

Effects of Solvent and Concentration of Borohydride for the Preparation of PtRu/C Electrocatalysts for Direct Methanol Fuel Cell Anodes – A Factorial Design Study

Polanco Nataly Soares de Oliveira^{1,a}, Tusi Marcelo Marques^{2,b},
Brandalise Michele^{3,c}, Oliveira Neto Almir^{1,d}, Spinacé Estevam Vítoro^{1,e}

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.

^anataly_polanco@hotmail.com, ^bmmtusi@gmail.com, ^cmbtusi@gmail.com, ^daolivei@ipen.br,
^eespina@ipen.br

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Abstract. A factorial design study was performed to evaluate the influence of the BH_4^- :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 BH_4^- :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 BH_4^- :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 BH_4^- :PtRu molar ratio than of the solvent used.

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].

The preparation and characterization of electrocatalysts aiming fuel cell applications are themes very addressed in the scientific literature. However, the measure of the effects of each studied parameters is not evaluated in these articles. They are related only a comparison among the studied materials and explanations about the results. 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 [2,3].

The impregnation method, here called borohydride reduction method, is one of the most widely studied methods for the preparation of electrocatalysts [4,5]. This method is simple to perform, relatively reproducible and effective in the preparation of smaller particles [5].

The use of factorial design in the synthesis of electrocatalysts is little used and papers about this issue are few. In a few articles from the area, Freitas et al. [6] measure the effect of the preparation variables on the electrode surface areas of Pt electrodes obtained using the polymeric precursor method on Ti substrates using a factorial design 2^3 . The factorial design indicated that the main effect for citric acid:ethylene glycol ratio is more significant than those calculated for temperature and Pt: citric acid ratio effects.

Hyun et al [5] evaluated the effect of NaBH₄ concentration on the characteristics of PtRu/C catalysts prepared by the impregnation method. The obtained electrocatalysts showed different surface compositions and different particle sizes and level of dispersion. Therefore the use of adequate NaBH₄ concentration possibility adjusting optimal surface composition and the active metal surface area. However, the effect of the parameters studied (amount of borohydride and solvent) was not evaluated.

Thus, in this work it was evaluated (using a factorial design 2³) the influences of BH₄⁻: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. The electrocatalysts were prepared using H₂PtCl₆.6H₂O and RuCl₃.xH₂O as metal sources, NaBH₄ as reducing agent and carbon Vulcan XC72 as support. The metal sources were dissolved in a mixture of water/2-propanol (50/50, v/v) and the carbon support was dispersed in the solution. The resulting mixture was submitted to an ultrasonic bath for 5 min. After this a solution of sodium borohydride was added under stirring in one portion at room temperature. Finally, the obtained solid was filtered, washed with water and dried at 70 °C for 2 h.

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 BH₄⁻: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 (level)	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 Eq. 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 [3].

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 BH_4^- :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.

BH_4^- : 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. 1a presents X-ray diffractograms of PtRu/C electrocatalysts prepared by a borohydride reduction method in different conditions.

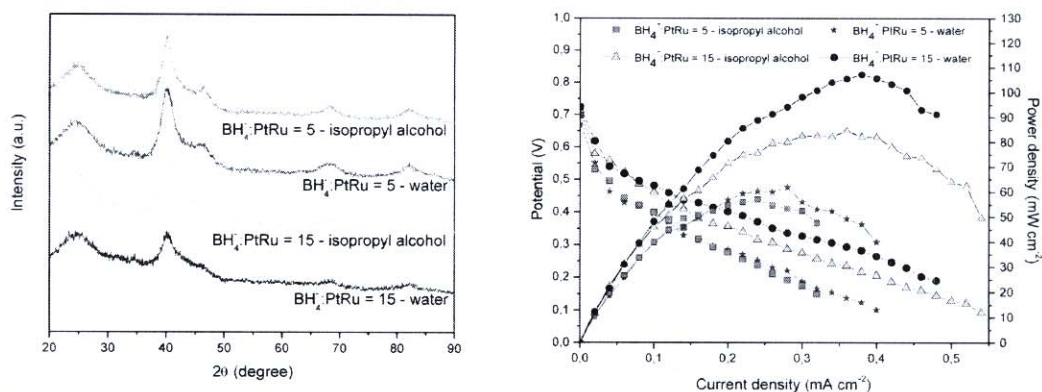


Fig. 1– (a) X-ray diffraction of PtRu/C electrocatalysts prepared by borohydride reduction in different conditions. (b) Performance of DMFC of 5 cm^2 using PtRu/C (load of 1,0 $\text{mg}_{\text{Pt}} \text{cm}^{-2}$) in the anode and Pt/C electrocatalyst of BASF (load of 1,0 $\text{mg}_{\text{Pt}} \text{cm}^{-2}$) 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 °C.

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° , 67° , 82° and 87° attributed to (111), (200), (220), (311) and (222) planes of face-centered cubic structure of platinum and its alloys [7]. Peaks associated to RuO_2 phases were not observed, however the presence as amorphous phases could not be discarded [7]. The mean crystallite sizes obtained using the Scherrer equation shown values in the range of 2-3 nm and an increase of BH_4^- :metal molar ratio from 5 to 15 seems to decrease the crystallite sizes for both solvents. Large particles are generally created under low concentrations of reducing agent (in this case, NaBH_4) because the nuclei growth is faster than the nucleation [5,8].

The Fig. 2 show images obtained by TEM and histograms with the distribution of particle sizes of the obtained PtRu/C electrocatalysts. 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 solvent affects on the course of nucleation and growth of the nanoparticles and the strength of their adhesion to the carbon support and its influence is associated to i) the strength of the metal

precursors adsorption at the carbon surface; ii) the nature of the solvated ions; iii) the energy of the liquid/solid (metal, carbon) interfaces; iv) the redox potentials of the reacting systems; and v) the strength of the adsorption of the solution components at the surfaces of the carbon and the growing nanoparticles [9].

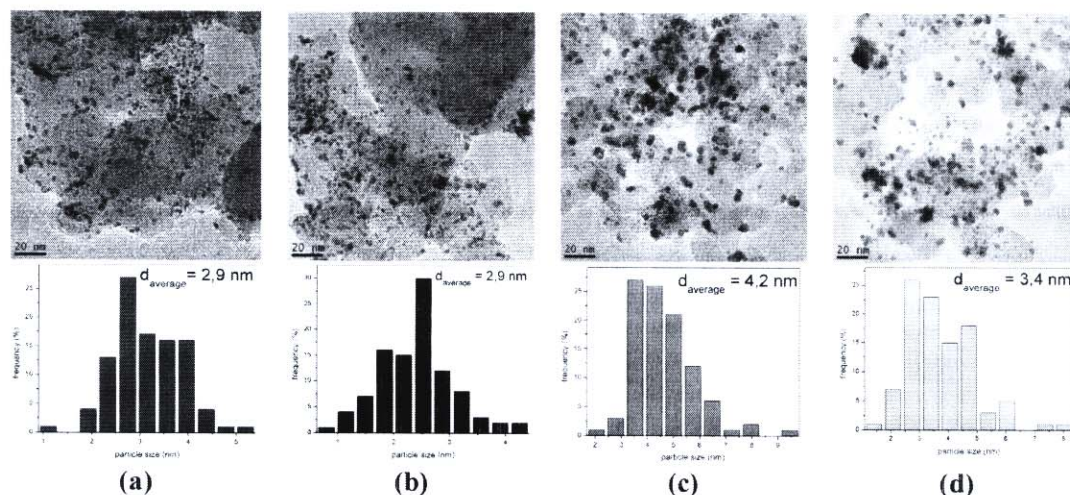


Fig. 2 – TEM micrographs and histograms of distribution of mean particle size of electrocatalysts prepared using (a) water and BH_4^- :PtRu molar ratio of 5, (b) water and BH_4^- :PtRu molar ratio of 15, (c) isopropyl alcohol and BH_4^- :PtRu molar ratio of 5, (d) isopropyl alcohol and BH_4^- :PtRu molar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

The Figure 1b presents the polarization curves and the power density vs current density of the PtRu/C electrocatalysts. 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) \approx 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. Additionally, lower concentrations of NaBH_4 generate nanoparticles with surface rich in Ru decreasing the activity [5,10].

Hiromi et al. [11] related that the dissociative adsorption of methanol is to easily occur on the Pt surface rather than the Ru surface at room temperature. However, a minimum of number of the neighboring site of the Pt and Ru atoms is needed. Jow et al. [12] reported that the optimum Ru surface content on the Pt–Ru electrocatalysts prepared by co-electrodeposition is 25 atom%.

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		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.

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 borohydride concentration (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

In this work they were prepared PtRu/C electrocatalysts in different conditions to evaluate the influence of solvent and borohydride concentration in the maximum power density obtained in single DMFC's using the obtained electrocatalysts like anode. All PtRu/C electrocatalysts presented in diffractograms peaks associated to Pt_{fcc} phase and absence of Ru phases. It was observed that lower concentration of borohydride leads to larger particles, while the use of water like solvent generate smaller particles and better distribution of this particles in the carbon support. The PtRu/C electrocatalyst prepared using water as solvent and a BH_4^- :metal ratio of 15 showed the better performance in single DFMC, probably, due the smaller particles combined to a good distribution of particles in the support and ideal superficial composition of nanoparticles. It was possible to measure the effects of solvent and borohydride concentration in the maximum power density os single DMFC's by the factorial design 2^2 . The main effect for concentration of borohydride (BH_4^- :PtRu ratio) is more significant than those calculated for solvent effect. The interaction effect of the two analyzed parameters was smaller than the main effects, however this interaction effect can not be considered negligible.

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