International Conference on Renewable Energies and Power Quality (ICREPQ'17)
Malaga (Spain), 4th to 6th April, 2017
Renewable Energy and Power Quality Journal (RE&PQJ)
ISSN 2172-038 X, No.15 April 2017

Electrocatalytic performance comparison of Pt/V and Pd/V electrocatalysts for ethanol oxidation reaction

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Abstract

Direct ethanol fuel cells (DEFCs) operate at low temperature, which makes the oxidation and reduction reactions slower, requiring electrocatalysts able to accelerate these reactions. In the present work, commercial Vulcan carbon (V) supported Pt and Pd catalysts were compared as electrocatalysts for ethanol oxidation reaction (EOR) in acidic and alkaline medium, respectively. Cyclic voltammetries obtained in presence of ethanol showing a better catalytic performance for the Pd/V electroctalyst compared to the Pt/V electrocatalyst. The maximum current density related with the EOR in a 1.0 mol L^{-1} ethanol + 1.0 mol L^{-1} NaOH solution was 236.9 A g Pd^{-1} for Pd/V. The better performance of the Pd/V electrocatalyst can be associated with a lower Pd nanoparticles sizes and higher particles dispersion onto the Vulcan carbon surface in the Pd/V electrocatalyst. The onset potential for the EOR was 0.2 V *vs.* SCE for the Pt/V sample and -0.6 V *vs.* Hg/HgO for the Pd/V sample.

Key words

Energy conversion, Direct Ethanol Fuel Cells, Pt catalyst, Pd catalyst, Ethanol oxidation reaction.

1. Introduction

Direct ethanol fuel cells (DEFCs) show a wide potential as technology to produce clean energy, especially for provide an efficient fuel conversion with low pollutants emission. These are systems that operate at low temperatures and convert chemical energy directly into electricity. Ethanol presents a great advantage in respect to its use, since Brazil can produce ethanol from sugar cane at extremely competitive prices [1, 2].

DEFCs operate at low temperature, which makes the oxidation and reduction reactions slower, requiring electrocatalysts able to accelerate these reactions. DEFCs can operate in acidic or in alkaline medium. In the acidic DEFCs, platinum is well known as the most suitable anodic catalyst for ethanol oxidation reaction (EOR), because of its excellent catalytic activity and stability [3], but the use of platinum based catalysts have the disadvantage of being very expensive. On the other hand, in alkaline DEFCs the fuel oxidation and oxygen reduction reactions are faster compared to the acidic DEFCs. The inherently faster kinetics in alkaline DEFCs allows the use of non-Pt electrocatalysts such as Pd, making them potentially low cost in comparison to others electroctalyst that use platinum based electrocatalysts [4]. In addition, the use of a non-Pt electrocatalyst on the cathode eliminates the oxidation of the fuel that may be transported from the anode, which makes the cathodic potential much higher than that in acidic DEFFCs [3]. Besides, the exchange membranes used in alkaline FCs have lower fuel permeability and allow better water management. Thus that simplifies the cell design, since the ionic current happens due to the hydroxide ions conduction [4, 5, 6].

In the present work, we compared the electroctalytic performance of Pt and Pd Vulcan supported electroctalysts for EOR.

2. Materials and methods

A. Electrocatalysts preparation and characterization

The synthesis of Vulcan carbon supported Pt catalyst sample (Pt/V) was already explained in a previous work [7]. Impregnation/reduction method was employed, using ethylene glycol as reduction agent and $H_2PtCl_6.6H_2O$ salt as catalyst precursor. Adequate amounts of support (V) and salt were mixed together to obtain the electrocatalyst Pt/V. Vulcan carbon supported Pd catalyst sample (Pd/V) was prepared based on previous works [8,6]. Briefly, 10 mL of ethylene glycol was added to 0.3 g of carbon material (V) and ultrasonicated for 30 min. The mixture of 10 mL of ethylene glycol: water (75:25 v/v) was used to dissolve a known amount of palladium (II) chloride salt ($PdCl_2$), added to the carbon slurry and mixed thoroughly for 15 min. A mixture of sodium borohydride ($NaBH_4$) and ethylene glycol ($HOCH_2CH_2OH$) with a 1:10 M ratio was slowly added to the carbon black catalytic slurry with vigorous stirring and then heated at 35 °C for 4 h. The electrocatalyst was left to cool, filtered and then washed with deionized water until a neutral pH was obtained. The electrocatalysts was dried in a muffle furnace at 105 °C until constant mass. The Vulcan carbon (V) corresponds to a commercial Vulcan XC-72 (Cabot Corporation). Thermogravimetric analysis (TGA) was performed on the samples using Shimadzu TG-50 equipment in a dynamic air atmosphere, in the temperature range of 25 to 800 °C, at constant heating rate of 10 °C min^{-1}, with sample masses between 8.0 and 10.0 mg in a platinum crucible. The constant mass at the end of the thermogravimetric curve was related to the amount of catalyst present in the sample. X-Ray diffraction (XRD) was performed using Rigaku Ultima IV with $K_{\alpha 1}$ X-ray radiation of Cu (1.54 Å). The diffractograms were recorded for a 2θ in range of 30-90° with step size of 0.02° and scan time of 2 s per step. Morphological information for the samples was obtained with JEOLJEM 2010 TEM, operating at 200 kV. The electrochemical measurements of the Pt/V and Pd/V samples were carried out in a 1.0 mol L^{-1} ethanol + 0.5 mol L^{-1} H_2SO_4 solution and in a 1.0 mol L^{-1} ethanol + 1.0 mol L^{-1} NaOH solution respectively. Measurements were carried out at room temperature in a standard three-electrode cell with a Pt wire as counter electrode, and using a potentiostat/galvanostat AUTOLAB PGSTAT 302N as was described in our previous work [9]. Saturated Calomel Electrode (SCE) reference electrode was used for the experiments in acidic electrolyte and Hg/HgO reference electrode in alkaline medium. As working electrode, a graphite disk was used. Its geometric area was 0.29 cm^2, and it was coated with a suspension of 1.0 mg of electrocatalyst powder in Nafion®. All the cyclic voltammetries were performed with scan rate of 10 mV s^{-1}, and in a potential range from -0,14 to 0,96 V *vs.* SCE for the Pt/V sample [10] and from -0.9 to 0.3 V *vs.* Hg/HgO electrode for the Pd/V. Prior to the electrochemical experiments the solutions were deaerated by N_2 purging for 10 min. In order to avoid the oxygen presence in the medium, nitrogen stream was led inside the solution during all of the electrochemical experiments.

3. Results and discussion

From TGA curves in air atmosphere it is possible to estimate the Pt and Pd metal load in the prepared electrocatalysts [11, 12]. The Pt mass content of 36 % and Pd mass content of 13 % was determined from the remaining mass in the TGA curves (Figure 1) of the Pt/V and Pd/V samples, respectively. Taken into account the amount of metal salt used in the synthesis, a metallic mass content of 40% was expected for both electrocatalysts. The lowest Pd° mass content in the Pd/V it may be associated with a lower Pd^{2+} reduction reaction rate.

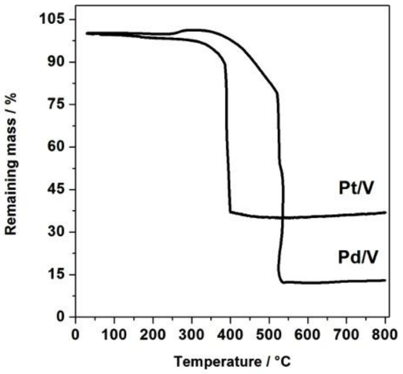

Figure 1. TGA curves in air atmosphere of the prepared samples.

Figure 2 compares the XRD diffractograms of Pt/V and Pd/V samples. In Figure 2a it can be seen the diffraction peaks located at 39°, 46°, 68°, 81° and 87° which correspond to the planes (1 1 1) (2 0 0) (2 2 0) (3 1 1) and (2 2 2) of platinum, representing a typical platinum cubic face centered crystal structure [13, 14, 15]. For Pd/V sample (Figure 2b), the peaks at 40.0°, 46.6°, 68.0°, 81.94° and 86.48° are indexed as (111), (200), (220), (311) and (222) crystal planes of the face-centered cubic (fcc) structure of Pd [16]. The equation 1, based on the Bragg's law [17] and valid for crystalline cubic symmetry, was used to estimate lattice parameter *a* as follow:

$$a = \frac{n\lambda}{2\, sen\, \theta} \cdot \sqrt{h^2 + k^2 + l^2} \qquad \textbf{(1)}$$

where, *n* represents the reflection order (it was considered *n = 1* - first order reflection), λ is the wavelength (1.5418 nm for Cu-Kα radiation), θ is the half of 2θ of the four peaks and *h, k, l* are the Miller index for (111) (200) (220) and (311) planes. For each planes, the determined *a* lattice parameter value was 3.92 Å for the Pt/V sample and 3.90 Å for the Pd/V. These values are in agreement with what has been reported in the literature for both types of samples [13, 14, 15, 16].

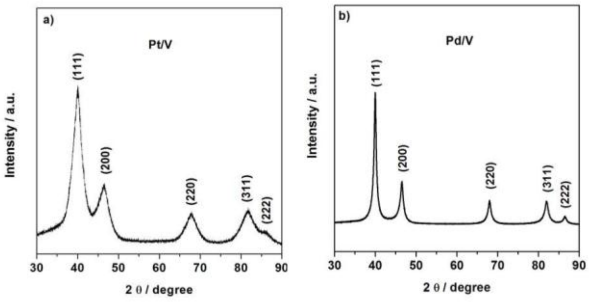

Figure 2. X-ray diffraction patterns of a) Pt/V sample and b) Pd/V sample.

TEM micrographs of the Pt/V and Pd/V samples are shown in Figure 3. In the sample Pt/V, a higher agglomeration of the Pt catalyst particles on the support surface was observed (Figure 3a), compared with the higher Pd catalyst dispersion that was observed for the Pd/V sample (Figure 3b). The average sizes of Pt and Pd nanoparticles for Pt/V and Pd/V were estimated to be 5.2 and 4.3 nm, respectively. These results show that the ethylene glycol and sodium borohydride reduction method produces nanoparticles in the desired size range for applications in fuel cells.

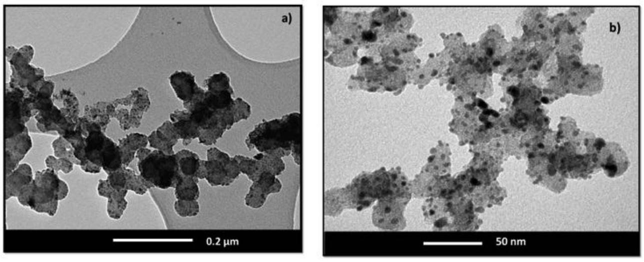

Figure 3. Images obtained from TEM a) Pt/V and b) Pd/V.

The voltammograms obtained for the Pt/V and Pd/V samples are shown in the Figure 4. Both samples voltammograms shows two oxidation peaks, one in direct scan, and the other in reverse scan. This voltammetric profile has been reported elsewhere [14, 18, 19]. The peak in the direct sweep can be related to the EOR, whereas the one in reverse sweep could be associated to incompletely oxidized carbonaceous residues on the catalyst surface [14, 18, 19].

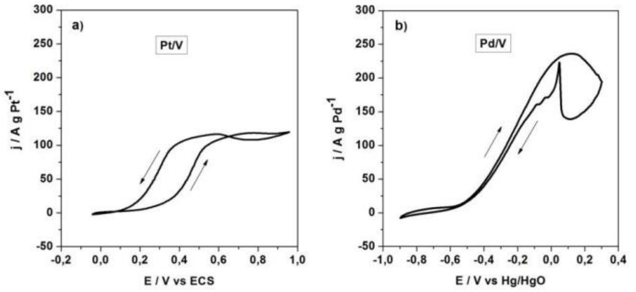

Figure 4. Cyclic voltammograms obtained in presence of ethanol of the a) Pt/V sample in acidic medium and b) Pd/V sample in alkaline medium.

From the voltammograms is possible to determine the maximum current density per catalyst mass (j_{max}) related to the EOR. Pd/V showed higher j_{max} than the Pt/V sample, 119.0 A g Pt^{-1} for and 236.9 A g Pd $^{-1}$. The higher current density for the Pd/V electrocatalyst can be associated with the lower Pd nanoparticles sizes and higher particles dispersion onto the Vulcan carbon surface. This current density value is higher than those reported by other author for some Pt [7, 14], PtSn [14] Pd/C [5, 6], PdAu [5] and PdRu [20] electrocatalysts. Furthermore, the EOR onset potential (Eonset) was 0.2 V *vs.* SCE for the Pt/V sample and -0.7 V *vs.* SCE for the Pd/V sample.

4. Conclusion

Pt/V and Pd/V electrocatalysts for EOR in acidic and alkaline medium were prepared by the impregnation/reduction method. The Pt/V sample has shown a poor dispersion with Pt particle agglomeration, while the Pd/V has shown better particle dispersion. The EOR electrocatalitic activity of the Pt/V sample was much lower than that was determined for the Pd/V sample. The maximum current density related with the EOR in a 1.0 mol L^{-1} ethanol + 1.0 mol L^{-1} NaOH solution was 236.9 A g Pd^{-1} for the Pd/V sample, while the maximum current density in a 1.0 mol L^{-1} ethanol + 0.5 mol L^{-1} H_2SO_4 solution for the Pt/V sample was 119.0 A g Pt^{-1}.The E_{onset} for the EOR was 0.2 V vs. SCE for the Pt/V sample and -0.7 V *vs.* SCE for the Pd/V sample.

Acknowledgement

The present work was carried out with support of CAPES (project CAPES /UdelaR N° 044/2011). A. Cuña thanks the Brazilian CAPES (Bolsista CAPES/Brasil) and E. Leal da Silva thanks the Brazilian CNPq (Bolsista CNPq/Brasil 152027/2016-5 - PDJ).

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