMFC research [3–10], was also evaluated. Thus, MEAs with Pd/C catalysts and 59%NI [12] were prepared according to Table 4.

The mixtures of catalyst and ionomer were carried out using ultrasound for 30 min and applied on the GDL MF15 (gas diffusion layers patented at IPEN: Patent No: PI 1106530-3) by hand painting. The electrodes were then kept in a stove at 80 °C for two hours and afterwards were hot pressed to both sides of a Nafion 115 membrane. This procedure was performed by first heating the MEA to between 105 and 125 °C and then applying a pressure of 1.000 kgf·cm^{-2} for 2 min [12,33,83].

The evaluations of MEAs were carried out in a single fuel cell between the open circuit potential (OCPs) and the potential of 300 mV. The polarization curves were obtained by the temperature of hydrogen (H_2) being varied between 25 and 90 °C and by the temperatures of oxygen (O_2) and the single fuel cell being varied between 5 and 15 °C below each H_2 temperature, seeking the best performance of each MEA. However, due to the large amount of data obtained, it was decided to present the higher reproductive polarization curves obtained at 40, 60, and 80 °C (H_2 temperatures) in this article and present the other polarization curves as Supplementary Data. The values of OCPs and current densities, obtained at the potential of 500 mV (Cd_{500mV}) in all temperatures studied, were also presented. The potential of 500 mV was chosen for being compatible with the region of the electric double layer of palladium catalysts [42–45,85] and also compatible with the operating potential of power modules [12,34,54].

Since the specific surface area (SSA) of each catalyst has an influence on fuel cell performance, to simulate the proportionality that could be obtained if all catalysts had the same specific surface area, the current densities obtained from MEAs at 500 mV were also presented divided by the specific surface areas of the respective catalysts (Cd_{500mV}/SSA), in order to evaluate some effect of the catalyst layer thickness on MEA performances.

The single fuel cell experiment was carried out using H_2 with purity 5.0, supplied with a flow rate of 160 ml·min^{-1} at 1 atm, and O_2 with purity 4.0, lied with a flow rate of 80 ml·min^{-1} at 1 atm, both saturated with pure water.

Since the performance comparison between platinum and palladium catalyst isn't the focus of this article, to allow this kind of comparison, the performances obtained from MEAs using palladium catalyst as described and MEAs using commercial platinum catalyst (Pt/C 20%), in cathode and anode sides using 0,4 mgPt·cm^{-2} and 35%NI in catalyst layers [12,34], are presented in Supplementary Data. The Pt/C catalyst was purchased from BASF Company, and the electrodes and MEAs were prepared and evaluate de in the same conditions described above.

Results and discussion

The patterns of X-ray diffraction of the synthesized catalysts (Fig. 1) showed peaks with 2θ values of 40.1°, 46.4°, 68.1°, and 82.0° corresponding to the planes (111), (200), (220), and (311), characteristic of the face-centered cubic structure of palladium, and broad peaks near 25° in 2θ corresponding to the carbon Vulcan XC72 used as support in the syntheses.

The lattice parameter calculated for all palladium catalysts from plane 220 was 0.3887 nm, which was very close to the reference value of 0.3890 nm [38]. From the images obtained by Transmission Electron Microscopy of the Pd/C catalysts (Fig. 2), the diameters of the metal particles and their respective specific surface areas were estimated.

The images obtained by TEM showed an irregular distribution of palladium on the substrate and also the formation of

Table 3 – Volume of ionomer calculated from the catalyst volume, determined by the sum of the metal and carbon volumes.

Pd/C catalyst	Catalyst volume on the electrode[a]	Nafion ionomer on the electrode		Ratio between catalyst and ionomer		Thickness of the catalyst layer[b]
				by mass percentage	by volume	
%	mm^3 cm^{-2}	mg cm^{-2}	mm^3 cm^{-2}	%NI	u. a.	μm
10	13.670	6.456	5.693	61.7	2.40	193.6
20	6.094	2.878	2.538	59.0	2.40	86.3
40	2.306	1.089	0.960	52.1	2.40	32.7
60	1.043	0.493	0.435	42.5	2.40	14.8

[a] From Table 2.
[b] Calculated with Equation (2).

Table 4 – Composition of catalyst layer prepared with Pd/C 10, 20, 40, and 60% according to the fixed mass percentage of 59.0%NI determined experimentally for Pd/C 20% [14]].

Paladium		Carbon		Pd/C	Nafion ionomer	Ratio between catalyst and ionomer[a]		Thickness of the catalyst layer[b]
						by mass percentage	by volume	
mg cm^{-2}	%	%	mg cm^{-2}	mg cm^{-2}	mg cm^{-2}	%NI	u. a.	μm
0.4	10	90	3.600	4.000	5.756	59.0	2.69	187.5
0.4	20	80	1.600	2.000	2.878	59.0	2.40	86.3
0.4	40	60	0.600	1.000	1.439	59.0	1.81	35.7
0.4	60	40	0.267	0.667	0.959	59.0	1.23	18.9

[a] Calculated from Table 2 data.
[b] Calculated with Equation (2).

agglomerates, confirming the results of previous studies [12,13,37,38]. Table 5 presents the percentages of metal mass determined by EDX, the average particle diameters ($\overline{x}$) of palladium, and their estimated specific surface area [51,52].

The metal load compositions of the catalysts (Table 5) were close to the nominal values. Among the specific surface areas estimated, Pd/C 20% had the highest value followed by Pd/C 10%, while Pd/C 40% and Pd/C 60% had lower and similar values.

After characterizations, electrodes and MEAs were prepared according to the two criteria of ionomer calculation described in the experimental part (according to catalyst volumes and masses) and were evaluated in single fuel cells. When catalyst layers were prepared according to a fixed mass percentage (59%IN), it is clear from Table 4 that the volumetric ratio between catalyst and ionomer decreased from 2.68 to 1.23 as a function of the increasing metal loading percentage from 10 to 60%. On the other hand, from Table 3 data, it could be seen that using correlation by volume a ratio of 2.4 between the volumes of catalysts and ionomer was obtained, while the percentage by mass decreased from 61.7 to 42.5 as a function of the increasing metal loading percentage from 10 to 60%. Thus, the difference between these criteria is clear, and it is perceived that these variations occurred due to the difference between the densities of metal and support material. The differences in ionomer quantities calculated from both criterion results in the differences in the estimated thickness (Tables 3 and 4) obtained using equation (2).

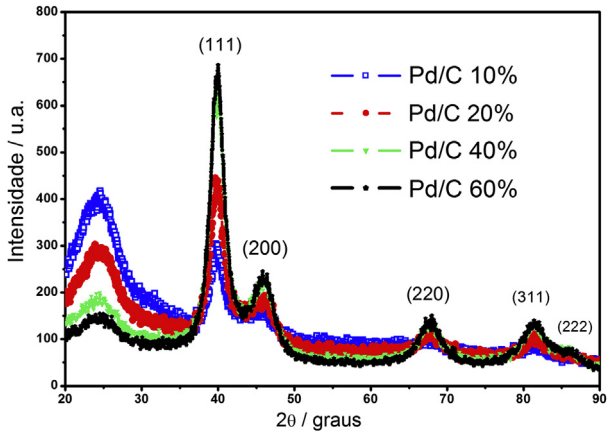

Fig. 1 – X-Ray diffractograms of palladium catalysts supported on carbon (Pd/C) with 10, 20, 40, and 60% of metallic masses.

The changing of the ratios between metal and carbon and the amounts of ionomer used with each catalyst also modified the thicknesses of the catalyst layers in MEA structures as presented in Tables 3 and 4. These differences in thickness changed the distances between the GDLs of each MEA and its membranes and affected its triple phase boundary in relation to managements of water, membrane moisture, and the reactant flow as well. In addition, the different specific surface areas of each catalyst (Table 5) also could significantly influence the results. Because of all these factors, the analysis of the results was made comparing the MEA performance with the standard of adjustment of Nafion ionomer obtained in our previous study (Pd/C 20% and 2.878 mgNI cm^{-2} or 59%NI) [12].

The MEAs prepared with Pd/C 10, 20, 40, and 60% using volume and fixed mass percentage as correlation criteria were evaluated from 25 until 90 °C (H_2 temperatures). The results obtained for H_2 at 40, 60, and 80 °C are presented in Figs. 3–5, respectively. Other temperature results are presented in the Supplementary Data.

Observing the polarization curves, it is clear that MEAs prepared according to the correlation by volume presented better performances than MEAs prepared by the fixed mass percentage criterion. The polarization curves obtained by other temperatures (presented in Supplementary Data) presented the same conclusion, in a general way. Thus, this criterion is more efficient to produce catalyst layers with different catalysts than a fixed mass percentage criterion. In order to compare MEA performances between 25 and 90 °C, the data shown in Figs. 6 and 7 present, respectively, the values of Open Circuit Potential (OCPs) and the values of Current density obtained at 500 mV (Cd_{500mV}).

From Fig. 6 it can be seen that all OCPs tended to decrease when the temperature increased, which can be related to membrane moisture and a joule effect in the fuel cell components. From Fig. 6 it can also be observed that MEAs with ionomer quantity calculated by catalyst volumes presented higher OCPs than MEAs with the same catalyst prepared using correlation by masses. These differences were greater in MEAs with Pd/C 10% between 25 and 90 °C and in MEAs with Pd/C 60% between 25 and 65 °C. Certainly, the differences observed in the evaluation of these electrodes are related with the ionomer quantity calculated from each method in evaluation,

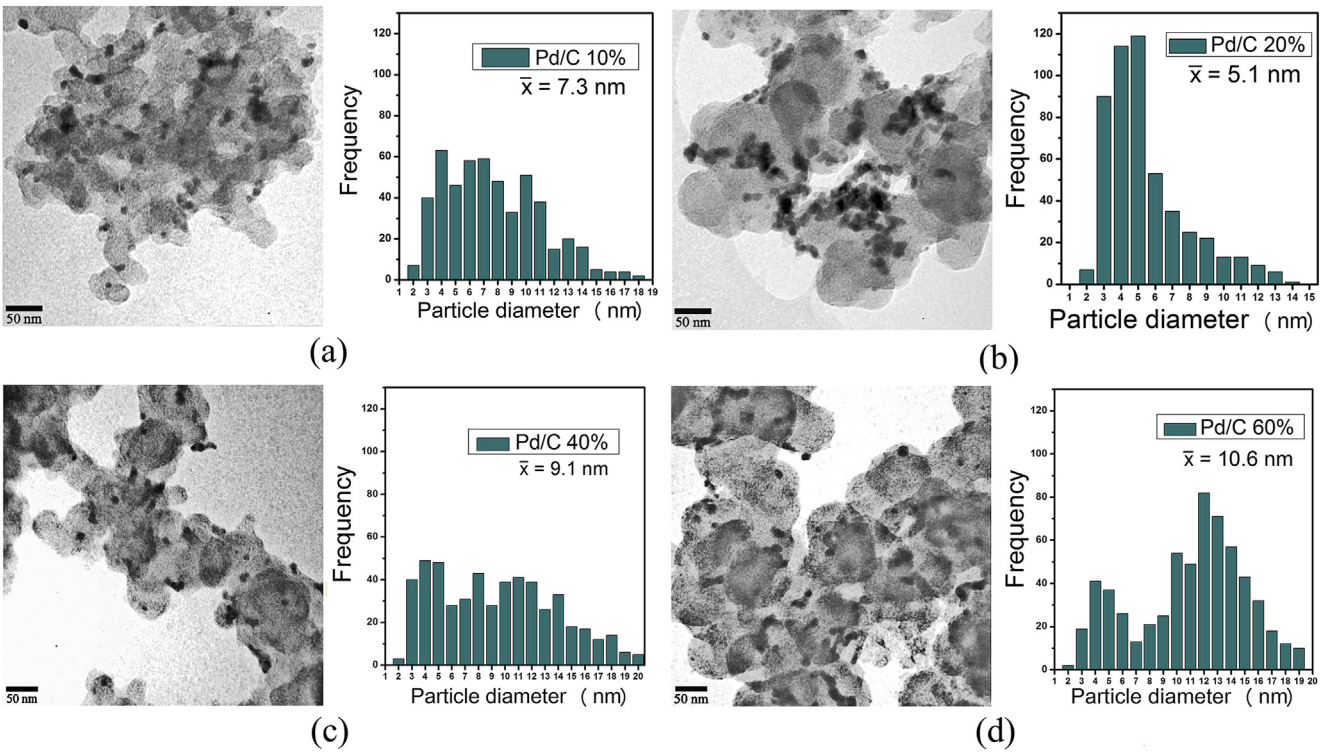

Fig. 2 – Images obtained by Transmission Electron Microscopy of Pd/C catalysts and their respective distributions of particle diameters. Metallic masses of (a) 10%; (b) 20%; (c) 40%; and (d) 60%.

which was the only difference between them. Obviously, the better performances obtained from MEAs prepared according with the ionomer quantities calculated from catalyst volumes means that this criterion results in the formation of more effectives triple phase boundary. By the other hand, the adjustment of ionomer quantity by mass was less effective in the OCPs than the adjustment by volume in all catalysts evaluated between 25 and 90 °C. MEAs prepared with correlation by volume also presented higher current densities at 500 mV (Cd_{500mV}) than MEAs prepared with correlation by mass in practically all conditions evaluated (Fig. 7). The performances obtained from MEAs with Pd/C 60% and Pd/C 40% prepared with correlation by volume (under and above 70 °C, respectively) were nearer those of the MEAs with Pd/C 20% than others, which demonstrates the major effectiveness of the correlation by volume, and also demonstrate the influence of operations conditions, like membrane humidification, in the performance of electrodes with different catalyst layer thickness.

From Fig. 7 it was also observed that the performance of MEAs with Pd/C 60% prepared with correlation by volume fell intensely above 65 °C (H_2). This behavior is still not completely understood, but analyzing Fig. 6 it can be seen that these comparative drops started in the open circuit potential. Since

Table 5 – Analysis of the composition of Pd/C catalyst with metal load of 10, 20, 40, and 60% by EDX; their average particle diameters; and specific surface areas.

Mass percent nominal value (%Pd)	Mass percent experimental value obtained by EDX (%Pd)	Average particle diameter (nm)[a]	Specific surface area ($m^2 \cdot g^{-1}$)
10.00	9.7 ± 0.3	7.3 ± 2.7	47.7 ± 3.7
20.00	19.9 ± 1.4	5.1 ± 1.8	58.1 ± 4.0
40.00	39.9 ± 0.2	9.1 ± 3.7	37.0 ± 3.5
60.00	59.6 ± 3.5	10.6 ± 3.9	36.4 ± 4.2

[a] Average size with average deviations.

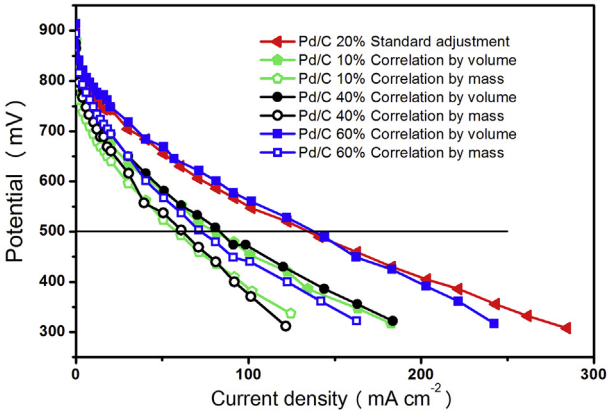

Fig. 3 – Polarization curves of MEAs prepared with Pd/C catalyst with metal loading of 10, 20, 40, and 60% and with Nafion ionomer quantity calculated according to catalyst masses and catalyst volumes. All MEAs were evaluated using H_2 at 40 °C and O_2 at 35 °C and single fuel cell at 30 °C.

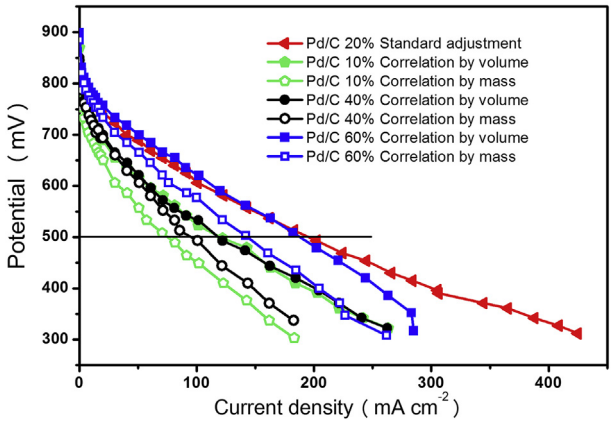

Fig. 4 – Polarization curves of MEAs prepared with Pd/C catalyst with metal loading of 10, 20, 40, and 60% and with Nafion ionomer quantity calculated according to catalyst masses and catalyst volumes. All MEAs were evaluated using H_2 at 60 °C and O_2 at 55 °C and single fuel cell at 50 °C.

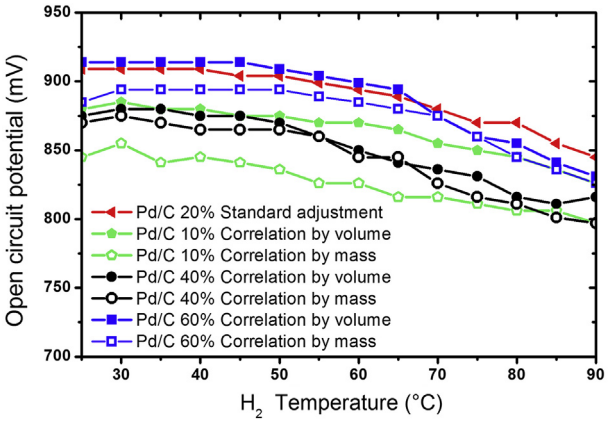

Fig. 6 – Open Circuit Potential of MEAs prepared with Pd/C catalyst with metal loading of 10, 20, 40, and 60% and with Nafion ionomer quantity calculated according to catalyst masses and catalyst volumes.

MEAs with Pd/C 60% prepared according to correlation by volume have less ionomer than MEAs prepared by mass correlation (Tables 3 and 4), these drops in performance above 65 °C can be related to other features such as the limited capacity of a thinner catalyst layer (around 15 μm from Table 3 data) performer a effective water management. In spite of this, above 70 °C the current densities obtained from MEAs prepared with Pd/C 60% and correlation by volume were similar to those obtained with correlation by mass, indicating that even in unfavorable operating conditions the volumetric criterion produces more effective MEAs. These results confirm the observation made from polarization curves and allow for the conclusion that to calculate the amount of Nafion ionomer to different catalysts using their volumes is more effective than to use the fixed mass percentage in order to compare them in fuel cell experiments. On the other hand, further additional studies can improve the calculation of volumetric correlation and make it even more efficient.

Considering that the specific surface area of palladium in each catalyst (Table 5) interfered in the current densities obtained at 500 mV in each MEA, to simulate the proportionality that could exist between the results if all the catalysts had the same SSA, in Fig. 8 the Cd_{500mV} value of each MEA is presented divided by the respective specific surface area of each catalyst (Cd_{500mV}/SSA).

From Fig. 8 it can be observed that if all catalysts had the same SSA, MEAs prepared with Pd/C 60% and Pd/C 40% and the quantity of ionomer calculated by volume would present higher performances than MEAs with Pd/C 20%, while MEAs prepared with these catalysts and the mass criterion would present performances similar to MEA with Pd/C 20%. Thus, it has been demonstrated that studies of catalyst layer thickness must adjust the amount of Nafion ionomer to each catalyst in order to compare their highest performances and that

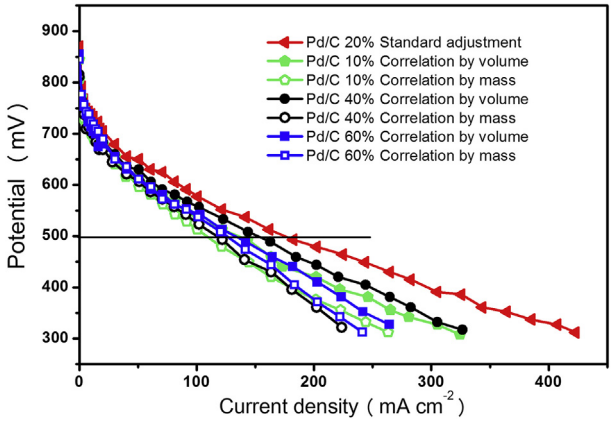

Fig. 5 – Polarization curves of MEAs prepared with Pd/C catalyst with metal loading of 10, 20, 40, and 60% and with Nafion ionomer quantity calculated according to catalyst masses and catalyst volumes. All MEAs were evaluated using H_2 at 80 °C and O_2 at 75 °C and single fuel cell at 65 °C.

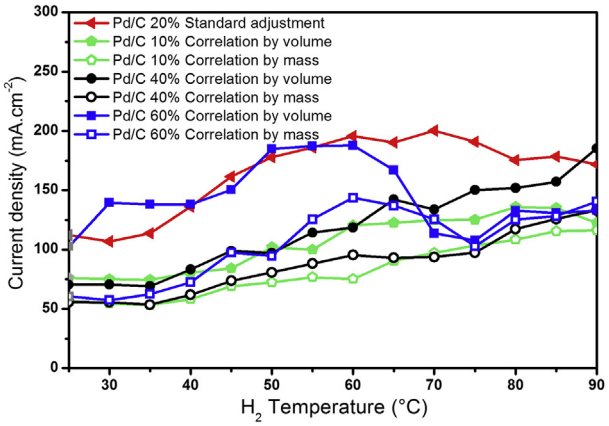

Fig. 7 – Current density obtained at 500 mV of MEAs prepared with Pd/C catalyst with metal loading of 10, 20, 40, and 60% and with Nafion ionomer quantity calculated according to catalyst masses and catalyst volumes.

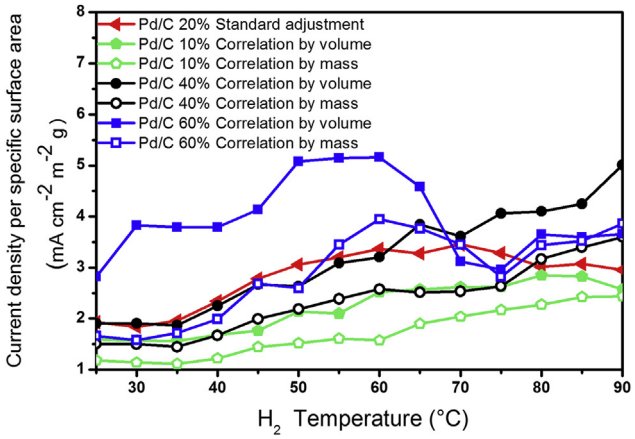

Fig. 8 – Current densities at 500 mV divided respectively by the specific surface areas of each catalyst (Cd_{500mV}/SSA). MEAs with amounts of ionomer calculated according to catalyst mass and catalyst volume criteria.

correlation by volume is much more effective than correlation by mass in this kind of study, i.e., it results in more effective triple phase boundary.

From the presented results it is also concluded that studies of catalyst layer thickness must also consider the temperature of each PEMFC application, because MEAs with Pd/C 60% and Pd/C 40% with catalyst layer thickness about 15 and 33 μm, respectively, showed better performance in different temperature ranges. Probably the adjustment of features such as GDL hydrophobicity and membrane thickness, among others, can lead to more efficient MEAs by each condition. It is important to point out that if experiments were performed only at 70 or 80 °C, most of these analyses would not be possible. Thus, it is concluded that the evaluation of MEAs in a wide range of temperatures enables more comprehensive analysis and the obtaining of a better understanding of their operation features.

The validation of the correlation by volume criterion by other support materials and others metals should be performed in future work, as well as the study of the most appropriate method [86–89] for determining the specific volume of catalysts or support materials.

As previously said, the Supplementary Data presents the performance evaluation of MEAs prepared according with the volume and mass criteria using Pd/C 10, 20, 30 and 40% between 25 and 90 °C, and additionally presents the performance comparison with these MEAs with others prepared using Pt/C 20% catalyst, as described in experimental section.

Conclusions

The ratio between metal and carbon support interfered in the amount of ionomer needed to obtain MEAs with higher performance, due to the different densities of these materials.

MEAs prepared with the adjustment of the quantity of Nafion ionomer in the catalyst layer, according to the catalyst volume criterion, determined by the sum of the volumes of its components (metal and carbon support), presented higher performance than MEAs prepared according to the use of a fixed mass percentage criterion, which is the method widely used in PEMFC research. Indicating that the MEA structures obtained from ionomer quantity calculated by the volumetric correlation criterion resulted in more effective triple phase boundary.

Dividing the MEA performances by the specific surface area of each catalyst showed that MEAs with the same catalyst (Pd/C 10, 40, or 60%) and ionomer quantity correlated by catalyst volume criterion presented higher performance than MEAs with ionomer quantity correlated by mass criterion, which indicates the importance of using the volumetric correlation in studies of catalyst layer thickness. MEAs with Pd/C 60% and Pd/C 40% with catalyst layer thickness about 15 and 33 μm, respectively, performed better in different temperature ranges. Studies of catalyst layer thickness must evaluate MEAs in a wide range of temperatures to obtain a better understanding of their features for each PEMFC work condition.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.ijhydene.2014.12.114.

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