International Congress of Science and Technology of Metallurgy and Materials, SAM – CONAMET 2014

# Pd/Ti electrocatalyst in  technological  significance reactions

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**Abstract**

New materials operating as future electrocatalysts into fuel  cells or in environmental remediation processes are continuously under research. Here we studied palladium modified electrodes, such as Pd/Ti and Pd/GC (glassy carbon), which are electrochemically built and used in chromate detection, in oxygen reduction and alcohols oxidation reaction. The palladium material electrodeposited at constant potential was characterized by X-ray diffraction, and scanning electron microscopy. The response of Pd/Ti nanoelectrodes,  by oxygen reduction was observed in alkaline and acid supporting electrolytes. The diffusion coefficient of $2 \cdot 10^{-5}$ cm$^2$/s with a transference of 4e$^-$ in 0.1M H$_2$SO$_4$ solution was calculated. A higher coefficient value in 0.05 M NaOH  was evaluated, because Ti substrate is also active in oxygen reduction in alkaline media. The reduction of Cr(VI) with Pd/Ti electrode proceeds at +0.58 V vs Ag/AgCl in H$_2$SO$_4$ 0.1M, with a diffusion coefficient of $2.2 \cdot 10^{-5} \pm 0.01$ cm$^2$/s and a linear range between 0.019 -0.69 mM Cr(VI). The lowest sensitivity 0.5 μM Cr(VI) was determined with Pd/Ti electrode in the range permissible by  drinking  water of 1 μM. The oxidation of alcohol molecules in alkaline environment showed by Tafel curves, the activity order on Pd/Ti electrocatalyts   is ethanol≅n-propanol >ethylene glycol. The calibration curve obtained by  anodic peak current density of cyclic voltammetries   upon an increasing alcohol concentration (3 to 90 mM alcohol)  in NaOH 0.05 M, permitted to evaluate   an activity of   PdTi(+0.1V)≈PdTi(-0.3V)>PdTi(-0.9V). The performance of Pd/Ti electrocatalysts was better when compared with a modified Pd/GC electrocatalyst, in the studied reactions.

## 1. Introduction

In aqueous systems, the dominant chromium species are Cr(VI) and Cr(III), present in wastewater drained from leather tanning, textile, electroplating, and electronic industries, and steel manufacturing [Nriagu J.O. (1888); Kachoosangi R.T and Compton R.G (2013)]. Since the  debate on  the environmental  convertibility  of  Cr(III) to the

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more hazardous carcinogen in  hexavalent state is on going, the ability to determine quantitatively hexavalent in chromium(III) substrates is of particular importance to many industries[C.Pellerin and S.M.Booker (2000)]. In order to protect human life and the environment from Cr(VI) toxicity, a permissible limit of 50 µg $L^{-1}$ (≈1 µM) in groundwater was set by the World Health Organization (WHO) [WHO, guidance (1993)]. Between numerous methods for determination of chromium in aqueous systems, electrochemical techniques are considered to be the most powerful methods in the presence of interferences [Metters J.P. et al (2012)]. Voltammetric methods are advantageous in the speciation of chromium since they offer a low detection limit [Jena B.K and Raj C.R (2008); Dominguez-Renedo et al (2008)]; the determinations can also be carried out without any additional separation step. In particular, we used cyclic voltammetry, differential pulse voltammetry, due to its high sensitivity and selectivity in the determination of Cr(VI) in acid media with new Pd/Ti and Pd/G electrodes.

It was reported [Xie S-W et al (2011)] that noble metal catalysts are relevant to alkaline or acid fuel cell technology, while oxygen reduction reaction systems are particularly relevant to chloralkali electrolysis and metal-air batteries [Erikson H. et al (2012)]. Therefore, prospects for the continued development of alkaline electrocatalytic systems, including alkaline fuel cells, seem highly promising, due to advantages in activity and material stability upon corrosion. Both, oxygen reduction and alcohols electrooxidation reactions with palladium electrodes in acid and alkaline medium have been systematically studied in the last five years [Alexeyeva N. et al (2011); Wang D. et al (2009); Cherevko S. et al (2012); Carrera Cerritos R. et al (2012)]. However, the effect of Ti substrate alone, and the combined Pd/Ti system, is still  unknown.  Here, we evaluate Ti, Pd /Ti and Pd/GC catalysts during  electrooxidation of ethanol, n-propanol and ethylene glycol,  to establish the appropriate fuel on the different electrocatalysts. In addition, we compare oxygen reduction in acid and alkaline electrolytes with Pd/Ti system.

## 2. Experimental

The substrate was a thin layer of pure titanium 2 µm of thickness supplied by Mateck, measuring 10 x30 x 1mm. In order to achieve a clean and reproducible surface, working electrodes have been washed with ultrapure water (18MΩcm) to obtain an Elix company Milli-Q system at room temperature. 5 mM $PdCl_2$ solutions (E. Merck, Darmstadt), dissolved in 0.1 M HCl, were prepared, adjusting the solution at a pH of 2.6. Electrochemical measurements proceeded with a three-electrode cell; the counter electrode was a high purity Pt wire; and  the reference electrode Ag/AgCl, KCl(3M). Electrochemical measurements were carried out using Metrohm Autolab B.V 302N equipment. The preparation of the working electrodes was based on the electrodeposition of Pd, from the electrolyte onto blade Ti metal as described above, and a constant potential of +0.1 V, -0.3 V and -0.9 V was applied during 300 seconds. An alternative palladium modified electrode was prepared depositing 5 mM $K_2PdCl_4$ at +0.05V for 200 seconds onto glassy carbon electrode (3 mm diameter). It was prepared once the working electrode was removed from the solution and rinsed with de- ionized water three times, so as to be sure of eliminating excess solution. Electrodes electrochemical characterization in alkaline (1 M or 0.05 M NaOH) or acid electrolyte (0.1 M $H_2SO_4$) was carried out by cyclic voltammetric, linear sweep voltammetry, linear polarization, and differential pulse voltammetry with 50 mV amplitude pulse and modulation time of 50 ms used in the detection in low limit. The characterization of the deposits built was performed by scanning electronic microscopy - SEM-FEG/CARL ZEIZZ-Sigma. X-ray diffraction tests were conducted on samples with a reflection diffractogram Philips PW1710 with radiation from copper, 40kV voltage and 30mA current. The patterns studied were in the range 2θ (from 20°to 90 °).

## 3. Results and Discussion

### 3.1- Characterization of Pd/Ti electrocatalysts

Fig.1 shows the typical SEM micrograph of palladium nanoparticles electrodeposited on Ti foil. Fig.1(a), shows the Ti substrate and Fig1(b) the typical micrograph of palladium by Pd/Ti(+0.1V) with an average size of 80 nm. A detailed image of nanoflower morphology corresponding to Pd/Ti(-0.9V) is the Fig 1(c). An increase in
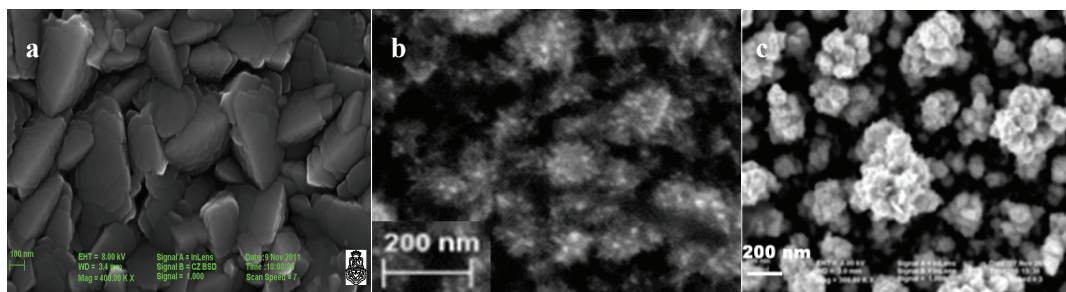
**Figure 1.** SEM image of a) Ti foil. b) Pd/Ti(+0.1V) and c) Pd/Ti (-0.9V), electrodeposits.

deposition overpotential produced an increase in particle size, and as reported previously [Fuentes A.S et al (2013)], all deposits closely followed the trend of 3D instantaneous nucleus and growth controlled by diffusion.

The Pd nano flowers supported on Ti film exhibited an XRD pattern of a typical face-centered-cubic (fcc) lattice, with the main Pd(111) peak at 39.85°. The (200) plane corresponding to the fcc structure of Pd° at 46.74° allowed calculating grain size (22.5 nm) and parameter of cell as 3.88728 Å. Further information on the synthesis and characterization of Pd/Ti systems may be found in [Fuentes A.S et al (2013)].

### 3.2. Cr(VI) reduction at Pd/Ti , Pd/GC electrocatalysts.

The response of various Cr(VI) concentrations in deoxygenated 0.1 M $H_2SO_4$ solution at Pd/Ti(+0.3 V) electrode, at room temperature is shown in Fig 2(a). The CVs revealed a reduction wave at +0.58 V (versus Ag/AgCl). The shape of the voltamogramms with the absence of oxidation peak in the potential range studied indicates a chemically irreversible reaction. However, the slight shift in the reduction peak to more negative values (less 20 mV) with further increase in Cr(VI) concentrations, would demonstrate a electrochemically reversible reaction. This is confirmed by the Tafel slope of ca. 112 mV per decade obtained from a plot of potential versus log (current). The corresponding plot of current density against an increasing concentration of hexavalent chromium, Fig 2 (b), was found to be linear between the range studied (0.019–0.695 mM); slope = 0.55 (mAcm$^{-2}$/ mM), intercept i(mAcm$^{-2}$) =0.03 and $r^2$ = 0.992. Pd/Ti(+0.1V) and Pd/Ti(-0.9V) electrodes maintained a similar activity. Further assays on Ti electrode without Pd deposited, did not show reduction activity of hexavalent chromium.

Fig. 3 (a) shows voltammetric responses with Pd/Ti(-0.3V) electrode of 0.695 mM Cr(VI) in deoxygenated 0.1 M $H_2SO_4$ at various scan rates: 5, 10, 20, 30, 50 up to 250 mV/s. The peak potential is not found significantly dependent on scan rates, with a shift of 36 mV from 5 mV/s to 50 mV/s, suggesting one electrochemically reversible reaction at Pd/Ti(-0.3V) electrode. This is confirmed by Tafel analysis, where the plot of potential (mV) versus log (current density) in CV at 5 mV/s produces a slope value of ca. 88 mV/dec, confirming electrochemical reversibility. The plot of density current vs scan rate square root, Fig. 3 (b), was found to be linear in the scan studied ($r^2$=0.99887) with a slope=0.00264, (Acm$^{-2}$/Vs$^{-1}$) suggesting that the reaction is diffusion rather than surface controlled. The reaction process might be rationalized as the one-step reduction of Cr(VI) to Cr(III). Then, the diffusion coefficient calculated by Randles–Sevcik equation [Bard A.J and Faulkner L.R (2001)], for a total three electrons and one electron transferred, was D= 2.21 $10^{-5}$±0.01 cm$^2$/s. This diffusion coefficient value was obtained for the reduction process of 0.2195 mM and 0.695 mM Cr(VI) at Pd/Ti(+0.1V) electrode. The reduction pathway considered was that suggested by [Welch C. et al (2005)] where the slow step proceeds via 1e$^-$ and 1H$^+$.

The voltammetric responses with Pd/GC electrode of 0.4128 mM Cr(VI) at various scan rates (5–150 mV/s) in deoxygenated 0.1 M $H_2SO_4$, revealed the potential peak at +0.52 V (vs Ag/AgCl) shifted only 40 mV to more negative values with further increase in scan rate, (graph not shown). This indicates one electrochemically reversible reaction with Pd/GC electrode, confirmed by Tafel analysis. Diffusion coefficient calculated by Randles–Sevcik equation for a diffusion-controlled reversible process was 1.464 $10^{-5}$ ±0.01 cm$^2$/s. The behavior of Pd/GC electrode upon the inclusion of additives of Cr(VI) in 0.1M $H_2SO_4$ was similar to that of Pd/Ti electrodes, but with a reduction maximum at +0.528 V vs (Ag/AgCl). However, the responses of glassy carbon (GC) electrode to solutions
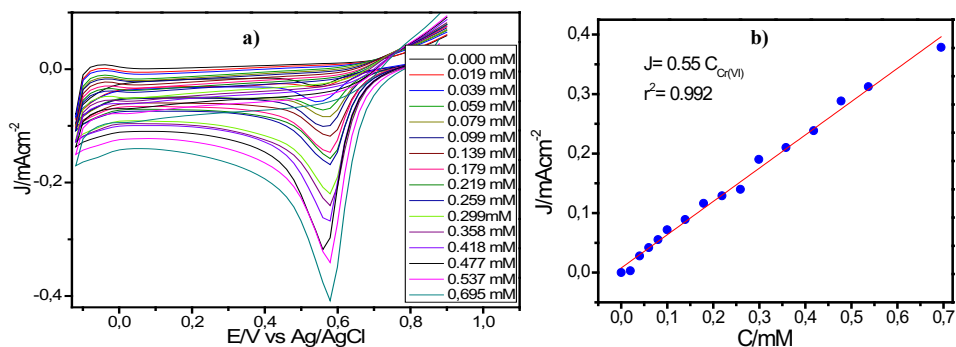
**Fig.2.** Pd/Ti (-0.3V) at 20mV/s in deoxygenated 0.1M $H_2SO_4$ solution **a)** upon increasing addition of Cr(VI),**b)** calibration curve.
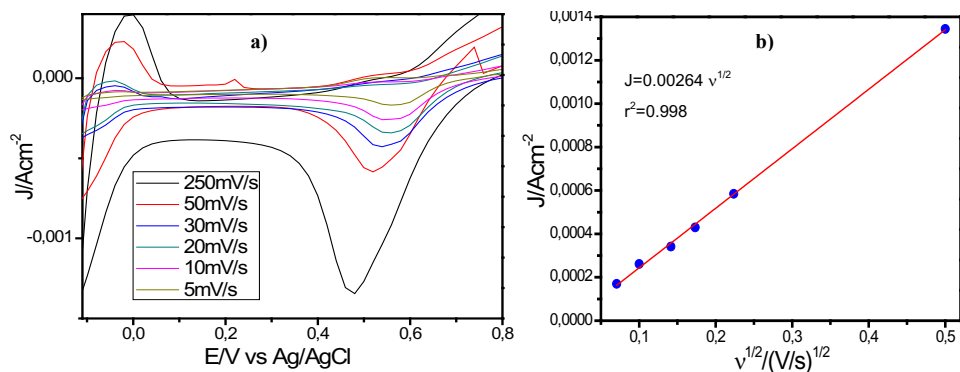


**Fig. 3.** Pd/Ti (-0.3V) in deoxygenated 0.1M $H_2SO_4$ solution , at **a)** several scan rates, **b)** calibration curve.

of 0.1 M $H_2SO_4$ containing additives of Cr(VI) (between 0.059-0.999 mM) revealed the presence of a pre-shoulder at +0.4V (vs Ag/AgCl) and a reduction wave at +0.63 V (vs Ag/AgCl), (CVs not shown).[Welch C. et al (2005)], by analyzing Cr(VI) with a glassy carbon electrode, argued that the more reversible wave might be tentatively attributed to the reduction of Cr(VI) to Cr(V), with further reduction to Cr(III) in another wave.

A detection limit of 19 μM was achieved with Pd/Ti and Pd/GC systems using the cyclic voltammetry for the more acidic 0.1 M $H_2SO_4$ solution. The recommended detection limit set out by EPA (1.0 μM) is significantly lower, showing that CV is not a sufficiently sensitive technique, being most valuable for the electrochemical characterization of the electrode. Thus, differential pulse voltammetry method was applied with a pulse amplitude (50 mV) and modulation time (50 ms) in 0.1 M $H_2SO_4$ and buffer solutions pH 4. The sensitivity by Cr(VI) with Pd/Ti electrodes was better in buffer pH 4. The calibration curve using the Pd/Ti(-0.3V) electrode, measured a slope= 7.67 μAcm$^{-2}$/μM; between a range from 0.49 μM to 6 μM Cr(VI) and a linearity factor of 0.99.

### 3.3.Oxygen reduction with Pd/Ti electrode.

The (CVs) profile with Pd/Ti(+0.1V) electrode in the nitrogen and oxygen saturated 0.1 M $H_2SO_4$ solution at 5 mV/s, allows comparing two profiles with an evident cathodic wave beginning at +0.55 V and one maximum peak at +0.4 V which may be attributed to the electrochemical reduction of oxygen molecules, Fig. 4(a). The shape of voltammograms suggests that oxygen reduction is a chemically irreversible reaction by the absence of a notable oxidation peak. Fig. 4(b) illustrates the effect of scan rate: 5, 10, 20, 50 and 100 mV/s, in oxygen saturated 0.1 M $H_2SO_4$ solution with Pd/Ti(+0.1V) electrode. The increase in scan sweep, shifts the peak potential only 17 mV from 5 to 100 mV/s. This proves that the potential is independent of scan rate; hence, it is likely that oxygen reduction is reversible electrochemically at Pd/Ti electrode in 0.1M $H_2SO_4$ solution. The linear relationship (0.992) between the reduction peak current and the square root of scan rate, indicates that oxygen reduction is also a diffusion-controlled process with this Pd/Ti electrode. The analysis given by reversible electron transfer [Bard.J.A and

Faulkner L.R (2001)], with the slope $=0.006$ $Acm^{-2}/Vs^{-1}$, an oxygen concentration of $1.2$ $10^{-6}$ $molcm^{-3}$, and a diffusion coefficient of $1.9$ $10^{-5}$ $cm^2/s$, calculated a *n* value near 4. Alternatively, by a n=4, the diffusion coefficient calculated was $2.08$ $10^{-5}\pm0.01$ $cm^2/s$. These results allow estimating that oxygen reduction reaction with Pd/Ti electrodes, occurs by transference of (4) electron yielding $H_2O$, rather than via (2) electrons to $H_2O_2$. However, the shape of voltagramms in broad reduction wave with maximum at +0.4 V and shoulder +0.1 V may suggest that two reactions take place during cathodic scan sweep. Some $H_2O_2$ may be produced, which is subsequently conversed to water. To confirm this, assays with hydrogen peroxide from 0.17 mM to 1 mM, were carried out in similar conditions in the presence and absence of oxygen. It was verified that the shoulder near +0.1 V derived from the reduction of $H_2O_2$ to $H_2O$ on nanoflowers of palladium in Pd/Ti electrodes.

A broad reduction wave is also observed in oxygen saturated 0.05 M NaOH solution due to Pd/Ti(+0.1V) electrode. Comparatively, Fig. 5(a), shows CVs at 5 mV/s of nitrogen and oxygen saturated atmosphere 0.05 M NaOH solution, where a notable reduction potential peak at -0.4 V (vs Ag/AgCl) is observed. Fig. 5(b)
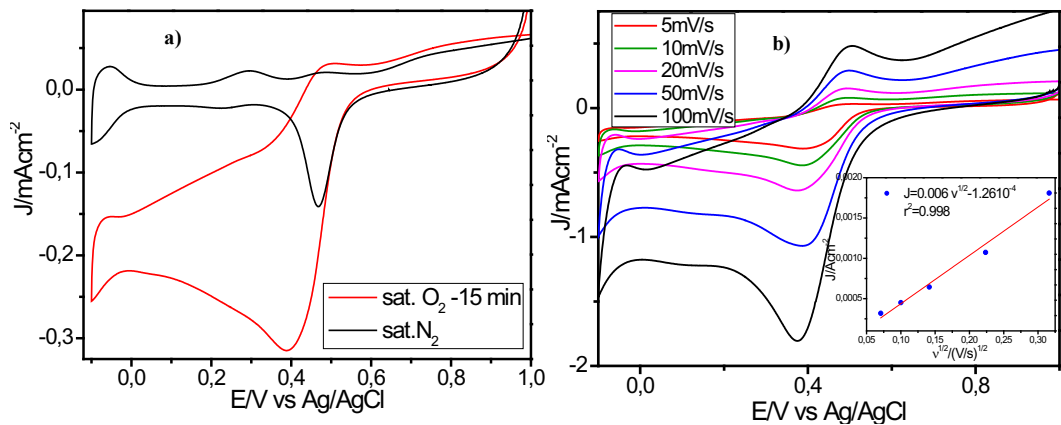


**Fig. 4.** CVs with Pd/Ti(+0.1V) electrode in 0.1M $H_2SO_4$, **a)** 5mV/s ,**b)** $O_2$ saturated solution at several scan rate.
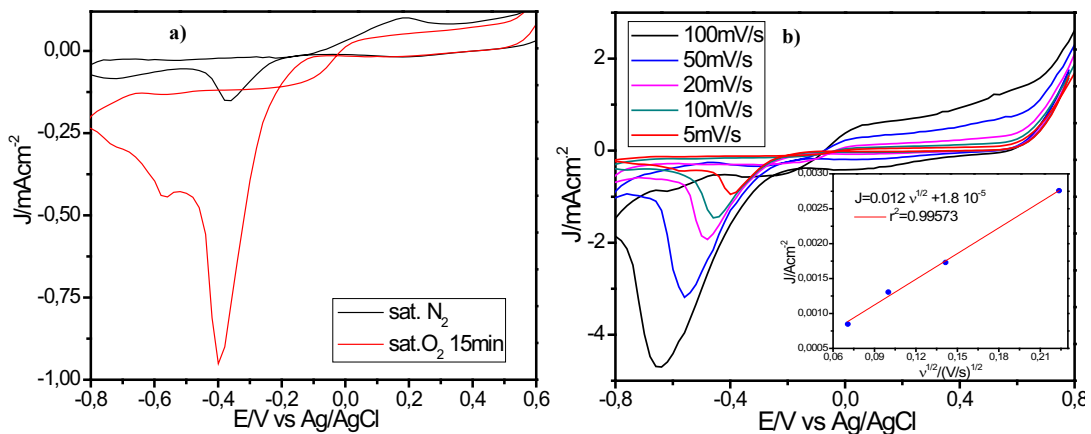


**Fig. 5.** CVs with Pd/Ti(+0.1V) electrode in 0.05M NaOH, **a)** 5mV/s ,**b)** $O_2$ saturated solution at several scan rate.

demonstrates the effect of scan sweep between 5-100 mV/s, with a shift of potential peak of 158 mV from 5 to 50 mV/s, indicating a quasi-reversible process. The slope calculated with Pd/Ti (+0.1V) electrode by the curve $J_{peak}$ vs (v) $^{1/2}$ was 0.012 (Acm$^{-2}$/ Vs$^{-1}$) with r$^2$= 0.9987. The equation applied [Bard J.A and Faulkner L.R. (2001)] evaluated a diffusion coefficient of 4.63 10$^{-5}$ ±0.03 cm$^2$/s by a charge transfer ($\alpha$ =0.5073), four (4) total electrons, and 1.22 10$^{-6}$ molcm$^{-3}$ of oxygen concentration. The greater diffusion coefficient in alkaline media may be attributed to enhanced ion transport and mobile charge transfer in alkaline electrolytes and to the different specific active area, since Ti substrate has activity in the oxygen reduction reaction. A similar behavior was evidenced with Pd/Ti(-0.3V) electrode; yet, Pd/Ti(-0.9V) electrode showed a behavior less reversible in both, acid and alkaline supporting electrolytes.

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

Fig. 6(a), 6(b) and 6(c) gathers CV curves at 20mV/s of Pd/Ti, Ti and PdGC electrodes respectively. The alcohols: ethanol(EtOH), n-propanol (PrOH) and ethylene glycol(EG), are assayed in 0.05 M NaOH and 1 M NaOH solution, at room temperature. The comparison of the CVs of the modified electrodes recorded in the blank solution (0.05 M or 1 M NaOH) with those obtained by adding quantities of corresponding alcohol clearly shows a significant alcohol oxidation as indicated by two well defined anodic peaks, one observed on the forward scan; the other on the reverse scan. The oxidation peak observed during the forward scan is ascribed to the oxidation of adsorbed alcohol molecules; it was used in the generation of calibration curves. A direct alcohol fuel cell, works at a negative potential such as -0.4 V [Yu H.E et al (2010); Antolini E and Gonzalez R.E (2010)]. In this case, the CVs profiles with Pd/Ti (+0.1V) in Fig. 6(a), with different alcohols at high or low concentrations, showed that at -0.4 V, the current density was greater in the order of EtOH> PrOH>EG, proving being more effective at electro-oxidizing ethanol and n-propanol than ethylene glycol with Pd/Ti (+0.1).     A similar performance was observed with Pd/Ti(-0.3V) and Pd/Ti(-0.9V) electrocatalysts.

Ti electrode, also demonstrated some catalytic activity by alcohols electro-oxidation, as observed in Fig. 6(b). Its ability to electrooxidize was similar to that of Pd/Ti electrocatalyst, in the order of EtOH≥PrOH>EG, but having a much lower density current. Palladium plated onto Ti blade, not only increased the activity by electrooxidation, it also made the electrode more stable with increasing additions of alcohols and use in several experiments. The performance of one Pd/GC electrode, by alcohols electro oxidation, was more distinctive than that of Pd/Ti electrocatalysts, since the former showed notable effectiveness by EtOH. In Fig 6(c), at -0.4 V, current density by EtOH is 10 times higher than that of PrOH and 100 times higher than that of EG. Pd/GC electrocatalyst showed the highest current density; however the deactivation of Pd/GC electrocatalyst upon several assays and increasing alcohol concentration was higher than that Pd/Ti. The changes in alcohol and supporting electrolytes concentration did not modify the tendency in electro oxidation activity by each alcohol with the palladium electrocatalysts assayed.

Table 1, describes the results of the calibration curves by current density(mAcm$^{-2}$) versus alcohol concentration from 3.4 mM to 90 mM, measured with Pd/Ti, Ti and Pd/GC electrodes, in 0.05 M NaOH solution. The behavior of each electrode upon increasing addition of ethanol, or 1-propanol or ethylene glycol was evaluated by the slope (as a measure of the activity) and linearity factor. A detailed analysis of the results allows determining the adequate fuel in each electrocatalyst. Fig. 7 and Fig 6(a), show the performance of Pd/Ti electrocatalysts with each alcohol molecule in 0.05 M NaOH solution.

The analysis based on the lowest alcohol oxidation potential indicates that the order is PrOH≈EtOH<EG and that the electrodes effectiveness satisfy: PdTi(-0.3)≅PdTi(+0.1)>PdTi(-0.9V). For EG, the maximum current density was above 5 mAcm$^{-2}$ (in 0.05 M NaOH) and about 19 mAcm$^{-2}$ (in 1 M NaOH). The evaluation of anodic voltammetric curves in Fig.6(a) and Fig.7, according to the Tafel plot, (log $J_{peak}$ vs E), provides insight into the electro-oxidation kinetic. Thus, in Table 2 , Tafel values for EtOH, EG and PrOH, in the range -0.6 V to -0.2 V are summarized. In this sense, [Liang Z.X et al (2009)] reported the Tafel plot of the ethanol electro oxidation in each potential region of palladium electrodes. The resulting value (≈120 mV/dec), was attributed to hydroxyl adsorption onto the Pd surface (forming Pd-OH$_{ads}$), assuming that this process competes with the ethoxi adsorption process. Our experimental value of 135 mV/decade, in the range (-0.6 V to -0.4 V) by Pd/Ti electrocatalysts, is quite close to the theoretical value and is also consistent with the overall rate equation model for ethanol oxidation proposed by the former

authors [Liang Z.X. et al (2009); Liu J. et al (2007)]. The slope value between -0.4 V to -0.2 V increases up to 400 mV/dec, this suggests that the kinetics is not only controlled by hydroxyl adsorption to the surface but it is affected by other surface reactions. In the same way, it is possible to evaluate n-propanol and ethylene glycol electro-oxidation, by Tafel plots, with distinctive potential ranges of each alcohol, as illustrated in Table 2. In Pd/Ti electrocatalysts, exhibiting smaller particle sizes, the Tafel plot for 1-propanol, derived from data of the rising part of the current voltage curve between (-0.5 V to -0.2 V), led a slope of 130 mV/dec. This Tafel value is comparable to that previously reported by [Nezhad K.G et al 2013] of 114 mV/dec ,in 1-propanol electro-oxidation, indicating the one-electron transfer is the rate- limiting step. The Tafel plot analysis of the left hand side of the ethyleneglycol oxidation peak (Fig. 6(a) and Fig 7), in a range -0.4V to -0.2V shows an average slope value of 118 mV/dec for Pd/Ti electrocatalysts having the smallest nanoparticle size. [Dalbay N. and Kadirgan F. (1990)] reported similar slopes values for Pd electrodes in alkaline media at EG concentrations from 0.01 M to 10 M.

The study by cyclic voltammetry of ethanol electro-oxidation with Pd/Ti and Pd/GC electrodes in 0.05 M NaOH solution, at various scan rates (5–100 mV/s) indicates diffusion controlled processes. The peak current density vs the square root of the scan rate calibration curve, built up with a Pd/Ti(+0.1) electrocatalyst gave a slope of $0.02398(Acm^{-2}/Vs^{-1})$ with $r^2$= 0.9937 (Figs. are not shown here). The ethanol oxidation with this Pd/Ti electrode was an irreversible diffusion–controlled reaction ($\Delta E$=217mV) from 5 to 50 $mVs^{-1}$. A diffusion coefficient of D= $(0.21\pm0.03)$ $10^{-5}$ $cm^2s^{-1}$ was calculated, with a concentration of 0.05 M EtOH, considering 2.8 as the number of transferred electrons as in [Liu J. et al (2007)] and $\alpha$=0.1721. Diffusion coefficient calculations were based on the ethanol electro oxidation mechanism proposed by [Liang Z.X. et al (2009), Carrera Cerritos R. et al (2012); Liu J. Et al (2007)]; in which the rate- determining step is the removal of the adsorbed ethoxi intermediate by the adsorbed hydroxyl ions to form acetate. Similar values of the diffusion coefficient were also obtained with Pd/Ti(-0.3V) and Pd/Ti(-0.9V) electrodes. For EG oxidation in a range (5-100 mV/s) in 0.05 M NaOH solution, the peak- current density approaches to an irreversible diffusion-controlled reaction. The dependence of $J_{peak}/(v)^{1/2}$ is checked with
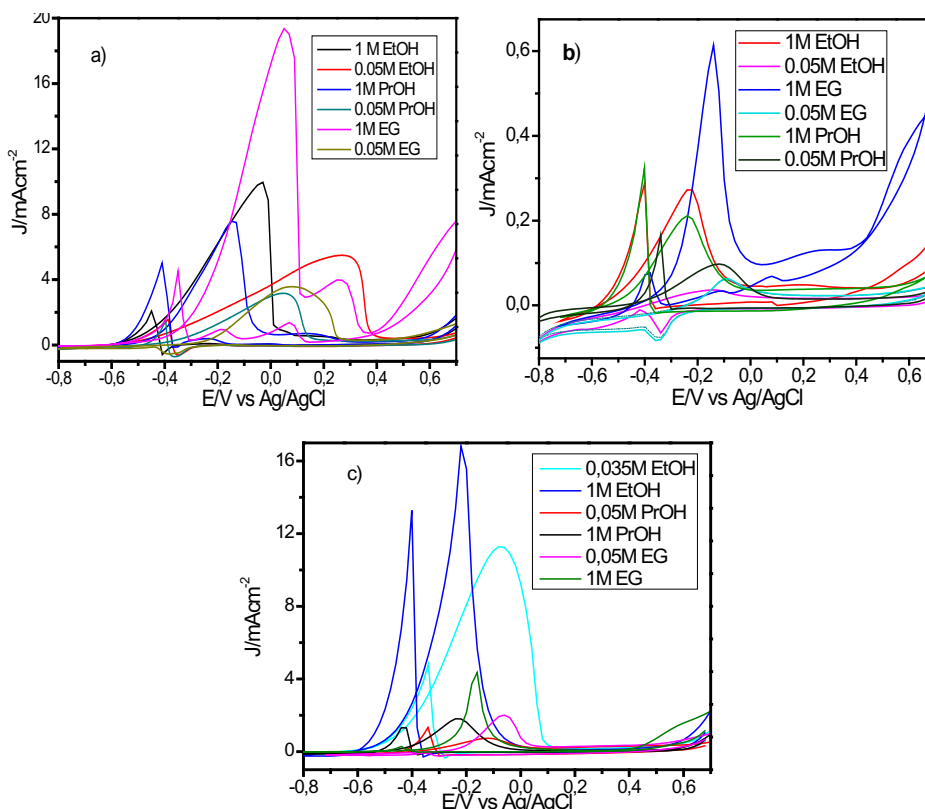


**Fig. 6.** VCs at 20mV/s of 1M alcohol+1M NaOH and 0.05M alcohol+0.05M NaOH with **a)**PdTi(+0.1V) ; **b)**Ti ; **c)** Pd/GC.
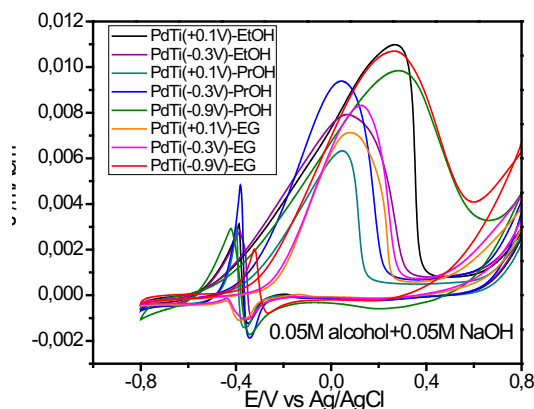
**Figure 7.** CVs of 0.05 M alcohols with Pd/Ti electrocatalysts in 0.05 M NaOH solution.

Pd/Ti(-0.9V) electrode and the slope value results 0.0198 (Acm$^{-2}$/Vs$^{-1}$) with  r$^2$=0.996; then, for  αn=0.5 and a concentration 0.05 M EG, a diffusion coefficient  (D=0.7 ± 0.01  10$^{-5}$ cm$^2$s$^{-1}$) is obtained.

Table 1.  Slopes  of  calibration curve J(mAcm$^{-2}$) vs C(mM) ,between 3-90mM alcohol ,  in  0.05M NaOH.

| Electrode , r$^2$= 0.96-0.99 | 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 | 0.0006 | 0.0013 | 0.0007 |
| Pd/GC* | 0.413 | 0.012 | 0.050 |

*From 3.4mM  to 22 mM  EtOH.

Table 2 – Tafel  slope , measured of CVs., with Pd/Ti electrodes in 0.05 M Alcohol+0.05M NaOH.

| Alcohol | Potential Range(V) | PdTi(+0.1V) mV/dec | PdTi(-0.3V) mV/dec | PdTi(-0.9V) mV/dec |
|---|---|---|---|---|
| EtOH | -0.6/-04 | 135.5 | 135.0 | 152.0 |
|  | -0.4/-0.2 | 419.5 | 414.0 | 652.0 |
| PrOH | -0.5/-0.2 | 131.8 | 133.5 | 317.0 |
| EG | -0.6/-0.4 | 205.0 | 201.0 | 306.0 |
|  | -0.4/-0.2 | 115.0 | 122.0 | 178.0 |

### *3.4.1. Linear polarization with Pd/Ti electrocatalysts in 0.05M NaOH solution.*

A comparison of alcohol electrooxidation activity on Pd/Ti electrode in alkaline media may be particularly important in order to establish the appropriate fuel on the different electrocatalysts. Fig. 8 shows, Tafel curves from the polarization curves assays of Pd/Ti(+0.1V) electrocatalyst  in oxygen-saturated 0.05 M NaOH solution + ( x) M alcohol with a scan rate of  1 mV/s,  being  (x=0.027 M and 0.054 M EtOH, 0.078 M PrOH, 0.056 M EG). The lowest point is the equilibrium potential which is the onset potential *(E$_{eq}$)* for alcohol electrooxidation. Fig. 8, shows that EG has the highest value of *E$_{eq}$* =-0.55 V on the Pd/Ti electrode.        Ethanol shows the   lowest value of *E$_{eq}$*=-0.8 V, and this potential is not significantly altered by alcohol concentration. 1-propanol (*E$_{eq}$*= -0.67V)  can be more   easily   electrochemically  oxidized   than   ethylene glycol. Then, the  oxidized order for alcohol
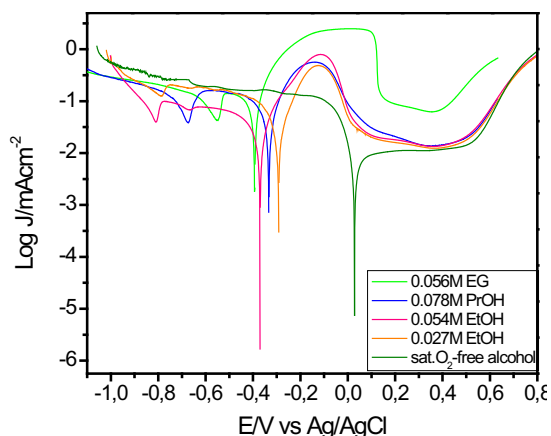
**Fig. 8** – Tafel curves, by alcohols oxidation and oxygen reduction , at 1mV/s in 0.05M NaOH

electrooxidation on the Pd/Ti(+0.1V) electrode is EtOH >PrOH >EG. Oxygen reduction reaction with Pd/Ti is involved in Fig. 8,   where the measures of Tafel slope were (60 mV/dec) at low current density. On the other hand, oxygen reduction with Pd/Ti in a free alcohol solution shows an onset potential of +0.025 V; however, when the reaction proceeds in the presence of alcohols a significant shift in $E_{onset}$ is observed. In addition, the shift is lower with 0.027 M EtOH than with 0.054 M EtOH (-0.29 V and -0.37 V) respectively.

## 2. Conclusions

Pd/Ti electrocatalyts are efficient by reduction or oxidation reactions in the adequate supporting electrolyte. The useful lifetime of Pd/Ti is greater than that of Pd/GC electrode in the reactions assayed. The activity by Cr(VI) reduction measured by each Pd/Ti electrocatalyst is  similar. The reduction potential of +0.58 V(vs Ag/AgCl) occurs at a more positive potential than that in Pd/GC electrocatalyst at +0.52 V. The Cr(VI) reduction with Pd/Ti is irreversible chemically and  reversible electrochemically diffusion-controlled reaction, and  diffusion coefficient is 2.2 $10^{-5}$ cm$^2$/s. Oxygen reduction reaction may be reversible electrochemically when the Pd/Ti catalyst works in acid media and a quasi reversible electrochemically  process in alkaline media. However, a notable activity is found  in alkaline media. Alcohols electro oxidation analyzed in low concentrations shows attractive results with current density in the  order of 5mAcm$^{-2}$ and a linear correspondence between 3 mM-90 mM in alcohol concentration in highly   diluted alkaline solutions. The performance of PdTi(+0.1V)≈PdTi(-0.3V)>PdT(-0.9V) when the more negative oxidation potential was required. Tafel curves supported the efficiency of alcohol electrooxidation as EtOH≥PrOH >EG with Pd/Ti electrocatalysts, since $E_{onset}$ had a more negative value for EtOH and  PrOH than that of EG. Oxygen reduction measured via polarization curve with Pd/Ti electrodes exhibits a positive onset potential of +0.025V, modified when an alcohol molecule is electrooxidized in the alkaline solution.

**Acknowledgement**

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