

CHEMOMETRIC STUDY OF THE EFFECTS OF $\text{PtRu}:\text{BH}_4^-$ MOLAR RATIO AND THE SOLVENT USED IN THE PREPARATION OF PtRu/C ELECTROCATALYSTS FOR DIRECT METHANOL FUEL CELL ANODES

N.S.O. Polanco¹, M.M. Tusi², M. Brandalise³, A.O. Neto⁴, E.V. Spinacé⁴

¹ Instituto de Pesquisas Energéticas e Nucleares – IPEN/CNEN-RS, São Paulo, SP, Brazil

² Universidade Regional Integrada do Alto Uruguai e das Missões – URI, Santiago, RS, Brazil.

³ Instituto Federal Farroupilha – IFF, São Vicente do Sul, RS, Brazil.
e-mail: mmtusi@gmail.com

ABSTRACT

A chemometric study was performed to evaluate the influence of the $\text{BH}_4^-:\text{PtRu}$ molar ratio (5 and 15) and the solvent (water or isopropyl alcohol) in the preparation of PtRu/C electrocatalysts for Direct Methanol Fuel Cell (DMFC) anodes. The obtained materials were characterized by Energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD) and transmission electron microscopy (TEM). For both solvents increasing the $\text{BH}_4^-:\text{PtRu}$ molar ratio from 5 to 15 leads to a decrease of the mean nanoparticle sizes and, using water as solvent, it was observed better distributions of the nanoparticles on the carbon support than using isopropyl alcohol. The DMFC maximum power density was obtained using a electrocatalyst prepared with a $\text{BH}_4^-:\text{PtRu}$ molar ratio of 15 and water as solvent. The analysis of the effect of interaction of the two parameters showed that the variations of the maximum power density was more dependent of the $\text{BH}_4^-:\text{PtRu}$ molar ratio than of the solvent used.

Keywords: PtRu/C , methanol, factorial design

Introduction

In the direct methanol fuel cells (DMFC) the methanol is fed directly into the fuel cell, without any previous chemical modification or purification, and it is oxidized at the anode, while oxygen is reduced at the cathode. The best results of these devices are reached using PtRu nanoparticles supported on carbon, denominated PtRu/C electrocatalysts. However the performance of PtRu/C electrocatalyst is strongly dependent of methods of preparation [1,2].

Hyun et al [3] evaluated the effect of NaBH_4 concentration on the characteristics of PtRu/C catalysts prepared by the impregnation method, here called borohydride reduction method. The obtained electrocatalysts showed different surface compositions and different particle sizes and level of dispersion. Therefore the use of adequate NaBH_4 concentration possibility adjusting optimal surface composition and the active metal surface area.

Unlike the multivariate analysis, the factorial design is a tool able to evaluate effects and interaction among effects caused by wished parameters on determined property. Another advantage of factorial design in relation to multivariate analysis is to reduce the number of experiments [4].

Thus, in this work it was evaluated (by chemometric methods) the influences of BH_4^- :metal ratio and the solvent (water or isopropyl alcohol) used in the preparation of PtRu/C electrocatalysts on the maximum power density of a single direct methanol fuel cell.

Experimental

PtRu/C electrocatalysts with 20 wt% of metal loading and Pt:Ru atomic ratio of 50:50 were prepared by a borohydride reduction method using different conditions. In this borohydride reduction method, a solution containing sodium hydroxide and sodium borohydride (NaBH_4) was added to a mixture containing a solvent, the metallic precursors ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$) and the carbon support Vulcan XC72. The conditions tested were: BH_4^- :metal ratios of 5 and 15 and water or isopropyl alcohol as solvent.

The obtained materials were characterized by energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD) and transmission electron microscopy (TEM). Membrane Electrode Assemblies (MEA's) were produced and the tests in single direct methanol fuel cells were performed at 100°C.

The Table 1 shows the levels of the BH_4^- :metal ratio (effect R) and levels of solvent (effect S).

Table 1 - Levels of the BH₄⁻:metal ratio (effect R) and levels of solvent (effect S).

Experiment	Solvent	BH ₄ ⁻ :metal ratio	Interaction
y ₁	water (+)	5 (-)	+ -
y ₂	water (+)	15 (+)	+ +
y ₃	isopropyl alcohol (-)	5 (-)	- -
y ₄	isopropyl alcohol (-)	15 (+)	- +

The effects of BH₄⁻:metal ratio (R) and solvent (S) in maximum power density besides the interaction between this two parameters (RS) were calculated using the Equations 1-3.

$$R = \left(\frac{y_2 + y_4}{2} \right) - \left(\frac{y_1 + y_3}{2} \right) \quad (1)$$

$$S = \left(\frac{y_1 + y_2}{2} \right) - \left(\frac{y_3 + y_4}{2} \right) \quad (2)$$

$$RS = \left(\frac{y_2 + y_3}{2} \right) - \left(\frac{y_1 + y_4}{2} \right) \quad (3)$$

The “y” in the equations are the responses in the experiments. Thus, the effects R and S are the difference between the mean response of superior (+) and inferior (-) levels of BH₄⁻:metal ratio (equation 1) or solvent (equation 2). The interaction of effects (RS) is calculated by difference between the mean response of superior (++) and inferior (- -) levels of BH₄⁻:metal ratio and solvent effects [5].

Results and Discussion

PtRu/C electrocatalysts (20 wt% of metal loading and Pt:Ru ratio of 50:50) were prepared using water or isopropyl alcohol as solvents and BH₄⁻:metal molar ratio of 5 and 15. The Table 2 shown the Pt:Ru atomic ratios obtained by EDX and the mean crystallite sizes of the obtained materials. All obtained materials presented Pt:Ru atomic ratios similar to the nominal values.

Table 2 - Pt:Ru ratio obtained by EDX and mean crystallite size of obtained materials.

BH₄⁻:metal molar ratio	Solvent	Pt:Ru atomic ratio (EDX)	Mean crystallite size (nm)
5	water	46:54	3
15	water	46:54	2
5	isopropyl alcohol	54:46	3
15	isopropyl alcohol	57:43	2

The Fig. 1 presents X-ray diffractograms of PtRu/C electrocatalysts prepared by a borohydride reduction method in different conditions.

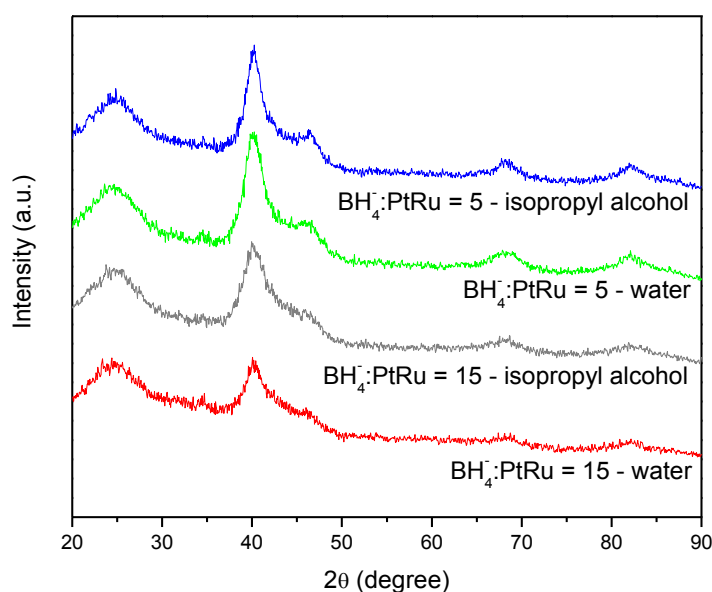


Figure 1 X-ray diffraction of PtRu/C electrocatalysts prepared by borohydride reduction in different conditions.

All materials showed a broad peak at about $2\theta = 25^\circ$ associated to carbon support and five peaks at about $2\theta = 40^\circ, 47^\circ, 67^\circ, 82^\circ$ and 87° attributed to (111), (200), (220), (311) and (222) planes of face-centered cubic structure of platinum and its alloys [6,7]. Peaks associated to RuO₂ phases were not observed, however the presence as amorphous phases could not be discarded [7,8]. The mean crystallite sizes obtained using the Scherrer equation shown values in the range of 2-3 nm and an increase of BH₄⁻:metal molar ratio from 5 to 15 seems to decrease the crystallite sizes for both solvents.

The Fig. 2 show images obtained by TEM and histograms with the distribution of particle sizes of the obtained PtRu/C electrocatalysts.

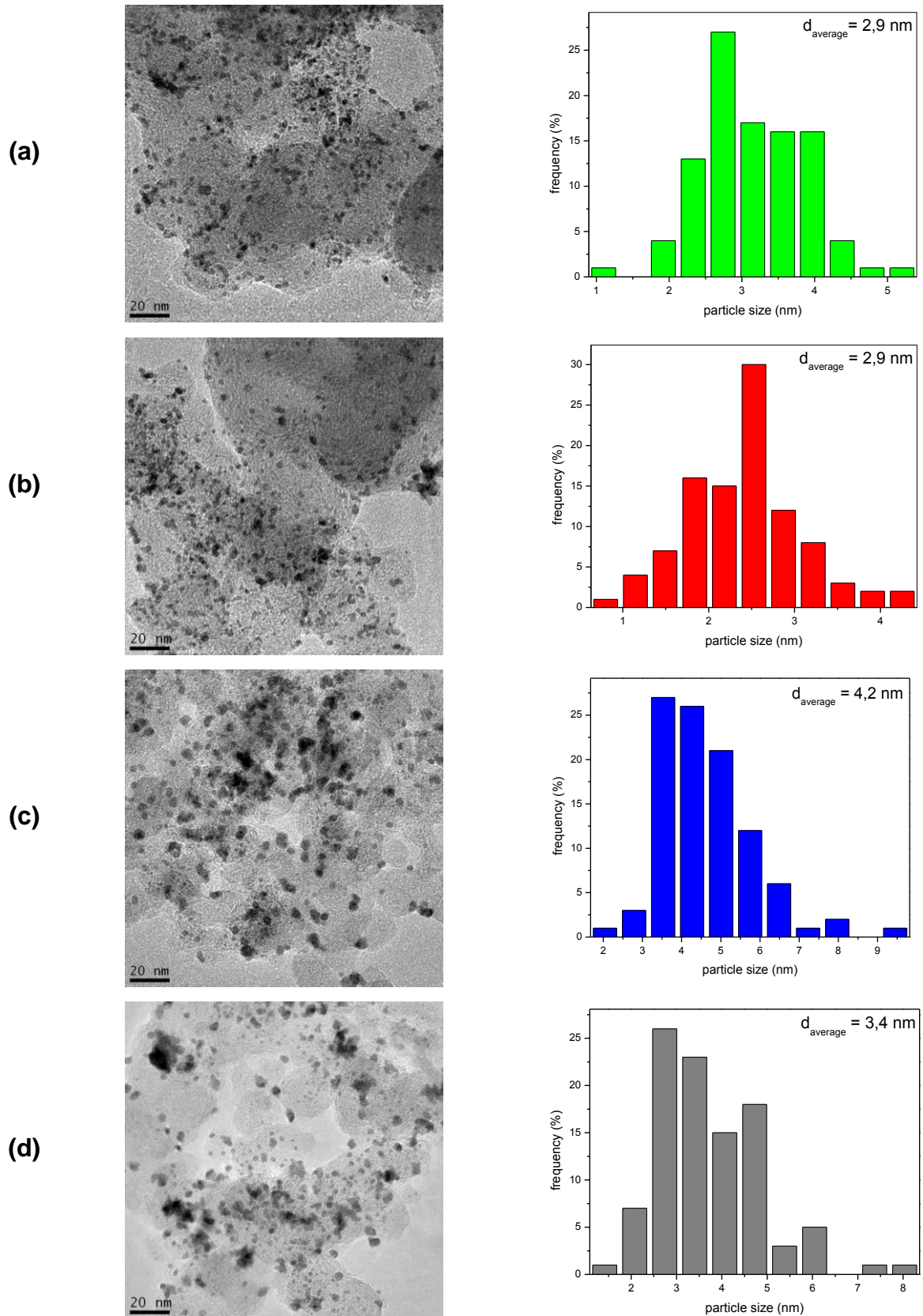


Figure 2 – TEM micrographs and histograms of distribution of mean particle size of electrocatalysts prepared using (a) water and BH_4^- :PtRu molar ratio of 5, (b) water and BH_4^- :PtRu molar ratio of 15, (c) isopropyl alcohol and BH_4^- :PtRu molar ratio of 5, (d) isopropyl alcohol and BH_4^- :PtRu molar ratio of 15.

The micrographs of the materials prepared in water reveal a good distribution of the metallic nanoparticles on the carbon support, while the electrocatalysts prepared using isopropyl alcohol as solvent showed some agglomerates of the nanoparticles. The histograms present a monomodal pattern of distribution of particle sizes. The mean particle sizes were 2.9 nm for both materials prepared using water as solvent. The material obtained using isopropyl alcohol as solvent and BH_4^- :metal ratio of 15 presented a mean particle size of 3.4 nm while the material obtained using isopropyl alcohol as solvent and BH_4^- :metal ratio of 5 showed an increase of the mean particle size (4.2 nm).

The Figure 3 presents the polarization curves and the power density vs current density of the PtRu/C electrocatalysts.

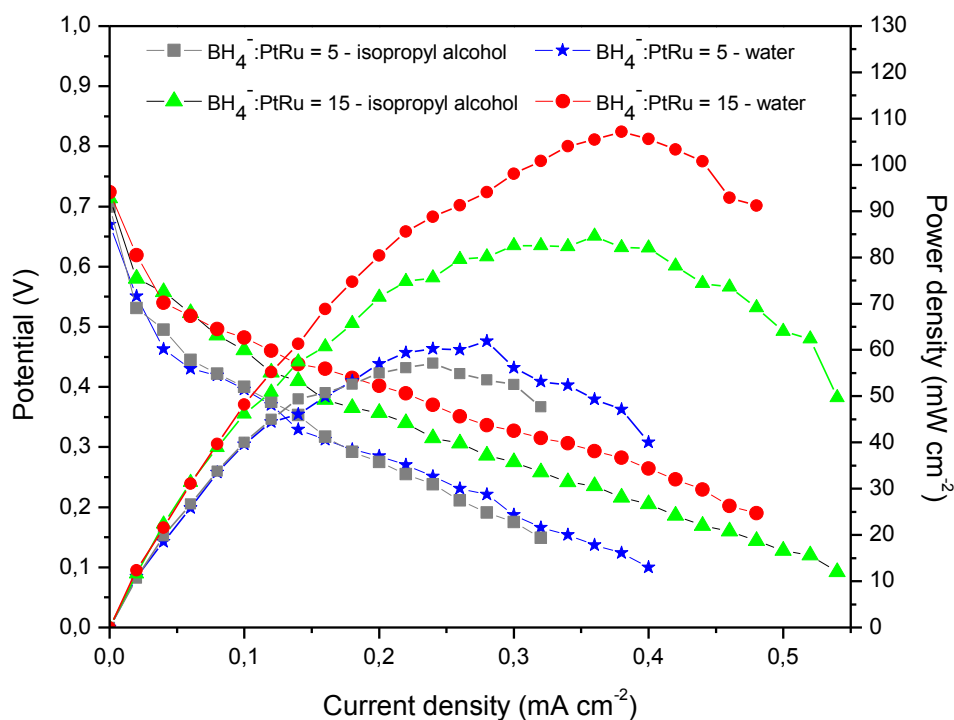


Figura 3 Performance of DMFC of 5 cm^2 using PtRu/C (load of $1,0 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$) in the anode and Pt/C electrocatalyst of BASF (load of $1,0 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$) in the cathode, Nafion 117 membrane, 2 mol L^{-1} methanol solution (flow of 2 mL min^{-1}), oxygen pressure of 2 bar and cell temperature of $100 \text{ }^\circ\text{C}$.

The maximum power densities obtained using the PtRu/C electrocatalysts were: PtRu/C (BH_4^- :metal = 15 - water) > PtRu/C (BH_4^- :metal = 5 - water) > PtRu/C (BH_4^- :metal = 5 - isopropyl alcohol) ~ PtRu/C (BH_4^- :metal = 15 - isopropyl alcohol). The results of single-DMFC tests can be explained by the smaller mean particle sizes and a better distribution of the nanoparticles on the carbon support of the PtRu/C electrocatalysts prepared using water as solvent.

The maximum power densities obtained by single cell tests (in duplicate) and mean maximum power densities are shown in Table 3.

Table 3 – Maximum power densities obtained by single cell tests (in duplicate) and mean maximum power densities used to calculate the influence of BH_4^- :metal ratio and solvent on maximum power density.

Experiment	BH_4^- :PtRu ratio	Solvent	Maximum power density (mW cm^{-2})		Mean maximum power density (mW cm^{-2})
y_1	5	water	57	60	58.5
y_2	15	water	102	107	104.5
y_3	5	isopropyl alcohol	52	57	54.5
y_4	15	isopropyl alcohol	85	86	85.5

As shown in Table 3, when water is used as solvent and the BH_4^- :metal ratio is increased from 5 to 15 (Experiments 1 and 2) the mean power densities increase from 58.5 mW cm^{-2} to $104.50 \text{ mW cm}^{-2}$ i.e. an increase of 46 mW cm^{-2} . When isopropyl alcohol is used as solvent and the BH_4^- :metal ratio is increased from 5 to 15 (Experiments 3 and 4) the mean power densities increase only 31 mW cm^{-2} . Thus, the effect of BH_4^- :metal ratio depends on the solvent used and vice versa (there are an interaction between this parameters). Using a BH_4^- :metal ratio of 5 (Experiments 1 and 3) the change of solvent results in a variation of 4 mW cm^{-2} in the maximum power density. Using a BH_4^- :metal ratio of 15 (Experiments 2 and 4) the change of solvent results in a variation of 19 mW cm^{-2} in maximum power density.

It is possible gives a geometric interpretation to the effects calculated previously by representation of the factorial design in a Cartesian system, with each parameter in an axis. The space defined by two parameters is a plan and the four experiments are put in the vertices of a square (Figure 4).

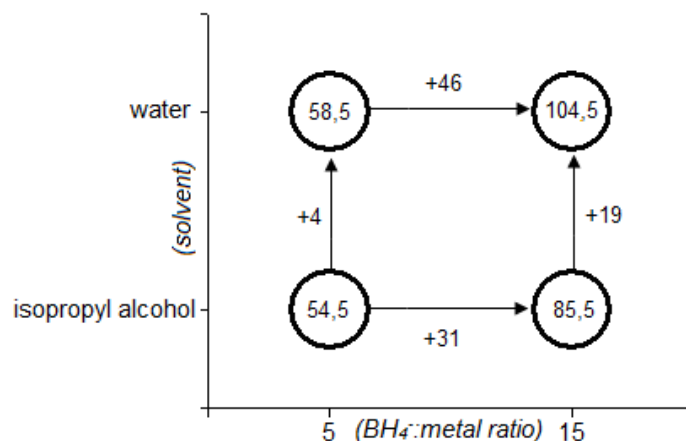


Figure 4 Diagram to interpretation of results of the 2^2 factorial design. The values in the vertices of square are the mean values of maximum power density obtained in the single cell tests.

Using the equations 1 and 2 and the data of Table 2 they were calculated the influences of solvent (S) and BH_4^- :metal ratio (R) separately. Also it was calculated the effect of interaction of the two parameters (BH_4^- :metal ratio and solvent - RS) on maximum power density (Table 4).

Table 4 – Calculated effects to 2^2 factorial design.

<i>Global average</i>	75.75 ± 1.37
<i>Main effects</i>	
R	38.50 ± 2.74
S	11.50 ± 2.74
<i>Effect of interaction</i>	
RS	7.50 ± 2.74

The main effect of BH_4^- :metal ratio (R) calculated was 38.5 mW cm^{-2} , while the main effect of solvent (S) calculated was 11.50 mW cm^{-2} . The interaction between BH_4^- :metal ratio and solvent (RS) calculated was 7.50 mW cm^{-2} . Therefore, the variations of maximum power density are more dependent of the BH_4^- :metal ratio (effect R) than of the solvent used.

Conclusion

A factorial design was performed and the effects of BH_4^- :PtRu molar ratio and the solvent used in the preparation of PtRu/C electrocatalysts by a borohydride reduction method were measured. In this study the main effect of BH_4^- :PtRu molar ratio was more significant than the main effect of solvent i.e. the variations in the maximum power density of a DMFC are higher for a variation of the amount of borohydride used in the reduction than for a changing of the solvent of the reaction medium. The interaction effect of the two analyzed parameters was smaller than the main effects, however this interaction effect can not be considered negligible

5. References

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