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**Electrochemical Activity of Pt/oxide-C Composites on the  
Oxygen Reduction Reaction**

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ABSTRACT

Pt-TiO<sub>2</sub>-C composites have been synthesized by photo-deposition and vapor-phase impregnation-decomposition methods. These electrocatalysts were characterized by XRD, H<sub>2</sub> chemisorption, TEM and XPS techniques. The main objective of this work was to compare the electrochemical activity of both composite materials on the oxygen reduction reaction taking a Pt/C sample as reference electrocatalyst. X-ray diffraction permitted to identify the crystallographic planes of Pt (*fcc*). TEM images showed Pt particle size less than 10 nm in all synthesized samples. Surface composition results (XPS) revealed a modification of Pt electronic properties depending of the preparation method. The platinum-oxide interaction on the Pt-TiO<sub>2</sub>-C samples promoted the electrocatalytic activity for oxygen reduction reaction compared with Pt supported on carbon.

*Keywords:* Pt/TiO<sub>2</sub>-C catalysts, Chemical vapor deposition, Oxygen Reduction Reaction



## 1. Introduction

The short life time of the electrocatalysts has recently been recognized as one of the most important issues to be addressed before PEMFC becomes commercially viable [1-7]. The degradation of Pt/C catalysts over time is mainly attributed to the loss of electrochemical surface due the corrosion and electro-oxidation carbon leading to significant electrochemical activity loss [7-9]. One alternative for increase the stability of the electrocatalysts is the use of more stable support. The emerging candidates as supports are the conducting oxides like  $\text{TiO}_2$  [10-15],  $\text{WO}_3$  [12, 16],  $\text{SnO}_2$  [17-18] and  $\text{NbO}_2$  [18] to produce stables oxide-carbon nanocomposites as substrates to Pt. These novel metal-oxide-carbon electrocatalysts have demonstrated an increase on the electrochemical stability and an enhancement on the ORR catalytic activity. For instance, the Pt/ $\text{TiO}_2$ /C composite present a higher electrocatalytic current per unit area than a conventional Pt/C [19-23]. This behavior was explained in terms of the presence of oxide produced modifications in the electronic properties of Pt surface, a synergetic effect of the interaction metal-oxide increases the electronic density of the Pt orbital, these changes are favorable for the oxygen adsorption and electrochemical activity [24-25], therefore Pt- $\text{TiO}_2$ -C could be used as promising stable catalysts in low temperature  $\text{H}_2/\text{O}_2$  fuel cells cathodes.

Recently, the photo-deposition method has been used for prepared electrocatalysts of Pt-C and Pt-oxide-C [11, 23, 26-29]. In order to improve the advantages obtained in the last researches, in this work we probed a new methodology as alternative method (vapor-phase impregnation-decomposition technique) to prepare actives and stable electrocatalysts for PEMFC. The use of this last technique mentioned produced well dispersed nanoparticles ranging from 1-10 nm depending on their chemical nature [30].

In the present research we have developed an experimental procedure to obtain and characterize 10%Pt-5% $\text{TiO}_2$ -C electrocatalysts prepared by photo-deposition and vapor-phase impregnation-decomposition methods. 10%Pt-C electrocatalysts were prepared by the same methods in order to compare each other. The solids physical properties were studied by XRD,  $\text{H}_2$  chemisorption, TEM and XPS techniques. The electrochemical activity was evaluated in the ORR at room temperature in acid medium.

## 2. Experimental

### 2.1. Pt- $\text{TiO}_2$ -C and Pt-C preparation by photo-deposition method

10 wt.% Pt-5 wt.%  $\text{TiO}_2$ -C (S1) catalyst was produced in two steps: i) first the  $\text{TiO}_2$ -C nanocomposite was synthesized by sol-gel method and ii) the nanoparticles platinum were photo-deposited onto  $\text{TiO}_2$ -C sustrate by irradiation. The  $\text{TiO}_2$ -C substrate was prepared following the L. Timperman et al.[1, 26-27] methodology. The synthesis of 10 wt.% Pt-C (S2) electrocatalysts was carried out following the same methodology described above using an alcoholic solution of  $\text{H}_2\text{PtCl}_6$  dispersed over Vulcan carbon as substrate. Under this condition the suspension was continuously stirred and irradiated by 3 h in  $\text{N}_2$  atmosphere. Then, the resultant suspension was heated at 100 °C overnight to remove the solvent by evaporation [27].

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**2.2. *Pt-TiO<sub>2</sub>-C and Pt-C preparation by vapor-phase impregnation-decomposition***

A thermal horizontal tube quartz reactor were used for the vapor phase impregnation decomposition (V) method. Platinum acetylacetonate (C<sub>10</sub>H<sub>14</sub>O<sub>4</sub>Pt, Aldrich), titania nanoparticles (rutile fase, Aldrich) and carbon Vulcan were mixed in the tube quartz at 10:5:85 weight ratio at room temperature to synthesized the 10 wt.% Pt-5 wt.% TiO<sub>2</sub>-C-V (S3). The vapor-phase impregnation-decomposition was carried out following the literature reports [30]. The sample 10 wt.% Pt-C-V (S4) were synthesized using the same conditions above mentioned using the 10:90 (Pt:C) weight ratio.

**2.3. *Physical characterization***

X-ray diffraction (XRD) patterns were collected on a Bruker D8 AXS equipment using a Cu anode (K $\alpha$ ,  $\lambda=1.5406$  Å) and a Bragg-Brentano configuration. The angle  $2\theta$  was varied from 30 to 90° with 0.2° min<sup>-1</sup> and 35 kV. Particle size distribution was obtained with a high resolution transmission electron microscopy using a JEOL-JEM-2200 field emission operated at 200 kV. XPS measurements were carried out using a JEOL JPS9010MC spectrometer with a MgK $\alpha$  radiation source of 1253.6 eV. The Pt (4f) and TiO<sub>2</sub> (2p) signals were collected by XPS technique. The position of the C (1s) peak (284.5 eV for the JEOL JPS-9010MC spectrometer) was used to correct the binding energies of Pt-C and Pt-TiO<sub>2</sub> electrocatalyst. XP spectra were fitted using XPS Peak v4.1 software.

**2.4. *Electrochemical measurements***

All electrochemical measurements were carried out at 25 °C in a single, conventional, three-electrode test electrochemical cell in a 0.5M H<sub>2</sub>SO<sub>4</sub> aqueous solution. A platinum mesh was used as the counter electrode, and Hg/Hg<sub>2</sub>SO<sub>4</sub>/0.5M H<sub>2</sub>SO<sub>4</sub> (MSE = 0.680 V/NHE) as the reference electrode. The potentials in this paper were related to normal hydrogen electrode (NHE). The electrochemical measurements were performed in a Potentiostat (EG&G PAR 263A) and a Pine MSR-X rotation speed controller. Glassy carbon disk with a cross-sectional area of 0.19 cm<sup>2</sup> was used as a support for the thin films and used as an ink-type working electrode. The catalytic ink was prepared with 1mg of catalyst, 6  $\mu$ l of 5 wt% solution Nafion® (Du Pont, 1100 EW) and 60  $\mu$ l of ethyl alcohol. For RDE experiments, 8  $\mu$ l of this sonicated mixture were deposited on glassy carbon electrode.

Before the ORR measurements, cyclic voltammetry (CV), in a nitrogen-saturated electrolyte, was performed to clean the electrode surface from 0.0 to 1.2 V at 50 mV s<sup>-1</sup>. Hydrodynamic experiments were recorded at oxygen atmosphere in the rotation range of 100, 400, 900, 1600 and 2500 rpm at 5 mV s<sup>-1</sup>. The current density was calculated using the geometric surface area.

The experimental techniques selected to determinate the Electrochemical Active Surface Area (EAS) were cyclic voltammetry in argon saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> at 50 mV s<sup>-1</sup> by integrating the hydrogen-adsorption/desorption region (EAS H<sub>upd</sub>) and the oxidation of the carbon monoxide (CO stripping) (EAS<sub>CO</sub>) [31]. In CO stripping technique, the electrode potential was held at 0.1 V/NHE and CO bubbled by 5 min. Thereafter, the electrolyte was saturated with argon in order to remove the CO from solution. Two cycles were done from 0.05 V to 1.2 V/NHE at 5 mV s<sup>-1</sup>.



### 3. Results and discussion

#### 3.1 X-ray diffraction

Fig. 1 shows the XRD diffraction patterns of Pt-TiO<sub>2</sub>-C-P (S1), Pt-C-P (S2), Pt-5TiO<sub>2</sub>-C-V (S3) and Pt-C-V (S4) electrocatalysts. The S1 and S2 powder electrocatalysts synthesized by photo-deposition method showed five diffraction peaks at  $2\theta$  values of 39.8°, 46.2°, 67.4°, 81.2° and 85.7° characteristics of the (111), (200), (220), (311) and (222) planes of face-centered cubic structure of platinum. For S1 electrocatalyst not sharp peaks corresponding to titanium oxide were observed, indicating that TiO<sub>2</sub> deposited are very small nanocrystals or have an amorphous structure.. The samples S3 and S4 prepared by vapor-phase impregnation-decomposition method showed a breadth XRD peaks of the fcc platinum structure. S3 catalyst showed other peaks at  $2\theta$  vales of 36.1°, 41.2°, 44.0°, 54.3°, 56.6°, 69° (indicated by asterisks in Fig. 1) that can be ascribed to the (101), (111) (210), (211), (220), (301) planes of TiO<sub>2</sub> (rutile phase commercial).

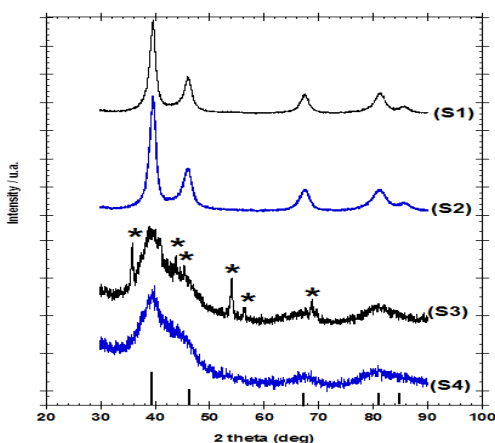


Figure 1. X ray difraccion patterns of 10 wt.% Pt-5 wt.% TiO<sub>2</sub>-C-P (S1), 10 wt.% Pt-C-P (S2), 10 wt.% Pt-5 wt.% TiO<sub>2</sub>-C-V(S3) and 10 wt.% Pt-C-V(S4) electrocatalysts synthesized by photo-deposition (upper) and by vapor-phase impregnation-decomposition (bottom). The (\*) corresponding to crystallographic position of TiO<sub>2</sub> rutile phase.

#### 3.2 TEM images

Fig. 2 presents a TEM images of Pt/TiO<sub>2</sub>/C (S1 and S3) and Pt/C (S2 and S4) electrocatalysts synthesized by both methods. The micrograph of S1 catalyst prepared by photo-deposition method reveals a selective deposition of Pt nanoparticles onto TiO<sub>2</sub> surface (platinum nanoparticles on the carbon Vulcan is not observed). The dispersion of TiO<sub>2</sub> prepared by sol-gel method onto the carbon was non-homogeneous. Sample S2 shows a good dispersion of Pt nanoparticles onto the carbon substrate with a particle size about 5-10 nm was observed on the sample S2 prepared by same methodology. The catalysts S3 and S4 prepared by vapor-phase impregnation-decomposition showed boht

similar morphology and distribution of metallic particles. They had a small average platinum particle size between 3-4 nm with a homogeneous distribution onto the carbon..

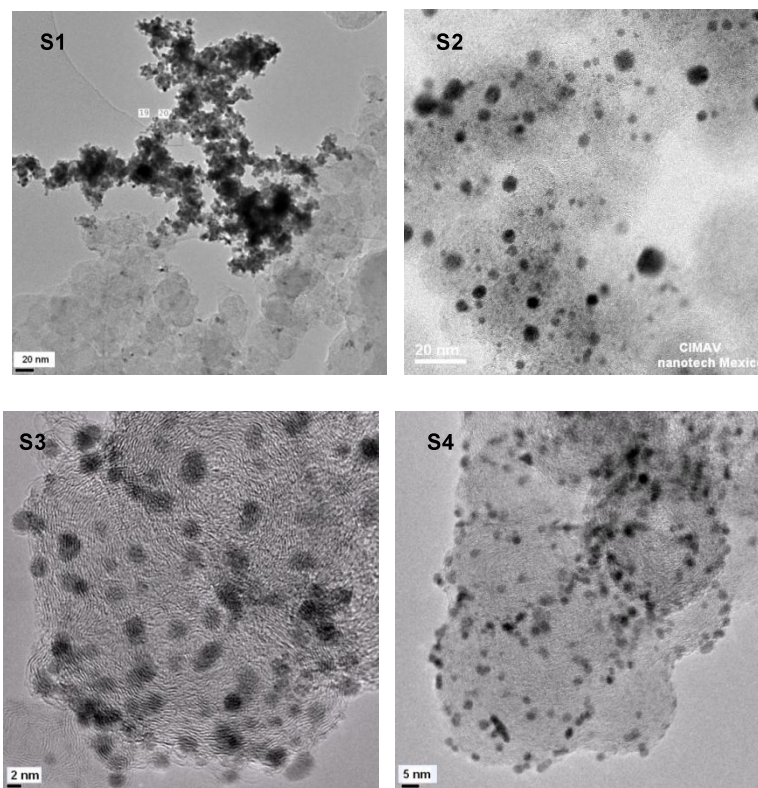


Figure 2. TEM images of 10 wt.% Pt-5 wt.% TiO<sub>2</sub>-C-P (S1), 10 wt.% Pt-C-P (S2), 10 wt.% Pt-5 wt.% TiO<sub>2</sub>-C-V(S3) and 10 wt.% Pt-C-V(S4) electrocatalysts.

### 3.3 XPS analysis

Fig. 3 shows XPS details of the Pt 4f signal of (a) Pt-TiO<sub>2</sub>-P and (b) Pt-C-P catalysts prepared by photo-deposition compared with (c) Pt-TiO<sub>2</sub>-V and (d) Pt-C-V materials synthesized by vapor-phase impregnation-decomposition method. The aim of this technique is analyze the metal-oxide interaction (Pt-TiO<sub>2</sub>) using both synthesis methods, the results were compared with XP spectrum of Pt-C. The BE value reported for Pt<sup>0</sup>4f<sub>7/2</sub> is about 71.2 eV [33].

In the fig. 3(a) Pt-TiO<sub>2</sub>-P XP spectra, the binding energy (BE) of values of 71 eV and 74.2 eV were associated to the 4f<sub>7/2</sub> and 4f<sub>5/2</sub> signals of metallic Pt (Pt<sup>0</sup>), whereas the fig 3 (b) Pt-C-P XP spectra of the material prepared with the same methodology by (photo-deposition) show a shift up in this values at 71.3 eV and 74.6 eV. This becomes evidence that Pt deposited on TiO<sub>2</sub> has different electronic properties, as compared to Pt deposited on carbon substrate. Also is observed that two doublets were necessary to fit the fig. 3(b) XP spectra the 4f signal. The doublets were assigned to different oxidation states of Pt according to literature data [30, 34-35]. Signals 4f<sub>7/2</sub> at 72.4 eV and



4f 5/2 at 75.8 eV were associated to oxidized  $\text{Pt}^{4+}$  and  $\text{Pt}^{2+}$  in PtO particles. It is rather related to incorporation of Pt into  $\text{TiO}_2$  structure, which cause lattice strain and observed BE shifts [23]. The presence of the oxide in the photo-deposition method helps to reduce the Pt precursor to metallic platinum, according to Eq. 1-3. This is not observable in the Pt-C sample prepared using the same methodology,  $\text{Pt}^0$  and PtO are deposited on carbon substrate.

XP spectras of fig 3(c) Pt- $\text{TiO}_2$ -V and fig. 3(d) Pt-C-V show similar results, the presence of  $\text{TiO}_2$  modifies the electronic properties of Pt. A shift down in the values of BE of metallic platinum ( $\text{Pt}^0$ ) of 4f 7/2 at 71.3 eV and 4f 5/2 at 74.3 eV was observed in Pt- $\text{TiO}_2$ -V sample. The 3(d) Pt/C-V catalyst present a BE of  $\text{Pt}^0$  4f 7/2 at 71.5 eV and  $\text{Pt}^0$  4f 5/2 at 74.8 eV, also this material show one doublet of oxide platinum ( $\text{Pt}^{2+}$ ) at 76.0 eV.

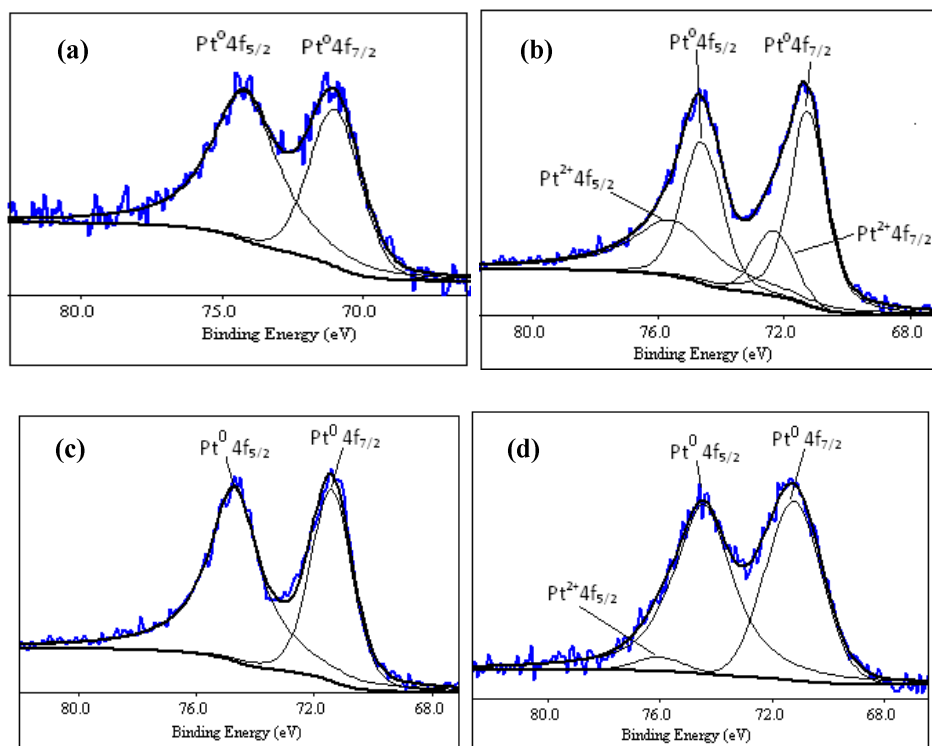


Figure 3. Pt 4f signals of XPS spectra of (a) 10%Pt- $\text{TiO}_2$ -P, (b) 10%Pt-C-P, (c) 10%Pt- $\text{TiO}_2$ -V and (d) 10%Pt-C-V electrocatalysts.

### 3.4 ORR electrochemistry

Fig. 5 displays the ORR activity of Pt- $\text{TiO}_2$ -C compared with Pt-C prepared by photo-deposition and vapor-phase impregnation-decomposition in oxygen saturated 0.5 M  $\text{H}_2\text{SO}_4$  at a rotating speed of 900 rpm at 25°C. As observed, the Pt- $\text{TiO}_2$ -C electrocatalysts show a shift of the EDR curves toward more positive electrode potentials versus the Pt/C, prepared using both methodologies. Table 1, summarize the kinetic parameters deduced for the ORR on the Pt-

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TiO<sub>2</sub>-C and Pt-C electrocatalysts in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 25°C. The interaction of Pt-oxide substrate shows an ORR kinetic current of 86.62  $\mu\text{A cm}^{-2}_{\text{Pt}}$  for Pt-TiO<sub>2</sub>-C-P while Pt-C-P reaches only 68.48  $\mu\text{A cm}^{-2}_{\text{Pt}}$ . Similar results were found in catalysts prepared by vapor-phase impregnation-decomposition, Pt-TiO<sub>2</sub>-C-V shows higher kinetic current (56.74  $\mu\text{A cm}^{-2}_{\text{Pt}}$ ) than Pt-C-V (46.72  $\mu\text{A cm}^{-2}_{\text{Pt}}$ ).

Table 1. Electrochemical parameters and active surface of Pt-C and Pt-TiO<sub>2</sub>-C electrocatalysts synthesized by photo-deposition and vapor phase impregnation-decomposition methods.

	EAS <sub>CO</sub> (cm <sup>2</sup> )	EAS (H <sub>upd</sub> ) (cm <sup>2</sup> )	E <sub>oc</sub> , V (NHE)	-b, (mV dec <sup>-1</sup> )	Koutecky- Levich slope (mA <sup>-1</sup> rpm <sup>1/2</sup> )	*j <sub>k</sub> a 0.9 V /NHE ( $\mu\text{A}/\text{cm}^2_{\text{Pt}}$ )
(S1)	0.83	0.86	0.99	105	107.6	86.62
(S2)	0.75	0.76	0.96	70	101.7	68.48
(S3)	4.1	3.9	0.98	69	112.0	56.74
(S4)	0.87	0.71	0.95	66	98.2	46.72

\*EAS from CO stripping

### 3.5 ORR electrochemistry

Fig. 5 displays the ORR activity of Pt-TiO<sub>2</sub>-C compared with Pt-C prepared by photo-deposition and vapor-phase impregnation-decomposition in oxygen saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> at a rotating speed of 900 rpm at 25°C. As observed, the Pt-TiO<sub>2</sub>-C electrocatalysts show a shift of the EDR curves toward more positive electrode potentials versus the Pt/C, prepared using both methodologies.

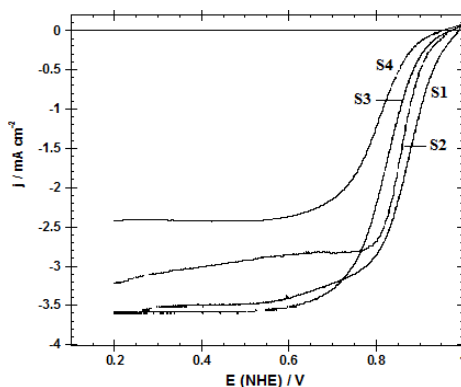
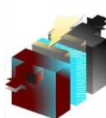


Figure 5. ORR curves of (S1) 10%Pt-5%TiO<sub>2</sub>-C-P, (b) 10%Pt-C-P, (c) 10%Pt-5%TiO<sub>2</sub>-C-V and (d) 10%Pt-C-V in oxygen saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> at 25°C, scan rate of 5 mV s<sup>-1</sup> and 900 rpm as rotating speed.

The influence of the oxide is observed in the open circuit potential (E<sub>oc</sub>) which is obtained for the different samples (Table 1). Pt-C materials showed E<sub>oc</sub>=0.95-0.96 V (NHE) range. A value of E<sub>oc</sub>=0.96 V (NHE) is typical of Pt electrodes. Pt-TiO<sub>2</sub>-C samples had higher open circuit potential (0.98-0.99 V (NHE) range) than Pt-C materials, this means that Pt-TiO<sub>2</sub>-C samples possess better oxygen adsorption capacity than Pt-C. Pt-TiO<sub>2</sub>-C-P sample presents a value of the Tafel slope around -0.120 V(NHE) dec<sup>-1</sup>, while the Pt-C-P, Pt-TiO<sub>2</sub>-C-V and Pt-C-V show a Tafel slope



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around  $-0.60\text{V(NHE)} \text{ dec}^{-1}$ , as the theoretical values for the first order reaction kinetics. These different values depend of the energy of the oxygen adsorption and means that the transfer of the first electron to the  $\text{O}_2(\text{ads})$  molecule is the determined step of the kinetic reaction. All prepared samples had a similar Koutecky-Levich (K-L) slope like theoretical value ( $100.7 \text{ mA}^{-1} \text{ rpm}^{1/2}$ ). Pt-TiO<sub>2</sub>-C-P and Pt-TiO<sub>2</sub>-V show higher K-L slopes ( $107.6$  and  $112 \text{ mA}^{-1} \text{ rpm}^{1/2}$ , respectively) than Pt-C-P ( $101.7 \text{ mA}^{-1} \text{ rpm}^{1/2}$ ) and Pt-C-V ( $98.2 \text{ mA}^{-1} \text{ rpm}^{1/2}$ ). From the RDE experiments a multielectron charge transfer process ( $n=4e^-$ ) for the oxygen reaction was determined

Table 1, summarize the kinetic parameters deduced for the ORR on the Pt-TiO<sub>2</sub>-C and Pt-C electrocatalysts in  $0.5 \text{ M H}_2\text{SO}_4$  at  $25^\circ\text{C}$ . The interaction of Pt-oxide substrate shows an ORR kinetic current of  $86.62 \mu\text{A cm}^{-2}_{\text{Pt}}$  for Pt-TiO<sub>2</sub>-C-P while Pt-C-P reaches only  $68.48 \mu\text{A cm}^{-2}_{\text{Pt}}$ . Similar results were found in catalysts prepared by vapor-phase impregnation-decomposition, Pt-TiO<sub>2</sub>-C-V shows higher kinetic current ( $56.74 \mu\text{A cm}^{-2}_{\text{Pt}}$ ) than Pt-C-V ( $46.72 \mu\text{A cm}^{-2}_{\text{Pt}}$ ).

#### 4. Conclusions

The smallest size nanoparticles of Pt (2-3 nm) with a homogeneous dispersion onto TiO<sub>2</sub>-C nanocomposite were obtained by vapor-phase impregnation-decomposition method. XPS results give an evidence that Pt deposited on TiO<sub>2</sub>-C substrate has different electronic properties than Pt deposited on carbon substrate. The electronic changes are related to incorporation and interaction between Pt and TiO<sub>2</sub> structure, which produced a synergetic effect. It generates that Pt-TiO<sub>2</sub>-C had better electrocatalytic activity for ORR than Pt/C.

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