



International Congress of Science and Technology of Metallurgy and Materials, SAM - CONAMET 2013

## Pd Nucleation and Growth Mechanism Deposited on Different Substrates

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### Abstract

Palladium, has an unique property between the noble metals, that is the higher capacity to adsorb onto the surface, and within its network, the hydrogen, resulting the Pd of crucial importance to many industrial processes such as catalysis, fuel cell, hydrogen storage and metal brittlement. Since the activity of a noble metal deposited depends strongly on the surface structure, this work is focalized to study the Pd<sup>0</sup> nucleation and growth mechanisms onto different substrates such as HOPG, and thin pure titanium films. Thus, the constant potential method was used in the nanostructures formation varying the potentials and times. The resulting material was characterized electrochemically and morphologically using scanning electron microscopy (SEM), X-ray diffraction (XRD). In agreement with the results, the existing mechanism onto both substrates, was (3D) Pd<sup>0</sup> instantaneous nucleation and growth controlled by diffusion, with a development of nanoparticles with defined morphology and narrow size distributions, which are potentially useful as electrocatalysts.

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Selection and peer-review under responsibility of the scientific committee of SAM - CONAMET 2013

**Keywords:** Electrodeposition, Palladium, Nucleation and growth models.

### 1. Introduction

The 21st century need clean energy technologies. Easily transportable storage of clean energy systems, are one

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of the keys to make the economy of the future. Nanotechnology promises to provide answers through the manipulation of matter and physical-chemical processes in tiny scales. Find innovations necessary for a transition to clean energy economies is one main challenges of nanotechnology. Electrodes formed by noble metal nanostructures, play a fundamental role in catalysis, fuel cells, by their large surface area and defined shapes [Simonov et al. 2003; Diculescu et al. 2007]. These metallic particles of *nano scale* distributed through the electrode, provide a large surface leading to an improvement the rate reaction. Since the activity of noble metals deposits depends strongly on the surface structure, studies on the mechanism of growth and structural characterization at atomic level are essential to develop a better understanding. In this sense, the microscopy techniques as scanning (SEM), tunnel effect (STM) and atomic force microscopy (AFM) had shown to be very useful tools for this type of characterization. Many metals had been investigated by the possible role of nanoparticles as electrodes and modifying its surface [Liu et al. 2001; Elias et al.2012, Penner et al.2002]. Among these noble metals as gold [Li et al. 2010, Osahka et al 2005], silver [Elias et al 2012; Penner et al 2002; Zoval et al. 1996] or platinum [Zoval et al. 1998], the palladium has a unique property that is its greater ability to adsorb over surface and within its network to hydrogen, which gives to palladium fundamental importance in many industrial processes as catalysis, fuel cell, hydrogen storage and metal brittlement [Adams et al 2011; Van Delft et al 2006; Lewis 1967 ]. Different studies on the electrodeposition of palladium have been developed, but information about deposition initial stage with the particles formation to nanometric scale is limited [Gimeno et al 2002; Gimeno et al. 2001]. Studies of metals electro-deposition are conditioned by the crystalline and surface structure of the substrate, as well as the energies of interaction of the metal atoms deposited with the surface atoms of the substrate, among other variables. The possibility of electrochemically controlling the chemical nature of the deposit and its physical characteristics are of interest for the preparation of new materials with specific and high-catalytic performance. That is why this work aims, study the mechanism of nucleation and growth of Pd on pyrolytic graphite substrates highly oriented (HOPG) and on semi-conductor titanium. Constant potential was used in the formation of nanostructures. Resulting material was electrochemically characterized and the morphology observed by (SEM), and the structure by X-ray diffraction (XRD).

## 2. Experimental procedure

Metallic Pd nanostructures were deposited over HOPG and Titanium foil. The substrate HOPG, was SPI-3 (7x7x1 mm) foil provided by SPI Supplies. Due to the laminated structure of HOPG, it can peel almost in the same way as mica, this presents edges of the terraces that act as a mold in the substrate (HOPG). The another substrate was a thin layer of pure titanium of 2 $\mu$ m of thickness of (10x30x1mm) supplied by the company Mateck. In order to achieve a clean and reproducible surface, working electrodes have been washed with ultrapure water (18M $\Omega$ cm) obtained an Elix company Milli-Q system at room temperature. It prepared 2 mM, and 5mM PdCl<sub>2</sub> solutions (E. Merck, Darmstadt) dissolved in 0.1 M HCl, adjusting the pH solution at 2. Electrochemical measurements were carried out using the Metrohm Autolab B.V.302N equipment, and it was used a three-electrode cell, the counter electrode was a high purity Pt wire, and the reference electrode Ag/AgCl, KCl (3M). Cyclic voltammeteries were carried out at scan rate 10 mV s<sup>-1</sup>, after elimination of dissolved oxygen, by bubbling N<sub>2</sub> for 20 minutes at room temperature. The preparation of the working electrodes based on the potentiostatic electrodeposition of Pd, from electrolyte described above. When was used as substrate the Ti film (Mateck), it immersed in 5mM Pd solution and it applied a constant potential of + 0.1V, - 0.3V and - 0.9 V during 300 seconds. When HOPG substrate was used, the potential remained constant to + 0, 1V and varied the deposition times : 10, 60, 180 and 300 seconds, using the 2mM Pd solution. Prepared once the working electrode was removed from solution and rinse with de-ionized water three times to be sure of eliminating any excess solution. The characterization of the formed deposits was done by scanning electronic microscopy - SEM-FEG/CARL ZEISS-Sigma, and X-ray diffraction tests conducted on samples with a Philips PW1710 reflection diffractometer using Cu K $\alpha$ ( $\lambda$ =1,5418 Å) radiation, 40kV and a current of 30 mA. Studied patterns were in the range 2 $\theta$  (20 ° to 90 °).

## 3. Results and Discussion

### 3.1. Evaluation of Pd species profiles that are electrodepositing .

Cyclic voltammetry was used to evaluate qualitatively the palladium electrodeposition onto HOPG and Ti substrates. Polarization curves, were obtained in the range  $-0.400 \leq E / V \leq 1$ . Voltammetric response (Figure 1 and Figure 2) is typical of a nucleation and growth process and there is evidence of adsorption peaks in the range of sobrepotential. During the first exploration towards the cathodic region (Figure 1) the main feature observed is the peak current in  $E \approx 0, 1V$  which is associated with the deposition of  $Pd^0$  on HOPG. Other cathodic current peaks observed in the potential distribution area  $-0.300 \leq E / V \leq -0.250$  which are characteristic of hydrogen adsorbed on the particles of Pd atoms [Gimeno et al. 2002; Gimeno et al. 2001; Schmidt et al 2001] prior to the emergence of the  $H_2$  evolution recorded in  $E \approx -0.350 V$ . In the reverse cycle and after the anodic peaks related to the  $H_2$  desorption procedures, a peak of anodic current density is observed at  $E \approx 0.580 V$  respect to the dissolution of Pd deposited previously. The anodic residual current observed in the anodic limit suggests the passivation of Pd particles. Similar behavior presents the Pd electrodeposition on the Ti sheet (Figure 2), who shows a crossover lines in  $E \approx 0.350 V$  which is the beginning of nucleation-growth, with the maximum at  $E \approx 0.150 V$ , which marks to the presence of  $Pd^0$  onto Ti film.

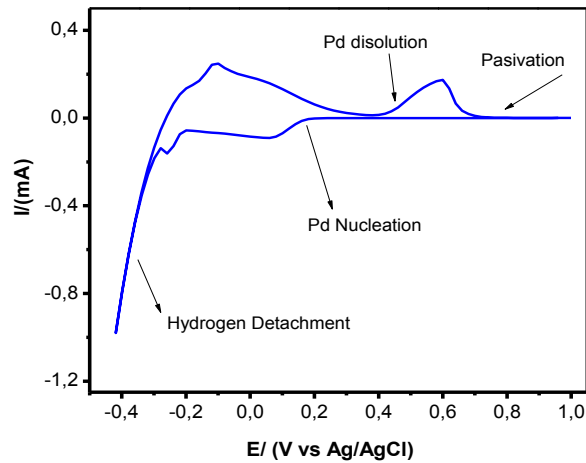


Figure 1. Cyclic voltammetry of 2mM  $PdCl_2$  + 0.1M HCl on HOPG.

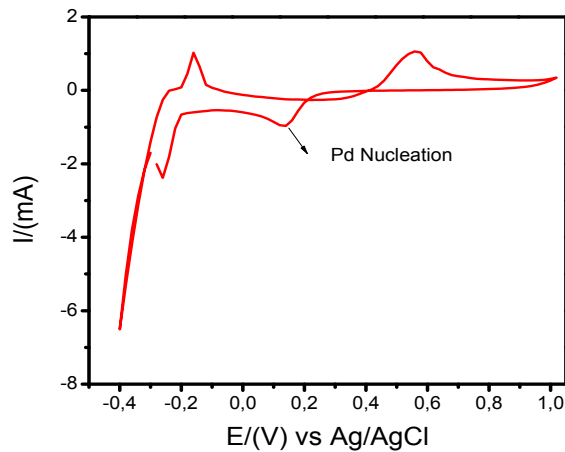


Figure 2. Cyclic voltammetry of 5 mM  $PdCl_2$  + HCl 0.1M on Ti film.

### 3.2. Kinetics and transport in electron transfer reaction

Since the transport to the surface of the electrode occurs almost always by diffusion there are equations that govern the diffusion speed within the boundaries of the layer of diffusion, as also a kinetic parameter governed by the transfer of electrons known as the charge transfer coefficient ( $\alpha$ ), whose value can be found using the kinetic study of the electrochemical reaction. For the calculation of the transfer coefficient, first instance assessed the conditions of the reactant system by cyclic voltammetry technique, analysis intervals were between -0.4 V and 1 V. From the dynamic behavior of the system with respect to a disturbance in the potential of analysis, are managed to detect characteristic areas of reduction and oxidation of the reactant species in the electrochemical system. Figure 1, shows that in the cathodic direction, there is an increase in the current at potentials close 0.1V reaching the reduction maximum at 0.2 V; this dynamic is attributed to the reduction of the ion  $\text{PdCl}_4^{2-}$  to  $\text{Pd}^0$ . The representation of Tafel equation, shown in Figure 3 as logarithm of current density  $J$  ( $\text{mA}/\text{cm}^2$ ) versus potential, it allowed to determine the exchange current density and the coefficient of electronic transfer ( $\alpha$ ). Later values are obtained from the slope of the curve ( $= \alpha F / 2.3 R.T$ ), at scan rate 10 mV/s. For Pd/HOPG systems at different deposition times, it can be seen that the results are comparable other publications [Gimeno et al. 2002, Schmidt et al 2001; Diculescu et al. 2007]. In table 1, are displayed the kinetic parameters of the Pd/HOPG and Pd/Ti systems for reduction in each applied potential and/or time zone. Since the ( $\alpha$ ) charge transfer coefficient is a measurement of the symmetry of the activation energy curve whose barrier must be overcome during a reaction both oxidation and reduction, the found value ( $\alpha$ ) suggests that the predominant structure of the active species in the electrolyte solution is the oxidized species, thus enabling the direction of reaction  $\text{PdCl}_4^{2-} + 2e^- \rightarrow \text{Pd}^0 + 4 \text{Cl}^-$  is directed towards the production of metallic palladium.

Table 1. Kinetics parameters by Pd/HOPG and Pd/Ti systems.

<b>Pd/HOPG</b>	$\alpha(n=2)$	$-\text{Log}J$ ( $\text{A} \cdot \text{cm}^{-2}$ )	<b>Pd/Ti</b>	$\alpha(n=2)$	$-\text{Log}J$ ( $\text{A} \cdot \text{cm}^{-2}$ )
<b>0.1V</b>			<b>300 s</b>		
10 s	0,275	0,960	0.1 V	0,296	1,5003
60 s	0,409	0,056	-0.3 V	0,264	1,6736
180 s	0,350	0,577	-0.9 V	0,243	1,9244
300 s	0,409	0,056			

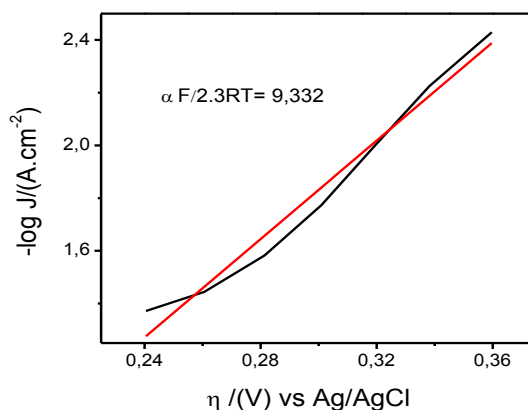


Figure 3. Tafel graphic at 10mV/s with Pd/HOPG, (0.1V for 10s).

### 3.3. Calculation of diffusion coefficient

The calculation of diffusion coefficient, defined the Pd transport regime present during the deposition. The results stored with the potential constant technique for an  $E_{app} = 0.1$  V at different times of electrodeposition, were used to construct a graph of current vs  $(\text{time})^{-1/2}$ . Accord this, it was concluded that the regime of transport of paladium ions from electrolyte was purely diffusional. It was evaluated the curve fit of the experimental data, according to Cottrell equation:

$$i = \frac{nFAD^{1/2}c^*}{(\pi t)^{1/2}} \quad (1)$$

from whose slope  $i$  vs  $t^{-1/2}$ , is evaluated the diffusion coefficient,  $D(\text{cm}^2/\text{s})$ . Where:  $n = 2$ ,  $F = 96400$  A s/mol,  $A = 0.001962$   $\text{cm}^2$  is the geometric area of HOPG, where the reaction occur, and the  $\text{Pd}^{2+}$  concentration in electrolyte  $c^* = 2 \times 10^{-6}$  mol/ $\text{cm}^3$ . The diffusion coefficients of Pd ions towards the cathode for the different electrodeposition times are in Table 2, whose values are close to those observed in the literature [N.Tasaltin et al. 2010]. It was observed a greater diffusion coefficient for the Pd/HOPG system to the longer deposition times even when the rate diffusion is made some independent of time, but arrival of the palladium ions may be favored by the types of defects presenting HOPG used as substrate as of the existence of nanostructures previously formed. For the case Pd/Ti, the diffusion coefficients were calculated by the assays at  $E_{app} = +0.1$  V,  $-0.3$  V and  $-0.9$  V and constant time of 300 s, with a  $c^* = 5 \times 10^{-6}$  mol/ $\text{cm}^3$ ,  $n=2$ , and  $A = 2\text{cm}^2$ . At greater cathodic overpotential the abrupt growth and a bigger nanostructure size was decreasing the ions diffusion rate from electrolyte in the time, may be favoring the adatoms diffusion in surface (see third and fourth column of Table 2). These numeric values are not comparables with Pd/HOPG because the higher concentration of  $\text{Pd}^{2+}$  in electrolytic solution and type of defects and properties of both substrates.

Table 2. Diffusion coefficient of  $\text{Pd}^{2+}$  from electrolytic solution.

Pd/HOPG	$D \times 10^{-5}$ ( $\text{cm}^2 \text{s}^{-1}$ )	Pd/Ti	$D \times 10^{-5}$ ( $\text{cm}^2 \text{s}^{-1}$ )
0.1V		300 s	
10 s	0,302	0.1 V	0,2909
60 s	0,135	-0.3 V	0,2164
180 s	0,705	-0.9 V	0,1227
300 s	1,100	----	----

### 3.4. Nucleation and growth proposed mechanisms of $\text{Pd}^0$ on HOPG or Ti.

The constant potential was used as a method of electrochemical deposition of Pd, and simultaneously as a method for the study of nucleation and growth mechanisms, taking into account the voltammetric results that inform us about of the species during the electrodeposition. In the experiments of Pd onto HOPG substrate, the potential used ( $E = 0.1\text{V}$ ) remained constant, that is to which the deposition of Pd is made present at different values of times (10s, 60s, 180s and 300s). Figures 4a and 4b, have the typical shape of a process of nucleation and growth, with the first nuclei which form islands (3D) as they can be seen in the SEM image inset Figure 4a, for 60s. In these conditions, the system makes a transition from a neither reaction state to a stable state controlled by the speed of mass transfer of ions palladium to the surface of the electrode. Such transition is always followed by a current transition to reach the steady state [B.Scharifker et al 1983].

The phenomenon of 2D or 3D instantaneous or progressive nucleation and growth forms are analyzed according to theoretical models proposed in the literature. [B.Scharifker et al 1983; Bewick, et al 1962; Fleischmann et al. 1963.

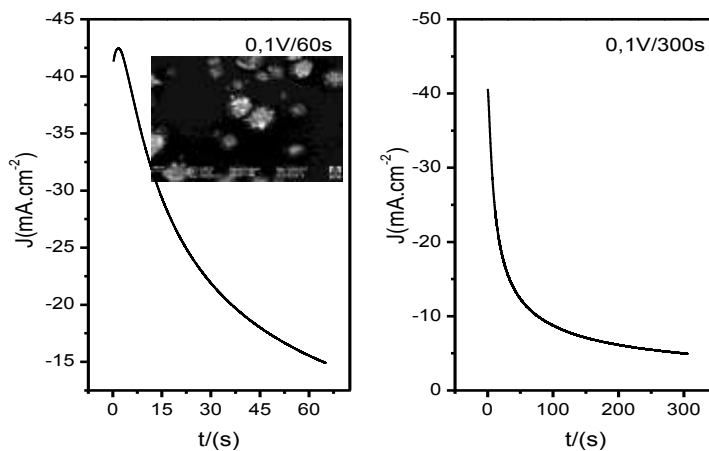


Figure 4: Pd/HOPG nucleation and growth for deposition times a) 60s and b) 300s.

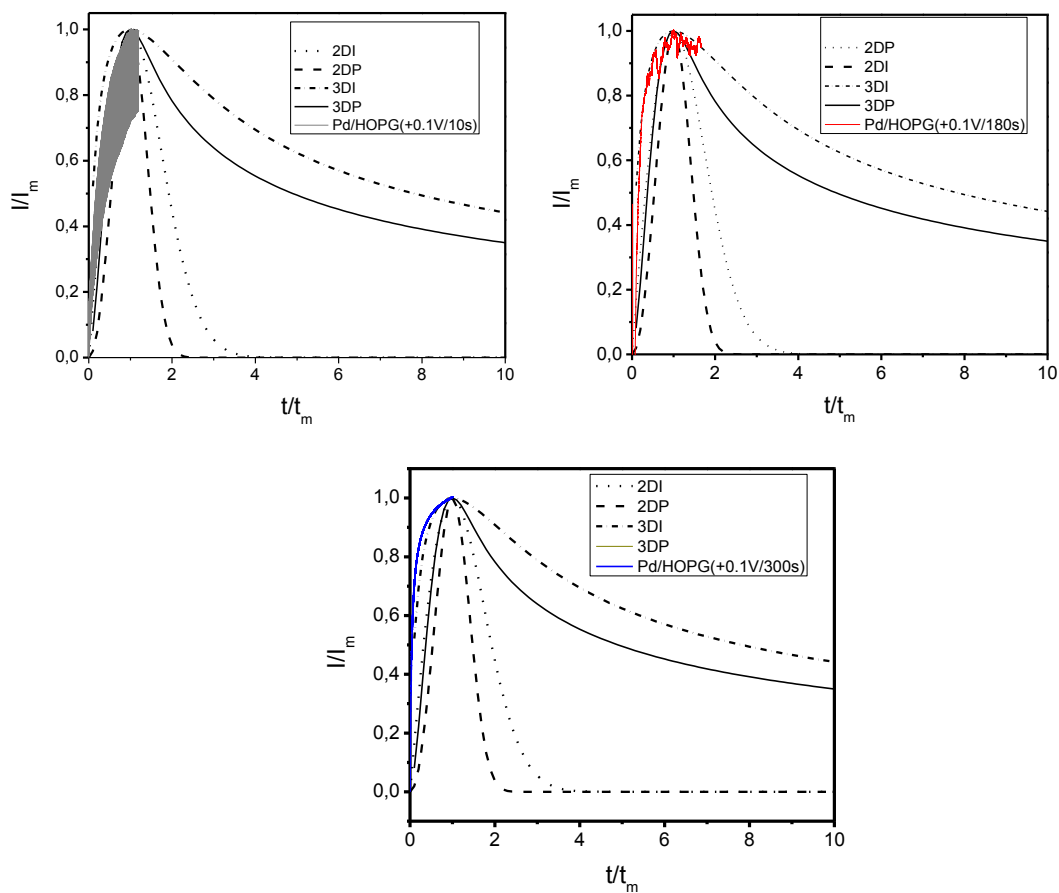


Figure 5. Dimensionless curves of  $I/I_m$  vs  $t/t_m$  by Pd/HOPG, at 0.1V a) 10s b) 180s c) 300s.

The representation of the experimental curves in dimensionless form  $I/I_m$  vs  $t/t_m$  allow comparison with theoretical limits values [Bewick, et al 1962; Fleischmann et al. 1963]. The figures 5a, 5b and 5c for Pd/HOPG, exhibit a typical form of 3D nucleation and growth controlled by diffusion. In short times they exhibit an increase in the current density, corresponding to the formation and growth of the nuclei, reaching a maximum  $I_m$  at a time  $t_m$ . 3D nucleation model and growth controlled by diffusion, has two cases limits: *instantaneous nucleation*, where all nuclei are formed after the step of the potential and *progressive nucleation*, where nuclei increase throughout the deposition process. Deposits of Pd on HOPG at 0.1 V and different times (Figure 5) are approaching instantaneous nucleation mechanism which is consistent with other authors [Rezaei et al. 2012]. In practice, the nucleation never is purely progressive or instantaneous, since these are highly idealized cases and instantaneous nucleation processes always have some progressive character.

Figure 6, shows the graph ( $I/I_m$ ) vs ( $t/t_m$ ) for Pd/Ti which allows you to find the best fit to the experimental data and assess the type of nucleation that operates during the deposition process. The curve corresponds to Pd/Ti with an applied potential of -0.3V for 300 seconds. It is observed to  $t < t/t_m$  coincidence with the theoretical curve of instantaneous nucleation, but for  $t > t/t_m$  stops in the final sections match the theoretical curve which is the existence of side reactions such as the reduction of  $H^+$  possible at negative potentials as -0.3V [Gimeno et al 2002, Palomar-Pardavé et al. 2005]. If it is analyzed the behavior of the adjustment of the model of Figures 5 a, b, and c and Figure 6 with the experimental data obtained for Pd/HOPG and Pd/Ti, it can be deduced that they closely follow the trend of 3D instantaneous nucleation and growth controlled by diffusion model proposed by Scharifker and Hills 1983 establishing a generation of nuclei very quickly, assuming that the number of active sites for nucleation reaches its maximum saturation instantly and then growth.

### 3.5. Morphological studies of Pd electrodeposited on HOPG and Ti

Instrumental analysis techniques allow to obtain a more detailed understanding of crystal structures of the deposits, that compounds are generated during the process and a vision of how deposits are distributed over the substrate. In this case it was used the scanning electron microscopy (SEM) capable of reproducing high resolution surface images. These three-dimensional images make this useful technique when it comes to the characterization of the type of dispersion of deposits on the surface of the substrate. From the images obtained after the electrodeposition of Pd on HOPG is observed that atoms which reach the surface preferentially adsorb at positions corresponding to the edges of the steps and/or defects of HOPG (Figure 7 a), with a size almost uniform approximately 50 nm. With the increase of deposition time (60 s) the Pd particles are directed on the edges of step of HOPG forming nanowires Figure 7 b. However, to greatest time of deposition (180 s), begin to assemble causing growth of the nuclei, resulting in this way in the formation of nanostructures (Figure 7 c) and even more compact is the formation of agglomerates atomic, resulting in the deposition of (300 s) (Figure 7d). Accord to these results, we can conclude that the deposition of Pd particles obeys the Volmer-Weber (formation 3D-Islands) model [Budevski et al. 1996].

SEM images in Pd deposits on Ti films (Figure 8), showed that electrodeposits are not directed to defects that had been on the surface but that are deposited in the area set out in a uniform way. The increases of sobrepotential from +0.1V to - 0.9V, generated bigger nanostructures by increase in the growth rate. The lowest sobrepotential + 0.1V (Fig. 8 a) generated nanostructures that tend to a spherical morphology, as so negative potentials of - 0.9V (Fig. 8 c) predominated nanoflowers formation, this would be related to the speed with which the Pd atoms diffuse along the surface, generating different structures.

### 3.6. Analysis of the microstructure by X-ray diffraction

Figure 9a, shows the pattern of X-ray diffraction of Ti substrate used in the electroplating. There are important diffraction lines in  $2\theta = 35.2; 38; 39.8; 52.5; 62.9, 70$  and  $81.5^\circ$ . Which means that it is a mixture of hexagonal and something cubic titanium phases. By adjustments to the patterns the more intense  $38^\circ$  line matches the (110) plane of (bcc) (JDSC 00-044-1288) pattern, but also coincides with the plane (hkl) (002) of the hexagonal structure

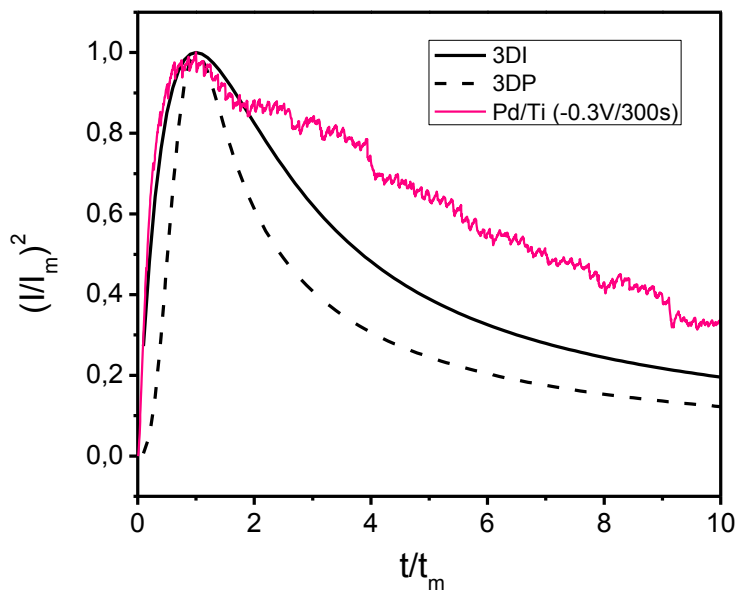


Figure 6. Adimensional curves  $(I/I_m)^2$  vs  $(t/t_m)$  in the setting of Pd/Ti experimental data

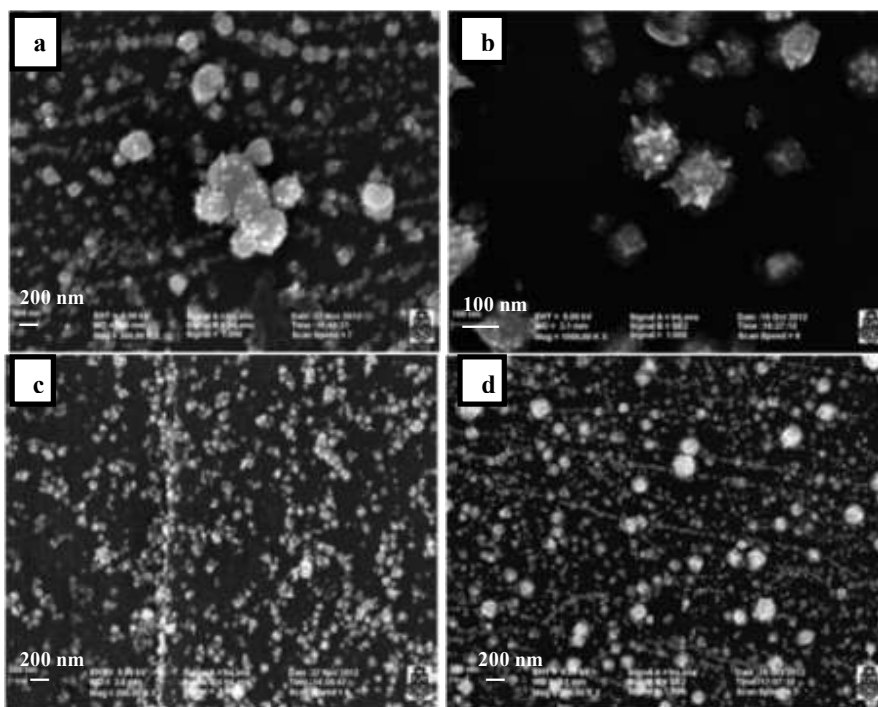


Figure 7: SEM Images by Pd on HOPG electrodeposition at a)10s b) 60s c) 180s and d)300s.



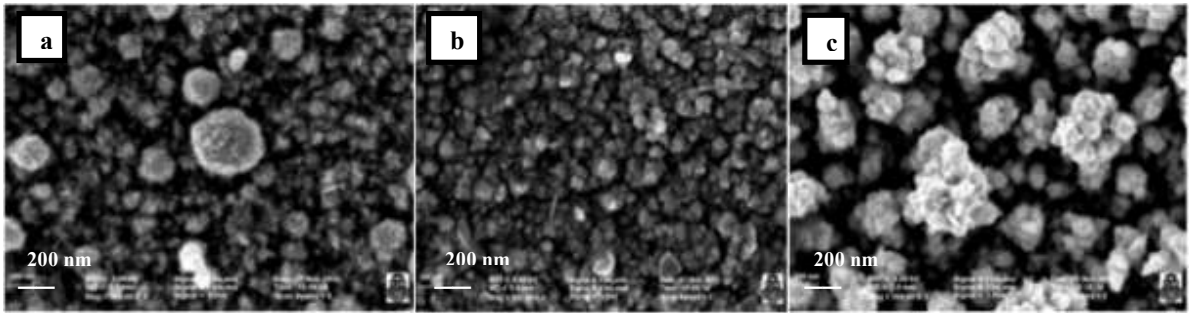


Figure 8: SEM images by Pd on Ti electrodeposition for 300s at a) 0.1V b) -0.3V c) -0.9V.

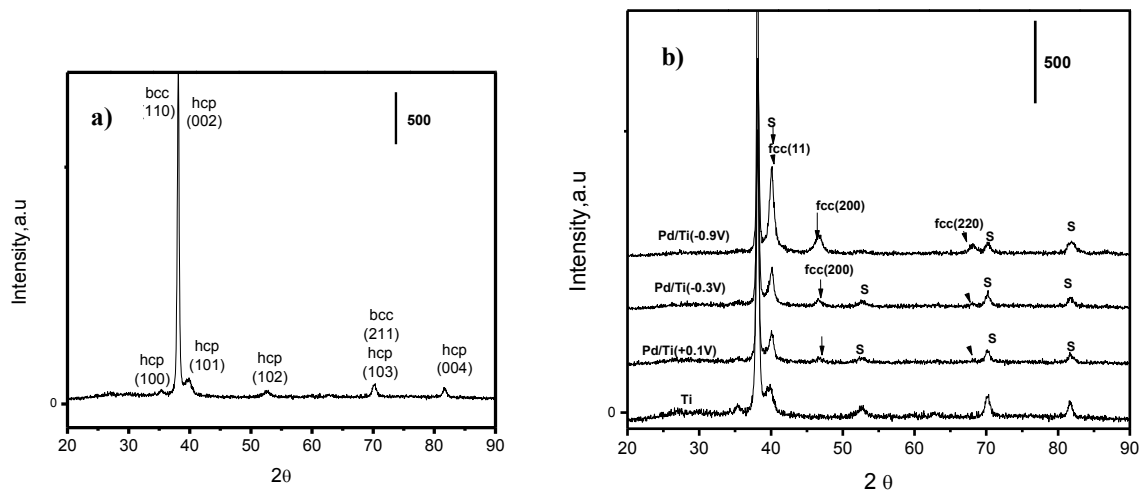


Figure 9. a) X-ray diffraction of Titanium substrate between  $2\theta$ :  $20^\circ$ - $90^\circ$ . b) Pd/Ti system electrodeposited for 300s at distinctive potentials

(JSDC 00-001-1197), to which also correspond the plans (100) to  $35.2^\circ$ ; (101) to  $39.85^\circ$ , (102) to  $52.59^\circ$ , to  $62.93^\circ$  the (110) and (103) to  $70.1^\circ$ . Grain size was calculated as 27.4 nm using the Scherrer equation in the most intense diffraction line. There isn't lines of crystalline  $\text{TiO}_2$ , as anatase, rutile or brookite.

Figure 9b, shows the diffractogram for the Pd/Ti corresponding the systems made at +0.1V; -0.3V and -0.9V for 300 seconds with the 5 mM solution of  $\text{Pd}^{+2}$ , superimposed on Ti substrate. Most intense peak of Pd $^\circ$  diffraction correspond to the structure (fcc) (JSDC-00-005-0681, 00-001-1201) with the more intense (111) plane superimposed on the hcp (101) plane of the substrate. The lonely line by (200) plane corresponding to the fcc structure of Pd $^\circ$  at  $2\theta = 46.737^\circ$  served us for calculation of grain size (22.5 nm) and the parameter of cell as 3.88728 Å. The deposited Pd didn't form oxides (JSDC 00-006-0515) since the diffraction lines of palladium oxides arise with maximum intensity at  $2\theta = 33.876^\circ$ . The Pd/HOPG nanostructures electrodeposited at various times, didn't show crystallinity by metallic deposit. The XRD of the system only showed diffraction lines that correspond to the substrate carbon substrate and neither phase Pd $^\circ$  or of its oxides. Thus, Pd crystallite size obtained by this way was too small size.

#### 4. Conclusions

It was effectible to electrodeposit nanostructures of Pd $^\circ$  on HOPG and Ti films, following defects substrate, applied potential, and deposition time. The crystalline palladium deposited on Ti has a fcc structure, with 23 nm

average grain size and a cubic cell parameter of 3.88728 Å. Accord to the experimental results obtained both substrates, the deposition kinetics, followed a typical 3D nucleation and growth controlled by diffusion. The palladium ions diffusion coefficient values are in same order  $10^{-5}$  cm<sup>2</sup>/s both substrates. The 3D Pd<sup>0</sup> instantaneous nuclei formation, had a development of nanoparticle-defined shapes: spherical on HOPG forming clusters, and cauliflower in Ti with narrow size distribution, which are potentially useful as electrocatalysts.

## Acknowledgements

Authors thank FONCYT- PICT0074 by financial support .

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