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**Topic: S06. Corrosión, protección y electroquímica.**

## **Pd/Ti electrocatalysts in technological significance reactions**

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## Pd/Ti electrocatalysts in technological significance reactions

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### ABSTRACT

Our goal is to present technologically important systems operating as future electrocatalysts into processes of remediation to environment or in fuel cell. Thus Pd/Ti nanoelectrodes, are applied i.e. in the chromate contaminant detection in acid electrolytes; or in the oxygen reduction reaction (ORR) or the alcohols oxidation reaction (AOR) in alkaline electrolyte. Pd/Ti electrodes were prepared at constant potential: +0.1V, -0.3V or -0.9 V by 300sec, from 5mM  $K_2PdCl_4$  solution onto Ti blade. Comparatively a modified Pd/GC ( $\phi=3mm$ ) electrode was prepared at +0.1V by 200sec. The materials were characterized by X-ray diffraction, and scanning electron microscopy. The response of Pd/Ti nanoelectrodes, by Cr(VI) detection, oxygen reduction, and the ethanol, n-propanol, ethylene glycol oxidation (AOR), was analyzed in function of analyte concentration, evaluating also the existence of diffusion control in electroactivity properties. The oxygen reduction wave at -0.4 V in NaOH 0.05M gave a current density two times than that measured at +0.4V in  $H_2SO_4$  0.1M, and the order of sensitivity was  $PdTi(+0.1) \approx PdTi(-0.3V) > PdTi(-0.9V)$  electrode. The small alcohol molecules oxidation in oxygen saturated alkaline environment showed by Tafel curves, the activity order of alcohol electro oxidation ( $E_{onset}$ ) on Pd/Ti electrodes is ethanol  $\geq$  n-propanol  $>$  ethylene glycol. Also, upon crescent addition alcohol concentration a linear range between 3.5-90 mM alcohol in NaOH 0.05M, indicated an order activity  $PdTi(+0.1V) \approx PdTi(-0.3V) > PdTi(-0.9V)$  electrodes. The reduction wave of Cr(VI) with Pd/Ti electrodes was near +0.57 V in  $H_2SO_4$  0.1M, and the calibration curve calculated between 0.019 -0.69 mM Cr(VI) gave a good linear correlation. The lowest sensitivity was 0.5-1.5  $\mu$ M Cr(VI). The performance (i.e. sensitivity, resolution, stability) of Pd/Ti nanoelectrodes, was better when compared with a modified Pd/GC electrode, in the interest reactions.

Maximum: 300 words.

Keywords: Pd/Ti electrodes, electroreduction reactions, alcohol electrooxidation.

### RESUMEN

Nuestro objetivo es presentar sistemas, tecnológicamente importantes, que operen como futuros electrocatalizadores en procesos de remediación al medio ambiente o en celdas de combustible. Así nanoelectrodos de Pd/Ti, se aplican en la detección de Cr(VI) en medio ácido, en la reacción de reducción de oxígeno (RO) y en la reacción de oxidación de alcoholes (OA) en electrolitos alcalinos. Los electrodos de Pd/Ti fueron preparados a potencial constante: +0.1V, -0.3V y -0.9 V por 300s, sobre una lamina de Ti (comercial), partiendo de una solución 5mM de  $K_2PdCl_4$ . Comparativamente se preparó un electrodo Pd/GC ( $\phi=3mm$ ) a +0.1 V/200s. Los materiales se caracterizaron por difracción de rayos X, microscopia de barrido electrónico. La respuesta de los nanoelectrodos Pd/Ti, en la detección de Cr(VI), reducción de oxígeno y la oxidación de etanol, n-propanol y etilenglicol, se analizó en función de la concentración del analito, evaluando control difusional en las propiedades de electroactividad. La reducción de oxígeno a -0.4 V en NaOH 0.05 M, mostró una mayor densidad e corriente que la medida a +0.4V en  $H_2SO_4$  0.1M, y el orden de sensibilidad fue  $PdTi(+0.1) \approx PdTi(-0.3V) > PdTi(-0.9V)$ . La oxidación de pequeñas moléculas de alcohol en medios alcalinos mostró por curvas Tafel, que el orden de actividad de electrooxidación del alcohol ( $E_{onset}$ ) para los electrodos de Pd/Ti es etanol  $\geq$  n-propanol  $>$  etilenglicol. La adición consecutiva de alcohol en un rango de concentración 3.5-90 mM en NaOH 0.05M, indicó un orden de actividad de los electrodos  $PdTi(+0.1V) \approx PdTi(-0.3V) > PdTi(-0.9V)$ . La reducción de Cr(VI) con los nanoelectrodos de Pd/Ti fue a +0.57 V en  $H_2SO_4$  0.1M, y la curva de calibración entre 0.019 - 0.69 mM Cr(VI) mostró buena correlación lineal. La menor sensibilidad de Cr(VI) fue 0.5-1.5  $\mu$ M. La eficiencia (ej. sensibilidad, resolución, estabilidad) de los nanoelectrodos de Pd/Ti, fue mejor que el electrodo modificado Pd/GC, en las reacciones de interés.

Máximo: 300 palabras.

Palabras Clave: electrodos Pd/Ti, electroreducción, electrooxidación de alcoholes,

### 1. Introduction

The environmental electrochemistry contribute successfully to environmental protection. Especially during the purification of dilute heavy metal ion-containing process liquids. The performance of an electrocoagulation system with iron electrodes for Cr(VI) removal from model wastewaters in laboratory scale was studied by [1]. Also removal of Cr(VI) from aqueous solutions by electrochemical reduction was studied

using steel rods connected in unipolar mode [2]. However, interesting is the performance of noble metals electrodes by notable stability at the corrosion. Thus Au, Ag nanoparticles were used in Cr(VI) detection showing low limit in detection [3-5]. In this work the electrochemical reduction of hexavalent chromium in acidic media is studied at various Pd/Ti, Pd/GC and GC (glassy carbon) electrode substrates.

Noble metals catalysts is relevant to alkaline fuel cell technology, while the oxygen reduction reaction systems are also relevant to chlor-alkali electrolysis and metal-air batteries. The use of alkaline media

presents advantages both in electrocatalytic activity and in materials stability and corrosion. Therefore, prospects for the continued development of alkaline electrocatalytic systems, including alkaline fuel cells, seem very promising. The alcohol electrooxidation on the Pd electrode in alkaline medium has been studied in the last five years[6-8]. However, the combined effect of substrate and noble metal in Pd/Ti system even was not reported, where evaluate the function of Ti in the different performance of nanoelectrodes in alcohol electrooxidation. Also, we compare the electrooxidation activity of saturated alcohols, such as, ethanol, n-propanol, the simplest diol ethylenglycol on Pd/Ti(+0.1V), Pd/Ti(-0.3V), Pd/Ti(-0.9V) and Pd/GC electrodes, just to find out the appropriate fuel on the different electrocatalysts.

## 2. Experimental

The substrate was a thin layer of pure titanium 2 $\mu$ m of thickness, supplied by the company Mateck whose dimensions are 10x30x1mm. 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 5mM PdCl<sub>2</sub> solutions (E. Merck, Darmstadt) dissolved in 0.1 M HCl, adjusting the solution at a pH 2.6. Electrochemical measurements proceeded with a three-electrode cell, the counter electrode was a high purity Pt wire, the reference electrode Ag/AgCl, KCl (3M). Electrochemical measurements were carried out using the Metrohm Autolab B.V 302N equipment. The preparation of the working electrodes based on the electrodeposition of Pd, from electrolyte described above onto blade Ti metal, applied a constant potential of + 0.1V, - 0.3V and - 0.9 V during 300 seconds. An alternative modified electrode was prepared depositing 5mM K<sub>2</sub>PdCl<sub>4</sub> at +0.05V /200sec onto glassy carbon electrode (diameter 3 mm). 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 electrodes electrochemical characterization in alkaline or acid electrolyte was carried out by cyclic voltammetric, linear sweep voltammetry, linear polarization, differential pulse voltammetry with amplitude pulse 50mV and scan rate 20mV/s (detection in low limit). The characterization of the deposits formed was done by scanning electronic microscopy - SEM-FEG/CARL ZEISS-Sigma. X-ray diffraction tests were conducted on samples with a diffractogram of reflection Philips PW1710 with radiation from copper, voltage of 40kV and a current of 30mA. Studied patterns were in the range 2 $\theta$  (from 20 $^\circ$  to 90 $^\circ$ ).

## 3. Results and Discussion

### 3.1-Characterization of Pd/Ti electrocatalysts

Fig.1 shows the typical SEM micrograph of palladium nanoparticles electrodeposited on Ti blade (Pd/Ti). Fig.1a shows the substrate Ti and Fig.1b typical micrograph of palladium nanoflowers by Pd/Ti(+0.1V) with an average size of 50 nm. Inset (left top) is kept an image detailed of nanoflowers morphology. An increase on deposition overpotential as Pd/Ti(-0.3V) and (-0.9V) produced an increase size, and as it was reported [9] all they closely followed the trend of 3D instantaneous nucleous formation and growth controlled by diffusion.

The Pd nano flowers supported on Ti film exhibit an XRD pattern of a typical face-centered-cubic (fcc) lattice structure didn't showed here. The Pd(111) peaks were used to calculate the grain size of Pd according to the Scherrer's equation. The average Pd sizes in Pd/Ti electrocatalysts were 27.4 nm.

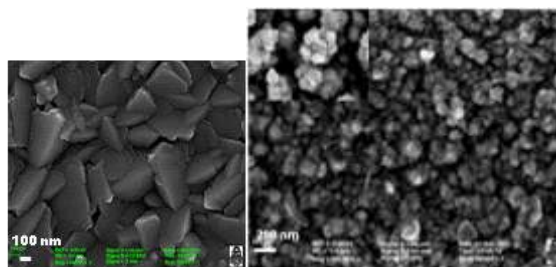
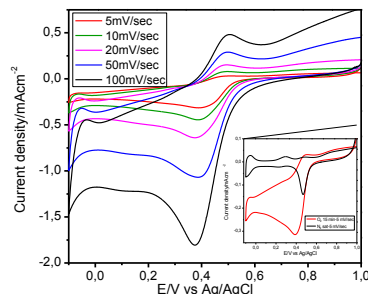
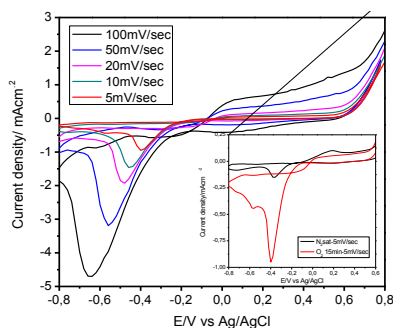


Figure 1. SEM image of a) Ti foil. b) Pd/Ti(+0.1V) electrodeposit

### 3.2. Oxygen reduction with Pd/Ti electrodes

The (CVs) profile with Pd/Ti modified electrode at: 5, 10, 20, 50 and 100 mV/sec, in H<sub>2</sub>SO<sub>4</sub> 0.1 M are showed in figure 2(a). An evident reduction peak was observed at about +0.4V. Inset was compared the Pd/Ti electrode at 5mV/sec in the nitrogen and oxygen saturated solution. Thus, one can confirm that the reduction peak at -0.4V is attributed to the electrochemical reduction of oxygen molecules. The well-defined voltammograms were displayed, with very similar profile to the reduction onto glassy carbon, but it was improved with higher activity by Pd nanosized. The performance of Pd/Ti (+0.1V) and Pd/Ti(-0.3V) electrodes in the oxygen reduction, was calculated by  $I_{\text{peak,Pd}/\text{GC}} \text{ vs } (\text{scan rate})^{1/2}$  with slopes between 0.00601 and 0.00596 ( $\text{Acm}^{-2}/(\text{Vsec}^{-1})^{1/2}$ ) respectively. The linear relationship (0.992) between the reduction peak currents and the square root of scan rates was gained, strongly verifying that oxygen reduction is also a diffusion-controlled process on these modified Pd/Ti (+0.1V) and Pd/Ti (-0.3V) electrodes. The analysis by Randles-Sevcik equation informed a  $n$  value equal 4, by a diffusion coefficient  $2.13 \cdot 10^{-5} \pm 0.03 \text{ cm}^2/\text{sec}$ . The wave reduction in 0.05M NaOH at -0.4 V by Pd/Ti(+0.1V) electrode is observed in Figure 2(b), with a shift of potential peak 158mV between 5-100mV/sec, indicating a quasi reversible process, and a slope  $0.013 (\text{Acm}^{-2}/\text{Vsec}^{-1})$  by the curve  $I_{\text{peak}} \text{ vs } \nu^{1/2}$ , with  $r^2 = 0.9957$ . The equation by an irreversible process evaluated a diffusion coefficient of  $2.23 \cdot 10^{-5} \pm 0.3 \text{ cm}^2/\text{sec}$  and  $n=4$  in alkaline electrolyte by electrodes Pd/Ti (+0.1 V) and Pd/Ti(-0.3V). The conduct by Pd/Ti(-0.9V) was less reversible in both electrolytes.

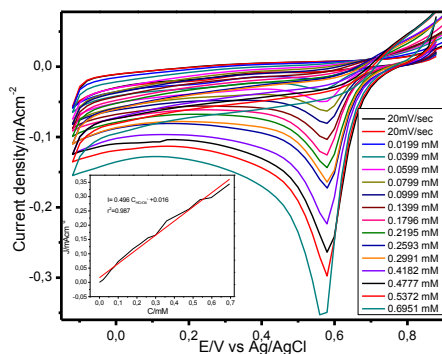




**Figure 2. Pd/Ti(+0.1V) in oxygen saturated a) 0.1 M H<sub>2</sub>SO<sub>4</sub> and b) 0.05 M NaOH solution.**

**3.3.Reduction Cr(VI) at Pd/Ti , Pd/GC electrodes**

The response of various Cr(VI) concentrations in 0.1M H<sub>2</sub>SO<sub>4</sub> at Pd/Ti(+0.1V) electrode (A = 2 cm<sup>2</sup>), was studied. Voltammetric profiles to scan rate (20mV/sec) are shown in Fig. 3. The recorded cyclic voltammograms revealed reduction wave at +0.58 V (versus Ag/AgCl). Recorded reduction peak was found to shift slightly to more negative values with further increase of HCrO<sub>4</sub><sup>-</sup> concentrations. This indicates a highly electrochemically reversible reaction, which is confirmed by the Tafel slope of ca.100 mV per decade obtained from a plot of potential versus log (current). The corresponding plot of peak current against increasing concentration of hexavalent chromium (see inset Fig 3) was found to be linear in the concentration range studied (0.019–0.695 mM) ; slope = 0.499 (mAcm<sup>2</sup>/ mM), intercept  $i_{(\mu\text{Acm}^{-2})} = 0,016$   $r^2 = 0,99$ . Besides, further assays over Ti electrode without Pd deposited, didn't showed a notorious reduction activity of Cr(VI).

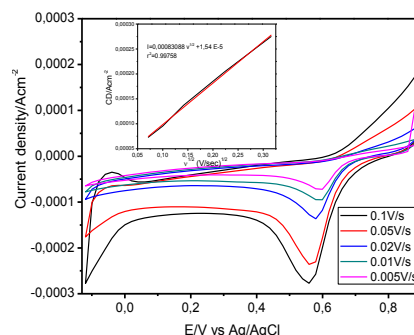


**Figure 3. Pd/Ti (+0.1V) in 0.1M H<sub>2</sub>SO<sub>4</sub> solution upon crescent addition of Cr(VI)**

The voltammetric responses (Figure 4) of 0.2195 mM Cr(VI) in 0.1MH<sub>2</sub>SO<sub>4</sub> to various scan rates (5–100mV/sec) obtained with Pd/Ti(+0.1V) electrode , revealed the reduction peak, was found to shift to more negative values with further increase of scan rate, from 0.586V (5mV/sec) to 0.56 V to (100mV/sec).However, the peak potential is not significantly dependent on scan rate ( shift only 20mV), that suggest on one electrochemically reversible reaction on Pd electrode, which is confirmed by the Tafel analysis. The plot of potential (mV) versus log (current density) produced a slope value of ca. 75-51 mV/dec , indicating the possible electrochemical reversibility. The reaction process might be

rationalized as the one-step reduction of Cr(VI) to Cr(III). The Randles–Sevcik plot(Inset Fig 4), for the reduction process of 0,2195 mM (molcm<sup>-3</sup>) Cr(VI) at Pd/Ti electrode ,calculated a slope of 0.00083098 (Acm<sup>2</sup>/Vsec<sup>-1</sup>) ,which was found to be linear in the scan rate range studied, suggesting that reaction is diffusion rather than surface controlled. Diffusion coefficient calculated by n<sub>e</sub>=3 and one electron transferred was D= 2.2 10<sup>-5</sup> ±0.2 cm<sup>2</sup>/sec. The reduction pathway considered was suggested by [5] where the slow step proceeds via 1e<sup>-</sup> and 1H<sup>+</sup>.

A limit of detection of 19 μM was achieved with Pd/Ti systems for the more acidic solution H<sub>2</sub>SO<sub>4</sub> 0.1M. The recommended limit of detection set out by the EPA(1.0 μM) is significantly lower, showing that cyclic voltammetry is not a sufficiently sensitive technique and is most valuable for the electrochemical characterization of the electrode. Thus, differential pulse voltammetry method was applied in buffer pH 4 , and the calibration curve for Cr(VI) solution in the range of concentration 0,49μM-5,99μM was  $I = 7.67C_{Cr(VI)} + 4.3$  , (r<sup>2</sup>=0.9811) for Pd/Ti(-0.3V) electrode.



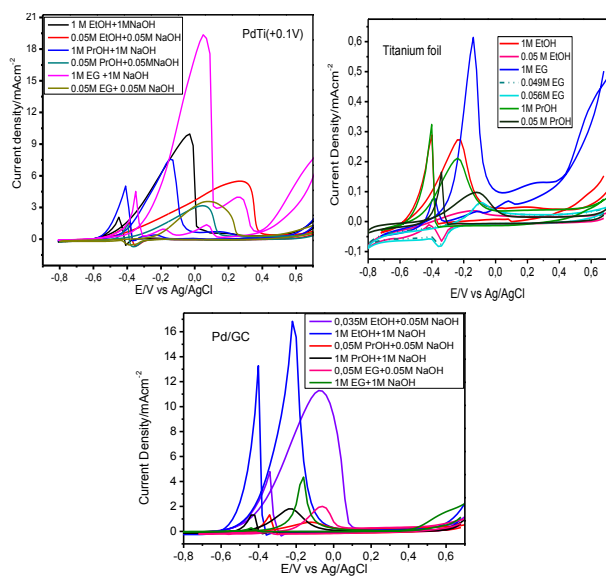
**Figure 4. Pd/Ti (+0.1V) in 0.1M H<sub>2</sub>SO<sub>4</sub> solution at several scan rates.**

The voltammetric responses of 0,42 mM Cr(VI) in 0.1MH<sub>2</sub>SO<sub>4</sub> to various scan rates (5–150mV/sec) obtained with Pd/GC electrode (didn't showed here), revealed the reduction peak, was found to shift to more negative values with further increase of scan rate, from 0.53V (5mV/sec) to 0.49V to (150mV/sec).However the peak potential is not significantly dependent on scan rate (shift only 40mV), that suggest on one electrochemically reversible reaction on Pd electrode, which is confirmed by the Tafel analysis. The reaction process might be rationalized as the one-step reduction of Cr(VI) to Cr(III). The Randles–Sevcik plot, for the reduction process of 0,4128 mM (4,18 10<sup>-7</sup> molcm<sup>-3</sup>) Cr(VI) at Pd/GC electrode ,calculated a slope of 0,0067(Acm<sup>2</sup>/Vsec<sup>-1</sup>), which was found to be linear in the scan rate range studied, suggesting that reaction is diffusion rather than surface controlled. Diffusion coefficient by n<sub>e</sub>=3 was D= 1.464 10<sup>-5</sup> ±0.2 cm<sup>2</sup>/sec. The responses of GC electrode to solutions of 0.1M H<sub>2</sub>SO<sub>4</sub> containing additives quantities of Cr(VI) revealed at low concentration the presence of a pre-shoulder at +0.4V (versus Ag/AgCl) , and a reduction wave at +0.63V versus Ag/AgCl) at highest concentrations Cr(VI) didn't shown here. Authors [5] analyzing Cr(VI) with GC electrode attributed that the wave more reversible might tentatively be attributed to the reduction of Cr(VI) to Cr(V), with further reduction to Cr(III) in another wave.

**3.4.Alcohol electrooxidation with Pd/Ti and Pd/GC electrodes**

Fig. 5(a) 5(b) and 5(c) gathers CV curves of the Pd/Ti(+0.1V) , Ti foil and PdGC electrodes respectively, at 20mV/sec , in 0.05 M NaOH

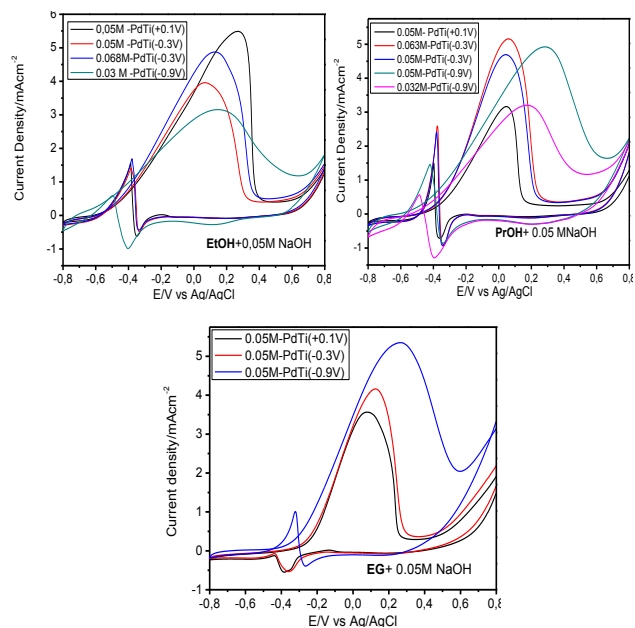
and 1M NaOH by (A): C<sub>2</sub>H<sub>5</sub>OH (EtOH), C<sub>3</sub>H<sub>7</sub>OH (PrOH) and C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>(EG), at room temperature. The comparison of CVs of the modified electrodes recorded in the blank solution (0.05M or 1 M NaOH) with those obtained in adding quantities of corresponding alcohol clearly demonstrates significant oxidation of alcohol as indicated by two well defined anodic peaks, one observed on the forward and other one, observed on the reverse scan. The observed oxidation peak during the forward scan is due to the oxidation of adsorbed alcohol molecules and it was used by the construction of calibration curves. The CV profile by 0.05 M Alcohol +0.05MNaOH and 1 M Alcohol+ 1M NaOH with PdTi(+0.1V) is showed in Fig 5(a). At low concentrations the EtOH measured the highest current density (5.5mAcm<sup>-2</sup>) and it is decreasing in order :EtOH>EG≥PrOH; but the lowest oxidation potential (0.04V) is by PrOH. The assays of crescent addition of each alcohol with this electrode in 0.05M NaOH ,(Figs didn't showed here), calculated slope values of I(mAcm<sup>-2</sup>)vs C(mM) (see Table 1) as being in order: EtOH>PrOH > EG. Then, in the assays at 1M ,Fig 5(a), the lower oxidation potential is by PrOH(-0.15V) and EtOH(-0.03V) than EG(+0.05V), but with a increased current sensitivity by EG (20mAcm<sup>-2</sup>) and EtOH(10mAcm<sup>-2</sup>). The Ti foil demonstrated catalytic activity by alcohol electrooxidation, as it is observed in the Fig.5(b). At low and high concentration the PrOH and EtOH maintained the lowest oxidation potential(-0.23V ; -0.15V) with current densities in order 0.6-0.04 mAcm<sup>-2</sup> quasi insignificant, but that reinforced the activity of the system Pd/Ti ,making this electrode more stable in front of crescent addition of the alcohols and use frequent in several experiments. The conduct of Pd/GC electrode ,Fig 5(c) by alcohols electrooxidation is similar to Pd/Ti nanoelectrodes, but i.e in 0.05M (A)+ 0.05M NaOH, the stability of electrode upon time of use and crescent alcohol concentration was reduced.



**Figure 5** –CV at 20mVs<sup>-1</sup>, in 1M (A)+1M NaOH, and 0.05M (A)+0.05M NaOH solution, a)PdTi(+0.1V) ; (b)Ti foil; (c) Pd/GC

The slope values of the calibration curves upon crescent addition of each alcohol molecule calculated with Pd/Ti: (+0.1), (-0.3V),(-0.9V), Ti foil and Pd/GC electrodes, in 0.05M NaOH electrolyte, between 3.43mM-90mM alcohols are described in the Table 1. The conduct of each electrode upon crescent addition of each specific alcohol molecule was something different, by this an analysis of each alcohol electrooxidation

activity on different Pd/Ti electrodes is necessary to find out the adequate fuel on the different electrocatalysts. By detail, the Figure 6, show the performance of electrocatalytic Pd/Ti systems with each molecule Fig 6(a) EtOH, Fig 6(b) PrOH and Fig 6(c) EG, in 0.05M NaOH electrolyte. The analysis through of lesser maximum oxidation potential (E<sub>ox</sub>) indicate that performance of PdTi(+0.1)>PdTi(-0.3)>PdTi(-0.9V) electrodes and would be better by PrOH and EG oxidation. The PdTi(+0.1) electrode showed a major sensitivity by EtOH electrooxidation but the oxidation potential maximum was displaced to 0.27 V as seen in Fig 6(a). The existence of a diffusional process was studied by voltammetric responses to various scan rates (5–100mV/sec) with Pd/Ti or Pd/GC electrodes in 0.05M NaOH electrolyte (the graphs didn't showed here). The results by ethanol oxidation showed that on Pd/Ti electrode is an irreversible controlled by diffusion process and a diffusion coefficient averaged D= 1.7±0.1 10<sup>-6</sup> cm<sup>2</sup>/s, can be obtained at 50 mM, with three Pd/Ti(+0.1V), Pd/Ti(-0.3V), Pd/Ti(-0.9) electrodes. The analysis by the calculate the coefficient was based in a ethanol electro oxidation mechanism in alkaline media proposed in literature [11].



**Figure 6** –CV at 20mVs<sup>-1</sup>, in 0.05M NaOH electrolyte, with PdTi:(+0.1V) (-0.3V),(-0.9V), a) EtOH, b)PrOH, c)EG

**Table 1** – Values of slope of linear regression J(mAcm<sup>-2</sup>) vs C(mM), between 3mM-90mM alcohol with r<sup>2</sup>=0.96-0.99.

Electrocatalysts	EtOH	PrOH	EG
PdTi(+0.1V)	0.221	0.053	0.036
PdTi(-0.3V)	0.105	0.064	0.072
PdTi(-0.9V)	0.108	0.080	0.080
Ti foil	0.0006	0.0013	0.0007
Pd/GC*	0.413*	0.012	0.050

\*Only between 3.43mM-22mM EtOH the curve was linear

### 3.41. Polarization Curves in NaOH 0.05M with Pd/Ti electrodes.

A comparison of alcohol electrooxidation activity on Pd/Ti electrode in alkaline media may be important just to find out the appropriate fuel on the different electrocatalysts. Fig. 8 shows the Tafel curves from the polarization curves assays of the Pd/Ti(+0.1V) electrode in 0.05 M NaOH oxygen-saturated solution + (x) M alcohol with a scan rate of 1mV/s, (x=0.027M and 0.054 M EtOH, 0.078M PrOH, 0.056M EG). The lowest point is the equilibrium potential which is the onset potential ( $E_{eq}$ ) for alcohol electrooxidation. The Fig. 8, show that EG has the highest value of  $E_{eq} = -0.55V$  on the Pd/Ti electrode. The oxidized order for alcohol electrooxidation on the Pd/Ti(+0.1V) electrode is ethanol > n-propanol > EG. The ethanol show lower value of  $E_{eq} = -0.8V$  (which isn't greatly modified by alcohol concentration) than other alcohols on the Pd/Ti electrode, showing that ethanol and 1-propanol ( $E_{eq} = -0.67V$ ) can be more easily electrochemically oxidized than ethylene glycol on the Pd/Ti electrode. The oxygen reduction reaction with Pd/Ti is involved in Fig 8, where the measurements of tafel slope was (60mV/dec) at low current density. By other hand, the oxygen reduction with Pd/Ti in a free alcohol solution show a onset potential of +0.025 V, but when the reaction proceed in presence of alcohols a significant shift in  $E_{onset}$  is observed. Besides, with 0.027 M EtOH the shift was lower than with 0.054 M EtOH (-0.29V and -0.37 V) respectively.

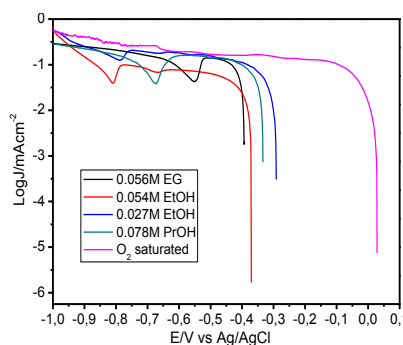


Figure 7 – Tafel curves, by alcohols oxidation and oxygen reduction , at 1mV/sec in 0.05M NaOH

## 4. Conclusion

Pd/Ti electrocatalysts are efficient by reduction or oxidation reactions in the adequate aqueous electrolyte. The time of life useful was greater than Pd/GC electrode in the reactions assayed. The oxygen reduction reaction may be reversible when the Pd/Ti catalyst work in acid media and a process de slow electron transfer occur indicating a quasi reversible

process in alkaline media. However a marked sensitivity by increase in current density is observed in alkaline media. The sensitivity by Cr(VI) reduction measured by three Pd/Ti electrodes was similar between them and the reduction potential of 0.58V occurs at more positive potential than Pd/GC electrode at 0.49V. The Cr(VI) reduction with Pd/Ti proceed via reversible electron transfer and a diffusion coefficient of  $2.2 \cdot 10^{-5} \text{cm}^2/\text{s}$  was calculated. The alcohols electro oxidation analyzed in low concentration showed attractive results with current density in order  $5 \text{mAcm}^{-2}$  and a linear correspondence between 3mM-90mM of alcohol concentration in very diluted alkaline solutions. The performance of PdTi(+0.1V)  $\approx$  PdTi(-0.3V) > PdT(-0.9V) when the more negative oxidation potential was required. The Tafel curves supported the efficiency of alcohol electrooxidation as EtOH > PrOH > EG with Pd/Ti electrocatalysts, because the  $E_{onset}$  resulted at more negative value by EtOH than PrOH and EG. The oxygen reduction measured via polarization curve with Pd/Ti electrodes present a positive onset potential +0.025V, that is modified when a alcohol molecule is electrooxidized in the alkaline solution.

## Acknowledgments

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