

# CHARACTERIZATION OF PALLADIUM NANOPARTICLES ANCHORED ON GRAPHENE OXIDE OBTAINED BY ELECTRON BEAM

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## ABSTRACT

Fuel Cells (FCs) are devices that convert chemical energy directly in electrical and thermal energy. There are two disadvantages in the process that difficult the implementation of these new power supply. The fuel, hydrogen, is highly flammable and it is difficult to transport and the catalyst is costly. FCs have been attracting worldwide attention because they are environmental friendly and potential as clean and efficient power source. However, their durability and cost have being identified as important issues in this power supply. The objective of this work is to provide a new material based on incorporation of palladium graphene oxide as catalyst. Graphene Oxide (GO) was synthesized from graphite by the modified Hummers method, in water/alcohol medium. The one-step method to incorporate nanoparticles on this nanomaterial was developed using by electron beam (EB). Additionally, this method also reduces the Graphene Oxide (GO). This nanocomposite were characterized by thermogravimetry (TG), Fourier transform infrared (FT-IR), transmission electron microscopy (TEM), x-rays diffraction (XRD) and its potential for electro catalysis were performed by cyclic voltammetry (CV) and amperometry (CA). The results showed that the incorporation of Pd on reduced GO (rGO) by electron beam was 20-40 % in mass. The process using EB and Pd nanoparticles supported on graphene oxide as a support are an alternative, in substitution of conventional methods to the production of electrodes for fuel cells.

## 1. INTRODUCTION

Fuel cells are electrochemical devices that convert chemical energy into electrical energy. They are an attractive alternative to conventional combustion engines for clean energy generation and they are classified on the type of electrolyte. [1]

Conventional fuel cells were not widespread due to the high cost and the use of hydrogen as fuel. Currently, the development of these cells are aimed at replacing the pure fuel gases by natural gas, methanol [2] and, more recently, ethanol. Among the alcohols, ethanol has been recognized as the most promising since it is less toxic. In addition, in Brazil this alcohol is produced on a large scale, obtained through sugar cane and it is easy to transport and storage.

Palladium (Pd) nanoparticle (NPs) have a high surface area-to-volume ratio and they have been used in various electrochemical studies [3], for instance Bambagioni et al. (2009) reported that palladium as an active metal for the electrooxidation of alcohol [4] and recently, Nagaraju et al. (2014) have studied the graphene as support for the palladium NPs for ethanol oxidation reaction, showing its potential as anode for fuel cells [5].

Graphene is a two-dimensional carbon-based nanomaterial with unique mechanical and physicochemical properties: high specific theoretical surface area ( $2630 \text{ m}^2 \text{ g}^{-1}$  per monolayer) [6], that increases its interfacial contact with other components [7]. This nanomaterial is chemically stable, with both excellent electrical ( $r = 64 \text{ mS cm}^{-1}$ ), and thermal conductivities ( $k = 5,103 \text{ Wm}^{-1} \text{ K}^{-1}$ ) [8], thermally stable, important property for electronic components, and high mechanical resistance [9]. These characteristics make graphene a material of wide application such as, electrochemical sensors [10] biosensors [11], capacitor electrodes [12].

In this work, we propose a new route for the synthesis of Pd incorporated on graphene oxide by simultaneous electron beam reduction of graphene oxide and palladium salt. This method is considered, facile and eco-friendly since there is no production of chemical waste, no use of toxic solvents and it is a quick method, compared to the chemical reagents.

## 2. METHODS

### 2.1. Reagents

The chemical reagents used in this work were of analytical grade. The graphite powder, NaOH,  $\text{H}_2\text{SO}_4$ , 30%  $\text{H}_2\text{O}_2$ , HCl,  $\text{KMnO}_4$ ,  $\text{NaBH}_4$ ,  $\text{Pd}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ , propanol, ethanol were used without any purification. The extra pure graphite powder is the brand Merck (99,9%).

### 2.2. Instruments

#### Electron beam

The samples were irradiated Dynamitron – Radiation Dynamics Inc. Radiation absorbed dose 1-300 kGy, dose rate  $1.6 \text{ kGy s}^{-1}$ , 0.4 mA and 1.5 MeV.

#### Thermogravimetry

The nanocomposite analyzed (SDT-Q600, TA Instruments) were carried out in platinum pan and for samples containing nanometal particles in alumina pan. The heat flow was  $20 \text{ }^\circ\text{C min}^{-1}$  from 50 to  $800 \text{ }^\circ\text{C}$  under a dynamic air atmosphere of  $100 \text{ mL min}^{-1}$ .

#### X-Ray diffractometer

X-ray diffraction (Bruker D8 advance) analyze were performed on the samples for characterization of the diffracted planes and the calculation of the interplanar distances between the layers as well as the estimate of the stacked plane quantity. Analyzes were performed with copper tube, from  $2^\circ$  to  $80^\circ$  at the Centro de Combustível Nuclear (CCN-IPEN / CNEN-SP).

#### Transmission electronic microscopy

In order to analyze the size and dispersion of the particles that are related to the specific surface of the metal, fundamental for the catalytic activity of the nanocomposite (JEM-2100, Jeol) at the Centro de Ciencia e Tecnologia de Materiais (CCTM-IPEN/CNEN-SP).

#### Infrared spectroscopy ATR

The presence of chemical groups that indicate alteration processes in the irradiated samples. The data were collected (Bruker, Alpha) at the laboratório de espectroscopia at the Instituto de Química of USP (IQ – USP).

### **Cyclic voltammetry and chronoamperometry**

The cyclic voltammetry studies were conducted at a scan rate of  $10 \text{ mVs}^{-1}$  in KOH ( $0.1 \text{ mol.L}^{-1}$ ) first in absence, then in presence of Ethanol (P.A.) and the chronoamperometry was recorded in presence of Ethanol at  $-0.35 \text{ V}$  for 1800 s (PGSTAT 30, Autolab) at Centro de Celula Combustivel e Hidrogênio (CCCH-IPEN/CNEN-SP).

### **2.3. Synthesis**

Preparation of Graphene Oxide

The Graphene Oxide (GO) was prepared from a graphite powder, by the well-known modified Hummer's method [13].

### **2.4. Preparation of Palladium/Graphene oxide**

The Pd/GO nanocomposite was synthesized in a single step. The graphene oxide was resuspended in a 100 mL becker containing water/isopropanol medium, ( $10$  to  $100 \text{ mg mL}^{-1}$ ) of solution in an ultrasonic bath, then  $20 \text{ mg mL}^{-1}$  of palladium salt was dissolved in the solution. After purging with nitrogen gas, the resulting GO suspensions were irradiated at room temperature by electron beam. The total dose (irradiation time) around  $300 \text{ kGy}$  at scan rate of  $1.6 \text{ kGy s}^{-1}$ .

### **2.5. Preparation of Palladium/reduced graphene oxide**

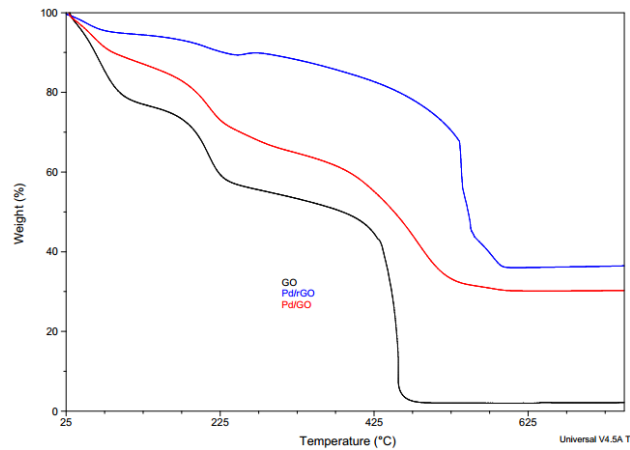
For the preparation the electrocatalyst Pd/rGO, the graphene oxide was previously reduced thermally at  $200 \text{ }^\circ\text{C}$  for 4h. The following incorporation of Pd on rGO was the same used before. The reduced graphene oxide was resuspended in a 100 mL becker containing water/isopropanol medium, ( $10$  to  $100 \text{ m./mL}^{-1}$ ) of solution in an ultrasonic bath, then  $20 \text{ mg mL}^{-1}$  of palladium salt was dissolved in the solution. After purging with nitrogen gas, the resulting rGO suspensions were irradiated at room temperature by electron beam. The total dose (irradiation time) around  $300 \text{ kGy}$  at scan rate of  $1.6 \text{ kGy.s}^{-1}$ .

### **2.6. Electrochemical Studies**

The electrochemical studies were carried out using a conventional cell with three-electrodes. As reference electrode Ag/AgCl ( $3 \text{ mol L}^{-1} \text{ KCl}$ ), a Pt plate as counter electrode and glassy carbon as working electrode. The analyzed solution had about  $12 \text{ mg.mL}^{-1}$  containing water and isopropanol and  $20 \text{ } \mu\text{L}$  Nafion. After 30 min in an ultrasonic bath,  $11 \text{ } \mu\text{L}$  aliquot was added on the working electrode and dry. All measurements were performed at room temperature ( $25 \text{ }^\circ\text{C}$ ).

## **3. RESULTS AND DISCUSSION**

Thermogravimetry (TG) was used to characterize and verify the amount of palladium on the graphene oxide. TG curve of GO (black), Pd/GO (red) and Pd/rGO (blue) are shown on Fig. 1.



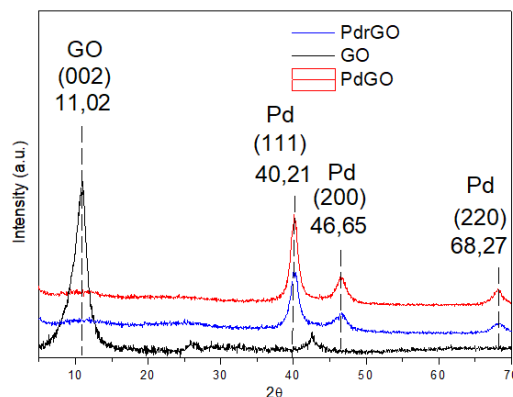
**Figure 1: Thermogravimetry of graphene oxide (GO), Palladium/GO and Palladium/rGO.**

In the GO sample the major weight was lost between 100 and 220 °C, indicating oxygen functional groups, For GO the weight loss was about 38 % and Pd/GO was 23.3 %. on the other hand, the weight lost for Pd/rGO was 7.1 % indicating a partial reduction of graphene oxide. The samples with palladium incorporated exhibited a residual mass and it can be related to the palladium. The next weight loss step below 630 °C was related to C-H groups. The percentages are shown in Table 1 [14-16], in the Pd salt, the mass of Pd was about 40 %.

**Table 1: Weight loss of the samples during thermogravimetry.**

Sample	H <sub>2</sub> O (%) ~100 °C	O <sub>2</sub> (%) ~220 °C	C-H residual (%)~450 – 630 °C	Pd (%)
GO	2.9	7.1	53.3	-
Pd/GO	2.8	23.3	40.1	35
Pd/rGO	2.7	38.0	55.6	30

XRD analyses were used to characterize the palladium and to confirm the reduction of GO Fig. 2 shows XRD for GO, Pd/GO and Pd/rGO.



**Figure 2: XRD of graphene oxide, graphene oxide decorated with palladium and reduced graphene oxide decorated with palladium.**

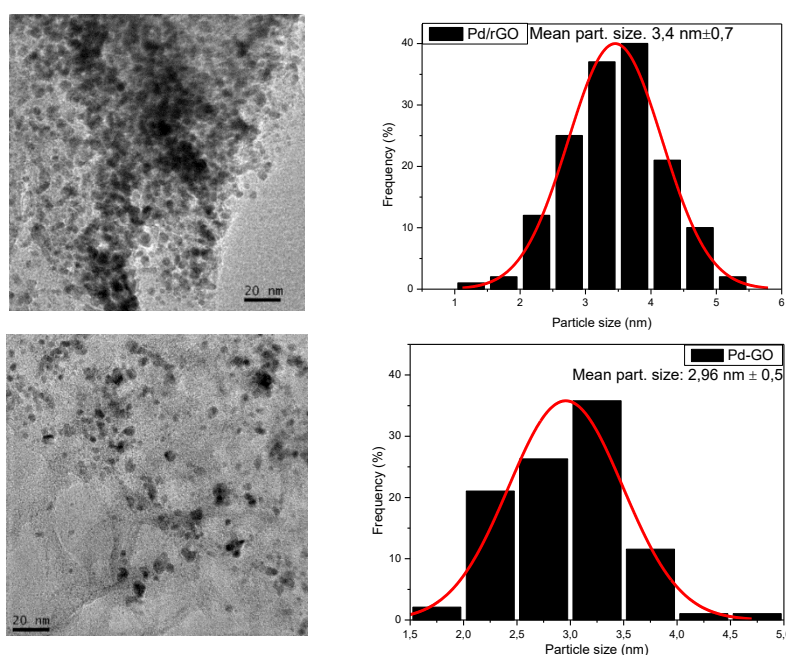
In XRD patterns, peaks at  $2\theta=40^\circ$ ,  $46^\circ$  and  $68^\circ$  respectively correspond to (111), (200) and (220) reflections of Pd face-centered cubic (fcc) crystal according to JCPDF# 88-2335 [17]. Furthermore, GO showed peak at  $2\theta=11^\circ$  is associated to (002) according to JCPDF# 75-1621 [17]. The space between the crystal plane was calculated to 0.820 nm using Bragg's law Eq.(1).

$$2 d \sin \theta = n\lambda \quad (1)$$

It is noteworthy that for graphite this value is 0.334 nm [18]. This increased distance between the crystal plane was due to the introduction of several oxygen-containing groups on each layer [19].

For samples with Pd, the peak attributed to GO was suppressed, this may be caused by the partial reduce of GO.

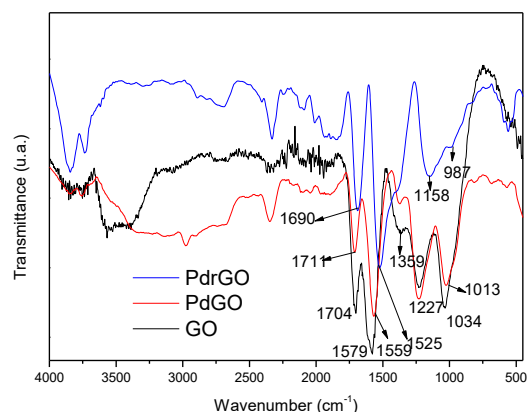
In order to analyze the nanoparticle distribution on the support and the nanoparticle mean distribution, TEM images (Fig. 3) for Pd/GO and Pd/rGO were obtained. The estimate was obtained by counting about 100 randomly chosen particles from different and relevant TEM images [20, 21] The figures show that images and also its histograms with nanoparticle size distribution and the mean diameter using the software: lince linear intercept 2.4.2 $\beta$ .



**Figure 3: TEM micrographs and histograms of the particle size distribution of Pd/GO and Pd/rGO.**

It was possible to observe that some Pd NPs were dispersed on the substrate (Figure 3) and some were agglomerated. The nanoparticles size is between 2.9 and 3.4 nm.

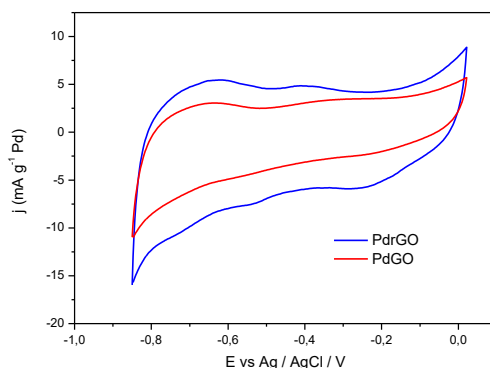
The nanocomposites FT-IR spectra are shown Fig. 4.



**Figure 4: FT-IR of graphene oxide (GO), GO decorated with palladium and reduced graphene oxide decorated with palladium.**

The bands at 1704 and 1711  $\text{cm}^{-1}$  indicated the presence of C=O, the bands at 1579 and 1559  $\text{cm}^{-1}$  is attributed to C-C stretching in graphitic domains. The spectrum reveals the presence of C-OH (1359  $\text{cm}^{-1}$ ), C-O-C (1227  $\text{cm}^{-1}$ ) and C-O (1034-1013  $\text{cm}^{-1}$ ) [21] The bands in the sample Pd/rGO were displaced to right side, this means may be a indication of formation C=C.

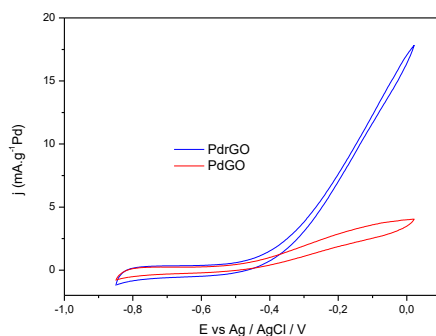
Electrochemical experiments were conducted by cyclic voltammetry (CV) in KOH 0.1 mol L<sup>-1</sup> saturated with N<sub>2</sub> (figure 5).



**Figure 5: Cyclic voltammograms of Pd/GO electrocatalysts and Pd/rGO in 0,1 mol.L<sup>-1</sup> KOH and scan rate of 10 mV.s<sup>-1</sup>.**

It was observed that for Pd/GO the current a decreased as expected, since GO is less conductive than rGO [22]. Furthermore, there are three characteristic peaks: hydrogen adsorption/desorption (-0.8 until -0.45 V), double layer and oxide formation/reduction (-0.3 V) [23, 24]

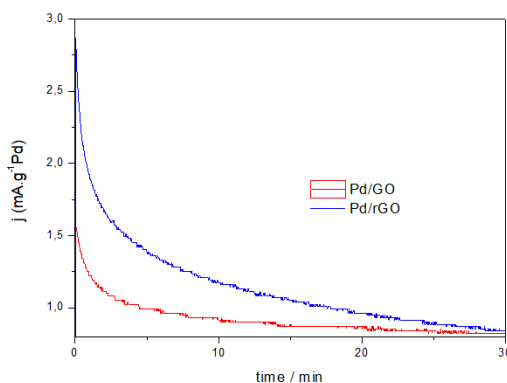
Figure 6 shows the CV of Pd/GO and Pd/rGO in presence of 1.0 mol.L<sup>-1</sup> ethanol and 0.1 mol L<sup>-1</sup> KOH.



**Figure 6: Cyclic voltammograms of Pd/GO (red) and Pd/rGO (blue) in presence of 1.0 mol.L<sup>-1</sup> of ethanol and scan rate of 10 mV.s<sup>-1</sup>.**

It was possible to observe the electrocatalytic activity of Pd/rGO toward ethanol electro-oxidation was better than Pd/GO one. It is also important to remain that graphene oxide due to containing oxygen-groups is not a good conductor [22].

The chronoamperometry was conducted to evaluate the stability of the electrocatalyst in a 0.35 V for 30 minutes.



**Figure 7: Current-time at -0.35 V in 1 mol.L<sup>-1</sup> ethanol and 0.1 mol.L<sup>-1</sup> KOH solution for Pd/GO electrocatalysts and Pd/rGO**

The Pd/rGO showed a good electrocatalytic activity. The current measured for Pd/rGO was little higher than the one obtained for Pd/GO.

### 3. CONCLUSIONS

Electron beam (EB) process showed to be an efficient method to prepare Pd/rGO, although studies must be made for search a good dose to decorate and to reduce the graphene oxide to reduced graphene oxide, which showed better current for the ethanol oxidation. This method EB is very promising for not produce chemical wastes and not use toxic reagents. The EB method produce particles size range from 2.9 to 3.4 nm.

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